U.D.C. 542+543-43

Advances in the Chemistry of Inorganic Films and the Interference Indicator Method

E.S.Vorontsov, V.K.Altukhov, A.N.Korneeva, and N.P.Peksheva

The fast developing field of chemical methods of preparation of inorganic films is reviewed, and a new method of investigating heterogeneous reactions (based on recent advances in the chemistry of inorganic films) is formulated, and termed the "interference indicator method". Specific features of the method are discussed, and examples are given of its application to studies of mechanism, kinetics, and catalysis in heterogeneous reactions; the limitations of the method, and its advantages and disadvantages, are also discussed. 106 references.

CONTENTS

I.	Introduction	596
II.	The interference indicator method	598
III.	Reactions in the metal-oxide-gas system	599
IV.	Reactions in the metal-oxide-liquid system	603
V.	Reactions in the metal-oxide-solid system. Carbo-thermic reduction	605
VI.	Limitations, advantages, and disadvantages of the method	606

I. INTRODUCTION

1. Inorganic Films on Solids

It has been known for a long time that the surface properties of solids can be improved by the application of inorganic coatings, which tend to prevent physical or chemical interactions between the solid and the surrounding medium and in this way extend the useful life-span of a large number of articles. Surface films on solids can also have decorative, protective, and complex physicochemical and electrophysical functions.

Interest in inorganic films has increased steadily during the last few years: for example, the publishing house "Mir" has produced the fifth (and almost certainly not the last) volume in the series "Physics of Thin Films" [1] during 1972. Whereas physicists are primarily interested in the physical and mechanical properties of thin layers of inorganic materials, chemists are concerned mainly with developing new and better methods of preparation of films having prescribed properties.

The increasing importance of thin films in science and technology stems not only from their decorative, protective, and mechanical properties when applied to everyday materials, but also from new developments in electrical and radio technology such as the microminiaturisation of integrated electronic circuits, which was made possible by the exploitation of thin films of metals, semiconductors, and insulators ("planar technology") [2,3].

The chemical composition of the films can be simple (single component) or complex (multi-component); their phase composition also can be simple (single-phase, homogeneous films) or complex (multi-phase, heterogeneous films). As regards electrical properties, we can distinguish metallic, semiconducting, and insulating (or dielectric) films. There is no generally accepted classification of the films in terms of thickness: for example, some workers [4] consider films between a monolayer and 100 Å in thickness as very thin, between 100 Å and 10 000 Å as thin, and above 1 μm as thick, whereas others [5] specify thin films (up to 400 Å), films of intermediate thickness (400–5000 Å), and thick films (over 5000 Å).

In this review we shall not be concerned with electroplated metal films, which are discussed systematically and in detail elsewhere [6]. The chemistry and technology of enamel films are also well known [7].

Chemical methods of preparation of thin films, relying on a wide range of reactions, have made considerable progress in the last few years. We have based our "interference indicator method" for the physicochemical study of heterogeneous chemical reactions [8-10] on these recent advances in the chemistry of thin films.

2. Chemical Methods of Preparation of Inorganic Films

The application of chemical reactions to the preparation of inorganic films is developing in the following directions.

1. The reaction between a solid and its gaseous or liquid environment, leading to the formation of a layer of product in whose composition the original solid is included. Oxide, sulphide, halide, and other films are produced on metals and semiconductors by this reaction. The method can be described schematically by the equations

$$A_{(s)} + B_{(g)} = AB_{(\text{film on A})}, \quad (1)$$

$$A_{(s)} + B_{(\text{soln.})} = AB_{(\text{film on A})}, \quad (2)$$

where $B_{(\text{soln.})}$ denotes a solution of B in any solvent.

For example, the oxidation of iron and its alloys in alkaline solutions and in water vapour is now widely used [11]. A salt-like film having strongly protective properties is formed when metals are phosphated [12].

The formation of oxide films on metals is described in detail in a number of monographs [13-18].

As a result of the development of semiconductor microelectronics, several papers on the growth of oxide films on Si and Ge have appeared in recent years. The preparation of films on silicon by oxidation in water vapour, in

dry or in wet oxygen, and also by anodic oxidation has been discussed by many workers[19-24].

2. The deposition of a film on a substrate, followed by chemical treatment to produce the desired properties. This method can be described schematically by the equations

$$A_{(film)} + B_{(g)} = AB_{(film)}, \quad (3)$$
$$A_{(film)} + B_{(soln.)} = AB_{(film)}, \quad (4)$$
$$AB_{(film)} + C_{(g)} = A_{(film)} + BC_{(g)}, \quad (5)$$
$$AB_{(film)} + C_{(soln.)} = A_{(film)} + BC_{(soln.)}. \quad (6)$$

For example, a metal film is deposited on a plastic, ceramic, alloy, or semiconductor, and it is allowed to react with a gas or a liquid to give an oxide, sulphide, selenide, telluride, halide, or more complex film.

On the other hand, one can deposit a layer of a compound on the substrate and convert it into a coating of simpler chemical composition by decomposing it or by allowing it to react with the surrounding medium. Copper–nickel coatings have been prepared[25-27] by reduction with hydrogen or carbon monoxide of mixed layers of Cu_2O and NiO, previously deposited on a ceramic or metallic substrate. This chemical procedure is interesting because it enables "hot" metallic coatings to be prepared without using molten alloy baths. Furthermore, the method is superior to electro-plating, which cannot provide complex metallic and metal-ceramic layers.

3. The most rapid progress has been made in the preparation of films by chemical deposition from the vapour phase. Reduction of a compound of the desired element, followed by condensation of the element on a substrate, is one important variant of this method:

$$AC + B = A_{(g)} + BC, \quad (7)$$
$$A_{(g)} = A_{(film)}, \quad (8)$$

where B is a reducing agent.

The growth of monocrystalline films of silicon on sapphire and on spinel ($MgO.Al_2O_3$) by reduction of $SiCl_4$ or decomposition of SiH_4, and the epitaxial relationships of the layer and the substrate, have been adequately discussed[28-37]. Silicon films offering the best crystallographic and electrical properties are obtained on sapphire previously heated to a high temperature in a hydrogen atmosphere.

Films of metals having a relatively high vapour pressure have been obtained[38] by chemical reduction followed by distillation and condensation at normal pressures, avoiding the need for relatively expensive vacuum equipment. The process can be described by the following equations:

$$MO_{(s)} + B_{(g)} = M_{(s)} + BO_{(g)}, \quad (9)$$
$$M_{(s)} = M_{(g)}, \quad (10)$$
$$M_{(g)} = M_{(film)}. \quad (11)$$

Many compounds (including oxides, sulphides, carbides, borides, silicides, and various intermetallic compounds) can be prepared by chemical vapour deposition. The reaction is usually carried out at atmospheric pressure. The growth conditions and the properties of the following films have been described: Si_3N_4,[39-47] rutile (TiO_2),[48,49] Ta_2O_5,[50] Nb_2O_5,[51] and Al_2O_3.[52-57]

We may consider the following reactions as typical of the chemical deposition of compounds from the vapour phase:

$$3SiCl_{4(g)} + 4NH_{3(g)} = Si_3N_{4(s)} + 12HCl_{(g)}, \quad (12)$$
$$2AlCl_{3(g)} + 3H_2O_{(g)} = Al_2O_{3(s)} + 6HCl_{(g)}, \quad (13)$$
$$2SiO_{(g)} + O_{2(g)} = 2SiO_{2(s)}. \quad (14)$$

In addition to reduction and oxidation, decomposition reactions can be used for chemical vapour deposition. Typical examples are:

$$Ni(CO)_{4(g)} \xrightarrow{200-300^\circ} Ni_{(s)} + 4CO_{(g)}, \quad (15)$$
$$SiH_{4(g)} \xrightarrow{800-1300^\circ} Si_{(s)} + 2H_{2(g)}, \quad (16)$$
$$CH_{4(g)} \xrightarrow{1000-2000^\circ} C_{(s)} + 2H_{2(g)}. \quad (17)$$

Involatile materials are commonly deposited by the procedure known as chemical transport. The term "chemical transport" denotes a process in which an involatile material is transported (in the form of a volatile compound) from one region of the system (called the source region) to another region (called the deposition or substrate region). The process consists of three steps: 1) conversion of the source material into a volatile compound by a chemical reaction; 2) transport of the compound to the substrate; 3) decomposition of the compound close to or directly on the substrate, and deposition of the source material on the substrate. For example[58]:

$$Ti_{(s)} + 2NaCl_{(g)} \rightarrow TiCl_{2(g)} + 2Na_{(g)} \quad (18)$$
$$TiCl_{2(g)} \rightarrow Ti_{(s)} + Cl_{2(g)} \quad (19)$$

Disproportionation reactions (in particular, of metal halides) are among the most widely used for chemical transport. They rely on the fact that many involatile metals can form an unstable, volatile, lower halide at high temperatures. Hence, when such a metal reacts with the higher halide at relatively high temperatures, the lower halide is formed, and the latter disproportionates to the metal and the higher halide when it reaches the lower-temperature region of the system. The metal is deposited on the substrate, and the higher halide is returned to the vapour phase, and can be transported back to the source region. This transport cycle can continue until the whole of the source material has been transported to the substrate. A known example of this process is the transport of silicon in the iodide system[59]:

$$Si_{(s)} + 2I_{2(g)} \rightarrow SiI_{4(g)}, \quad (20)$$
$$Si_{(s)} + SiI_{4(g)} \rightarrow 2SiI_{2(g)}, \quad (21)$$
$$2SiI_{2(g)} \rightarrow Si_{(s)} + SiI_{4(g)}. \quad (22)$$

Chemical transport by halide disproportionation reactions has been demonstrated for B, Al, Si, Ge, Ti, Cr, Ga, In, Zr.[60-62] The theory of transport reactions was developed by Schaefer and by Mandel and coworkers[63-66].

The preparation of metal, semiconductor, and oxide films by the thermal decomposition of metal–organic compounds has been actively developed during the last few years[67]. The method, which can call upon an enormous range of initial compounds, is best illustrated by the following reactions:

$$[(CH_3)_2CH-CH_2]_3Al \xrightarrow{\sim 250^\circ} Al + 3(CH_3)_2C=CH_2 + \frac{3}{2}H_2, \quad (23)$$
$$(C_6H_6)_2Cr \xrightarrow{\sim 350^\circ} Cr + 2C_6H_6, \quad (24)$$
$$(C_2H_5O)_4Si \xrightarrow{\sim 800^\circ} SiO_2 + 4C_2H_4 + 2H_2O. \quad (25)$$

The preparation of thin transparent films, of great importance to the optical industry, has been discussed by Suikovskaya[68]. Transparent films deposited on dense, opaque substrates produce a coloration due to the interference of light. In this way, heterogeneous chemical reactions accompanied by a change in the thickness (and hence in the colour) of a film can be made "visible".

II. THE INTERFERENCE INDICATOR METHOD

1. Indicators of Chemical Reactions

We shall use the Russian term "indikator", derived from the Latin "indicator", which means a pointer [69].

All chemical reactions are accompanied by physical effects: heat absorption or evolution, transport of elementary particles (including electrons), changes in weight, volume, and pressure of the reactants, etc. Explosions also produce light and sound effects.

We can often monitor the progress of a chemical reaction by observing changes in some physical property of the reaction system: this property acts as an indicator of (or a pointer to) the state of the reaction. For example, in potentiometric titrations the measured e.m.f. of the system is the indicator property of the system. In the dissociation of a carbonate in a vacuum the indicator property is the increasing pressure of CO_2, which grows to a constant value corresponding to the establishment of a dynamic equilibrium in the system. The inversion of cane sugar can be followed with a polarimeter by observing the rotation of the plane of polarisation of a beam of light passing through the optically active solution.

Often, however, reactions take place without visible change, and the choice of a physical property as an indicator of the path or of the extent of the reaction becomes difficult. Homogeneous reactions in solutions are of this type. In this case one adds to the reaction mixture special substances (indicators) having a property (such as colour) which can be easily monitored and which is sufficiently sensitive to the extent of the reaction.

In the chemistry of aqueous (including some non-aqueous) solutions the indicators are usually organic or inorganic compounds, capable of detecting the end-point of a titration by a colour change, by the appearance or disappearance of a turbidity, by luminescence, etc., or of giving an indication of the value of some physicochemical property of the system such as pH or redox potential. Indicators are usually added to the solution under study in small amounts [70].

During the last 15–20 years the isotopic (including radioactive) indicator method has become very popular: it is based on the "labelled atom" method proposed by Hevesy and Paneth in 1913. Isotopic indicators are substances in which the isotopic composition is different from the natural isotopic composition. They can therefore be used as tracers to study a wide variety of processes. Both stable and radioactive isotopes of the elements can be used as isotopic tracers, since both types of isotope can easily be detected and quantitatively determined [70].

The isotopic indicator method is extremely sensitive; the specificity of these indicators is so high that they can be used in processes involving mixing, migration, and chemical reaction in the most complex systems, including living organisms. The method has therefore been used in studies of the thermodynamics, kinetics, and mechanism of chemical reactions [71–73].

Of course, any indicator has advantages, disadvantages, and limitations. For example, many organic indicators in aqueous solutions are suitable only for identifying the equivalence point in titrations. Radioactive isotopes with very short half-lives have a very limited field of application as indicators; indicators which emit penetrating radiation are dangerous to life and require elaborate screening arrangements.

2. The Interference Colour of Films

One of the most characteristic physical effects of heterogeneous reactions such as oxidation on the surface of a compact monocrystalline or polycrystalline metal is the formation of iridescence (or "temper" colours). This phenomenon has been described in detail [13–18]; a brief discussion of its essential features is given below.

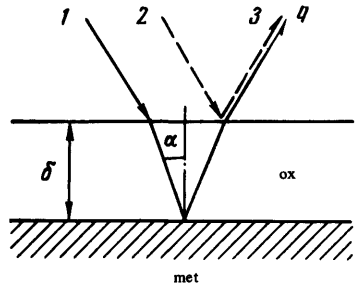


Figure 1. Formation of interference colours in films on metal substrates: *1*) and *2*) incident beams, *3*) and *4*) reflected beams.

When a metal is oxidised by a gaseous reagent (oxygen, chlorine, carbon dioxide, or sulphur, iodine, or water vapour) a transparent, invisible film of product is initially formed on the surface. As the films grows, its thickness becomes comparable with the wave length of visible light, and at this stage interference colours begin to appear.

If a beam of monochromatic light is allowed to strike at right angles the surface of a metal covered by a film, part of the radiant energy is reflected at the film–air interface, and the remainder is refracted into the film and reflected at the metal surface. The condition for destructive interference of the two beams is a phase lag by an odd number of half-waves (Fig. 1); in other words, colours will appear when

$$2\delta = \frac{\lambda}{2n}, \frac{3\lambda}{2n}, \frac{5\lambda}{2n} \ldots \qquad (26)$$

where δ is the thickness of the layer of products, λ is the wave length of the light in air, and n is the refractive index of the film.

If a phase change occurs as a result of the double reflection, it can be treated as a correction (c) to the optical path difference:

$$\delta = \frac{\lambda}{4n} - c; \frac{3\lambda}{4n} - c; \frac{5\lambda}{4n} - c \ldots \qquad (27)$$

Extinction of part of the visible spectrum by the film produces the complementary colour. As the reaction proceeds, and the film becomes thicker, the colour changes from yellow to blue, as shown by the data on the oxidation of iron [13] given in Table 1.

It follows from the condition for destructive interference that this colour sequence can be repeated as the film continues to grow, giving rise to a second-order spectrum. On some metals it is possible to observe spectra of order three, four, or even five. For example, the book by Bai and coworkers [18] on the oxidation of

titanium and its alloys quotes four distinct interference spectra for oxide films on this metal. Five iridescence spectra were recorded (Table 2) in our continuous observations [74] of the oxidation of titanium in air at 600°†.

Table 1. Interference colours on iron.

Heated in air at 400°		Film thickness, A
time, min	film colour	
1.0	Yellow	460
1.5	Orange	520
2.0	Red	580
2.5	Violet	680
3.0	Blue	720

On titanium, the first-order iridescence spectrum is much more intensely coloured than the higher-order spectra; the spectra of order two, three, and four have pinkish tones, and grey tones are observed at the end of the fifth-order spectrum, indicating a change from interference colours to the genuine colour of the oxide (rutile).

Table 2. Interference colours on titanium heated in air at 600°. (Roman numerals in brackets denote the order of the spectrum.)

Oxidation time	Film colour	Oxidation time	Film colour
0 min 45 s	Dark yellow (I)	63 min 40 s	Crimson
1 min 00 s	Brown	82 min 00 s	Violet
1 min 25 s	Violet	84 min 00 s	Violet-blue
2 min 25 s	Dark blue	88 min 10 s	Green
6 min 30 s	Light blue	113 min	Greenish yellow (IV)
17 min 00 s	Dark yellow (II)	116	Yellowish pink (IV)
22 min 05 s	Crimson	134	Crimson
30 min 00 s	Violet	158	Violet
32 min 30 s	Blue	160	Dark green
38 min 00 s	Dark green	183	Yellowish green (V)
49 min 40 s	Yellow (III)	210	Pink (V)

Because of the development of micro-electronics technology, which relies on thin films of semiconductors and of oxides (insulators), there is a growing awareness of the importance of films showing interference colours. Thin, coloured films on semiconductors such as silicon and germanium are used in practice in structures known as MOS (metal–oxide–semiconductor). [For all practical purposes, MOS technology relies on silicon, not germanium, as the substrate. (Ed. of Translation).]

3. Interference Colour as an Indicator of Heterogeneous Reactions

The colour of thin films on metals and on some semiconductors is a physical effect directly related to a heterogeneous reaction between the solid and its surrounding medium.

The interference colours of thin films have been discussed in depth in the scientific literature. However, most of the published work is concerned with the oxidation of metals by gaseous reagents (see, for example, Refs. 13–18), i.e. with only one type of chemical interaction.

† The temperatures are expressed throughout in degrees Celsius.

Von Wartenberg and Aoyama [75] used the tarnishing of the metal as an indicator in their study of the equilibrium composition of the gas phase in the Cr–O–H system. The interference colour of the oxide film could not be used as a reaction indicator in this work, because it was masked by radiation from the hot metal at the relatively high temperatures used by the authors.

A series of experiments carried out in 1965 by one of us and Agapova [76] demonstrated a reversible colour change when Fe, Ni, and Cu are reduced by hydrogen from their coloured films at relatively low temperatures:

Colour changes during oxidation →

Film colour: yellow brown violet blue

← Colour changes during reduction

That work [76] marked the beginning of a more general use of interference colours as indicators of heterogeneous chemical reactions. It became obvious that interference colours can give valuable information not only on the oxidation of metals, but also on their reduction from the oxides. Reduction reactions can therefore be made "visible", as well as oxidation reactions, by monitoring the colour changes of oxide films in a reducing medium.

Changes in the colour of the films can be seen also during thinning by chemical or electrochemical etching. This information is of fundamental importance in studies of the kinetics and mechanism of the interaction between oxides and electrolyte solutions, and should lead to better control of technological processes for the production of semiconductor and insulator films as well as yielding additional information on the nature of passivating films on metals.

Thus, the change of interference colour during the course of a reaction can be used as an indicator of the extent of reaction in the following systems:

solid–coloured film–gas,
solid–coloured film–liquid,
solid–coloured film–solid.

It is important to remember that a semiconductor, e.g. Si or Ge, can be used in place of the metal, and any other oxidation product, e.g. chloride or bromide, in place of the oxide. Thus, the range of heterogeneous systems in which interference colour can be used as an indicator is very wide indeed.

Several papers in which interference colours are used as indicators of chemical reactions have already been published, and we can therefore state that a new method of physicochemical research has been proposed and validated: the "interference indicator method".

We shall now consider some specific aspects of this method and some concrete results of its application.

III. REACTIONS IN THE METAL–OXIDE–GAS SYSTEM

1. Mechanism

Studies of reactions in the metal–oxide–gas system are very important in clarifying the mechanism of oxidation and reduction reactions of metals: this is particularly true of the theory of heterogeneous chemical reactions in general, and of the theory of metallurgical processes and of the rapidly developing micro-electronics technology in

particular. The use of the interference colours of oxide films as reaction indicators can lead to valuable practical results in these fields of technology.

The generalised equations for the oxidation and the reduction of metals

$$mM_{(s)} + \frac{n}{2}O_{2(g)} \rightleftharpoons M_mO_{n(s)}, \quad (28)$$

$$M_mO_{n(s)} + nB_{(g)} \rightleftharpoons mM_{(s)} + nBO_{(g)}, \quad (29)$$

describe only the quantitative relationships between the reactants, and give no indication whatever of the mechanism of the reaction. The mechanism consists of a series of simple acts and steps, such as diffusion of the reactants in the gas medium and in the layer of products, adsorption and desorption, the chemical act itself, and electron transfer.

The oxidation of metals begins with chemisorption of the oxidising gas, e.g. oxygen, on the metal surface. Oxygen atoms, being electron acceptors, extract electrons from the metal: all the subsequent events on the metal surface stem basically from this cause.

One of the consequences of oxygen chemisorption on a metal surface is the creation of an electric field [15,16] whose value can be as high as 10^7 V cm^{-1}. The electric field can pull cations from the metal lattice into the adsorption layer even at room temperature; its influence was first pointed out by Mott and Cabrera [77,78], whose theory gave the first convincing explanation of the formation of oxide films on metals at low temperatures (i.e. under conditions in which the transport of atoms by diffusion is negligibly small).

Interference colours are observed if a metal is heated after the formation of the primary (low-temperature) oxide film. The theory of Cabrera and Mott, as developed and refined by Wagner, Hauffe, Il'shner, and others [15], can account also for the formation of layers showing interference colours.

Thus, the formation and growth of coloured films is discussed in adequate detail in the theory of the oxidation of metals. However, nothing appears to have been published on the thermodynamics, kinetics, mechanism, and other physicochemical aspects of the reduction of these films to the metal. Some preliminary work in that direction has been done in our laboratory [9,76,79] by observing changes in the interference colours on Fe, Ni, and Cu in a reducing atmosphere.

We found that the reduction of Fe, Ni, and Cu from their coloured films in hydrogen or in carbon monoxide at relatively low temperatures gives colour changes in the opposite sequence to that observed during oxidation. Hence, heterogeneous reactions of the type

$$MO_{(s)} + H_{2(g)} = M_{(s)} + H_2O_{(g)}, \quad (30)$$

$$MO_{(s)} + CO_{(g)} = M_{(s)} + CO_{2(g)}, \quad (31)$$

do not lead to the formation of the product (M) at the oxide–gas interface. Reduction is accompanied by a decrease in film thickness from the direction of the metal substrate.

Our experimental results, combined with the main propositions of the Mott–Cabrera theory, lead to the mechanism shown in Fig. 2 for the reduction of a metal from thin oxide layers. This scheme differs from Richardson and Dancy's [80] in two respects:

1. It emphasises the role of disorder in the oxygen sublattice and of migration of oxygen anions under the influence of the electric field.

2. The disordering of the cation and the anion sublattice, and therefore the generation of the appropriate vacancies, is ascribed to the chemical (reduction) reaction itself.

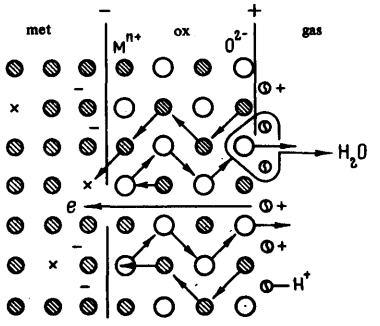


Figure 2. Reduction mechanism of thin metal oxide layers.

The relevance of our experiments, using the colour of the films as a reaction indicator to investigate the mechanism of the reduction of oxide films, is not confined to a reconsideration of the role of oxygen migration in these reactions [81]. The experimental results were used also to identify the site of reactions of the type

$$MO_{(s)} + B_{(g)} = M_{(s)} + BO_{(g)}. \quad (32)$$

Recent publications on the physical chemistry of pyrometallurgical reactions [82,83] attach great importance to the metal–oxide interface, which is assumed to be the reaction surface, i.e. the site of reactions of the type of reaction (32). Once the metal–oxide interface has been formed, reaction (32) is localised at this interface.

Our experimental results on the reduction of coloured oxide films, and the reaction mechanism shown in Fig. 2, are not consistent with the view that the surface-chemical reaction (32) occurs exclusively at the metal–oxide interface. After formation of a metallic phase the reaction is not completely localised at the interface, but it splits up into a series of simpler steps in three-dimensional space, for example:

$$B_{(g)} \rightarrow B^{n+}_{(ads)} + ne_{(ads)}, \quad (33)$$

$$ne_{(ads)} \rightarrow ne_{(m)}, \quad (34)$$

$$M^{n+}_{(ox)} \rightarrow M^{n+}_{(m-ox)}, \quad (35)$$

$$M^{n+}_{(m-ox)} + ne_{(m)} \rightarrow M_{(s)}, \quad (36)$$

$$O^{n-}_{(ox)} \rightarrow O^{n-}_{(ox-g)}, \quad (37)$$

$$O^{n-}_{(ox-g)} \rightarrow O^{n-}_{(ads)}, \quad (38)$$

$$O^{n-}_{(ads)} + B^{n+}_{(ads)} \rightarrow BO_{(ads)}, \quad (39)$$

$$BO_{(ads)} \rightarrow BO_{(g)}, \quad (40)$$

$$MO_{(s)} + B_{(g)} \rightarrow M_{(s)} + BO_{(g)}. \quad (32)$$

The above scheme is justified in our earlier papers [84,85]. Without claiming to be universally applicable, it does illustrate the complexity of the reduction of metal oxides with gaseous reagents, and in particular it shows how spatially separate steps can be combined in the overall mechanism.

One of the theoretical arguments in support of the role of the MO–M interface in surface-chemical reactions of type (32) rests on the application of the law of mass action [82]. We have removed some misconceptions in the application of the law of mass actions to these reactions [86,87].

We have dwelt at length on the mechanism of reactions (28)–(32) because of its relevance to the discussion to follow.

Table 3. Relative increase in the mean rate of oxidation of titanium with increase of temperature during the formation of a first-order coloured film. Mean rate at 500° taken as unity.

Temperature, °C	500	600	700	800
Time for the colour to change over the whole of the first-order spectrum, s	6000	390	70	30
Relative value of the mean rate of oxidation	1	15.4	85.7	200

2. Kinetics

Reaction rates can be inferred from the time for a given change in the colour of the film. For an oxidation reaction we can construct the kinetic curve (film thickness against time) by comparing the colours of films obtained by heating the metal in air or in oxygen for different times with the colours of standard samples.

Tamman [88] described the first experiment of this type. He measured approximate film thicknesses by comparing (in reflected light) the colour of the metal with that of a layer of air between glass plases. The interference colours of a layer of air of variable thickness are given in a table compiled by Rollet. The thickness of the film on the metal was calculated by dividing the thickness of the air gap showing the same colour by the refractive index n of the oxide (or other compound).

Useful kinetic data on the initial stages of oxidation of a metal can be obtained by simple visual observation of colour changes with time, using a stop-clock or a watch. Thus, we have shown [74] that the increase in the mean rate of the initial stage of oxidation of titanium with temperature can be estimated by comparing the times needed to develop the colour corresponding to the completion of the first-order spectrum at different temperatures (Table 3).

A quantitative indication of the retardation of the oxidation of titanium by the increasing thickness of the film of products can be obtained by noting the times needed for the completion of successive spectral orders (Fig. 3).

Depending on the nature of the reactants, on the oxidation temperature, on the range of thicknesses observed, and on other factors, film formation in an oxidising atmosphere is found to obey different kinetic laws (linear, parabolic, or logarithmic) [13–16]. For small changes in thickness (in the range 200–400 Å) the rate of growth is linear to a first approximation, and the mean rate of oxidation is close to the true rate.

Other conditions being equal, the mean rate of oxidation $\bar{V}$ of a metal can be expressed as an exponential function of temperature

$$\bar{V} = \frac{\delta}{\tau} = ke^{-E/RT}, \qquad (41)$$

where δ is the film thickness, τ is time, k is a pre-exponential factor, E is an apparent activation energy, R is the gas constant, and T is the absolute temperature.

For δ = const,

$$\lg\tau = \frac{E}{2.3RT} + C, \qquad (42)$$

and τ and E become the main kinetic parameters of the reaction.

Eqn. (42) suggests a new method of kinetic investigation, which avoids the need for measurements of the film thickness. By choosing a standard interference colour, the time needed to reach a prescribed thickness at different temperatures can be determined visually.

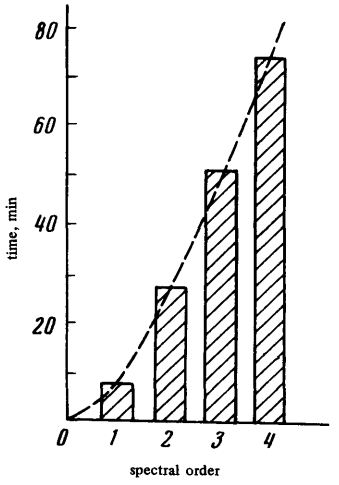


Figure 3. Inhibition of the oxidation of titanium in air at 600° by the increasing thickness of the oxide film.

Using previously published results [9,89], we have made a comparative study of the rates and apparent activation energies for the oxidation of Fe, Ni, and Cu. In the early stages of the reaction, we find that copper oxidises more easily than iron, and the latter more easily than nickel: the colour of the film begins to change appreciably at 200° on copper, at ~300° on iron, and above 400° on nickel.

The interference colour of oxide films has been used also to study the relative rates of oxidation and of Fe, Ni, and Cu [and reduction of their oxides], and also to compare the kinetic efficiencies of two gaseous reducing agents (hydrogen and carbon monoxide) [9,79]. We found that oxidised copper is reduced more easily than oxidised nickel, and the latter more easily than oxidised iron; of the two reducing gases, hydrogen was found to be the more effective.

3. Catalysis

The catalytic effect of the resulting metal on the reduction of an oxide with a gaseous reducing agent is well known: detailed discussions are given in Refs. 90 and 91.

However, the mechanism of the catalytic action is far from perfectly understood. Thus, some workers believe that acceleration of the reaction by the product is possible only when the metal and the oxide are in intimate contact: they assume that the catalytic properties are confined to the metal which is produced by the reaction as a new phase [92]. Other workers [93] report long-range catalytic effects by the product. Further study of these problems is desirable.

Our work with films showing interference colours suggests that it should be possible to observe very much more rapid colour changes in the presence of any agency (such as a catalytically active metal) capable of accelerating the reaction.

As a first step, we examined [10] the catalytic effect of platinum on the reduction of oxidised copper by hydrogen. The catalytic effect of platinum on a wide range of oxidation–reduction reactions is well known [94]. Plates of the electrolytic metal (99.9% Cu), 2 × 1 × 0.2 cm in size, were lapped, polished, and de-greased, and then oxidised in the air at 500° to give a thin, pale-yellow (almost white) film. This interference colour was taken as the standard for the experiment (~950 Å).

The films were then reduced in a hydrogen atmosphere until the interference colour disappeared and the natural colour of copper was restored. The reduction times of the standard film thickness at different temperatures and in the absence of the catalyst are listed in Table 4.

Table 4. Reduction time of a pale yellow film on copper as a function of temperature.

t, °C	200	250	300	350	400	Remark
τ, min	97	25	6	2	0.9	Mean value

The apparent activation energy corresponding to the data of Table 4 is 11.5 kcal mole^{-1}.

The experiment was repeated in the presence of the catalyst, consisting of platinum wires (bright, or coated with platinum black), placed in contact or out of contact with the film surface.

A catalytic effect of platinum on the reduction of oxidised copper was detectable in all the variants of the experiment. The strongest (and most localised) catalytic effect was noted in the experiments in which the wire was platinised and in contact with the sample (Table 5).

The powerful catalytic effect of platinised platinum on the reduction of oxidised copper is evident by simple inspection of Tables 4 and 5. Thus, 97 min were needed to reduce the film at 200° in the absence of the catalyst, whereas the natural colour of copper became visible in less than 7 s in the region adjacent to the contacting surface of Pt black. The acceleration factor for the reduction in the vicinity of the catalyst was 800 or more!

Two observations concerning the action of the platinum catalyst are noteworthy:

1. In the region 40–250° the temperature coefficient of the reaction rate is positive. In the presence of the catalyst the reaction proceeds at a measurable rate even at 40°.

2. At higher temperatures the catalytic activity of the platinum black is substantially lower. Hence, the temperature coefficient of the reaction rate in the presence of the catalyst shows two opposing effects: on the one hand, increase of temperature accelerates the reaction, and on the other hand it lowers the efficiency of the catalyst and thus it inhibits the reaction. We can therefore expect to find an optimum temperature, corresponding to maximum reaction rate. For the range of temperatures of our experiment (40–350°) the optimum is close to 250°.

Table 5. Reduction time of a standard film on Cu in the presence of a freshly platinised wire in contact with the sample.

t, °C	40	50	100	150	200	250	300	350
τ, min	12	3.5	0.75	0.25	0.116	0.0334	0.25	0.33

We have also found [95] that copper has a definite catalytic effect on the reduction of coloured films on copper by carbon monoxide as well as by hydrogen. The largest catalytic effect was obtained with hydrogen, using electrolytic copper as the catalyst.

We have also reported [96,97] a catalytic effect of Pt on the hydrogen reduction of coloured oxide films on Fe. The results are summarised in Table 6.

Table 6. Reduction time of a blue film on iron (to disappearance of colour).

τ, min \ t, °C	250	350	400
Without catalyst	>360	30	3
With catalyst, near contact area	0.333	0.256	0.067

It is evident from Table 6 that the reaction is accelerated by Pt: at 400° the acceleration factor is about 44, at 350° it is 110, and at 250° it is even greater.

In the region close to the platinum contact the reduction proceeds even at temperatures too low to give a significant reaction rate in the absence of the catalyst. Incipient reduction (corresponding to a barely visible colour change) was noted after 10 min at 25°, after 80 s at 50°, and after 35 s at 100°.

Further discussion of the mechanisms of the catalytic action of platinum on the reduction of an oxidised metal, based on observations of changes in the interference colours of the films, can be found in our earlier papers [8,10,97].

IV. REACTIONS IN THE METAL–OXIDE–LIQUID SYSTEM

1. Chemical Etching of Coloured Films on Iron

Uniform dissolution of the films on metals showing interference colours should be accompanied by a sequence of colour changes opposite to the colour changes observed during the growth of the films. This expectation has been confirmed experimentally.

Oxide films often need to be removed from metal articles as the first step in a series of technological operations. Hence, an understanding of the behaviour of films during dissolution has practical as well as theoretical importance.

Experiments with films showing interference colours can be expected to give more reliable results than experiments with thick films, which are liable to contain a greater number of defects such as pores, cracks, bubbles, chemical and structural inhomogeneities.

We believe that all the following questions can be answered by using films showing interference colours to study reactions in the metal–oxide–liquid system:

1. Is a given reagent a suitable etchant for the oxide film on a particular metal? If the etching rate is acceptable, colour changes will be noted in a relatively short time, otherwise the colour will remain unchanged for hours or days.
2. Is the etching action uniform? If the colour changes uniformly, the answer is in the affirmative. Selective etching is indicated by a spotty appearance of the interference colour.
3. Whis is the effect of the nature, concentration, and temperature of the acid?
4. Whis is the effect of convection, ultrasonic irradiation, electric field, etc. on the etching process?

We have used[98] interference colours as a reaction indicator to study the dissolution of oxide films on iron, the commonest of all industrial metals. Polished and de-greased plates of Armco-iron were oxidised in air to a standard interference colour (dark blue) corresponding to a thickness of 720–725 Å.[13] Etching of this film to the disappearance of the interference colour corresponds to a decrease in thickness by about 350 Å, which is of the same order as the thickness of the colourless natural film.

The samples were immersed in solutions of hydrochloric or sulphuric acid, and the colour of the film was continuously noted. The kinetic curves obtained are shown in Fig. 4.

It can be seen that coloured films on iron dissolve at approximately the same rate in hydrochloric and in sulphuric acid over our range of temperatures (20–60°) and concentrations (0.1–1.0 N). Increase of temperature from 20 to 60° increases the rate of the reaction by a factor of 5–6.

For a constant concentration of the etching solution, the etching time is an exponential function of temperature:

$$\tau = Be^{\frac{E}{RT}}, \qquad (43)$$

where B is a constant and E is the apparent activation energy of the dissolution process. The experimental results are satisfactorily described by a linear plot of $\lg\tau$ against $1/T$, which corresponds to the logarithmic form of Eqn. (43):

$$\lg\tau = \lg B + \frac{E}{2.3RT}. \qquad (44)$$

Plots of Eqn. (44) for etching in hydrochloric acid are shown in Fig. 5. The plots for dissolution of the films in sulphuric acid are very similar.

The apparent activation energy E calculated from these plots is 7500–8000 cal mole^{-1}.

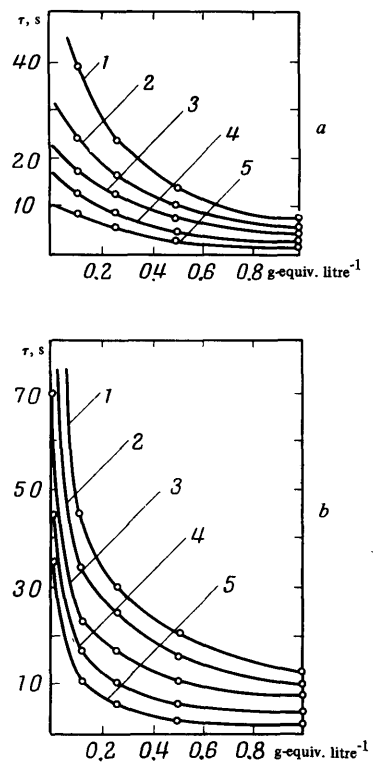


Figure 4. Time for disappearance of interference colour against acid concentration during etching in (*a*) HCl and (*b*) H_2SO_4 at different temperatures: *1*) 20°, *2*) 30°, *3*) 40°, *4*) 50°, *5*) 60°.

2. Behaviour of the Yellow Film on Titanium in Various Inorganic Acid Solutions

The high chemical stability of rutile (TiO_2) towards solutions of inorganic acids has been stressed in the literature[99,100]. Hence it is interesting to study the corrosion behaviour of titanium covered with a thin film of oxide, whose crystal structure is known[18] to be that of rutile.

We have examined the behaviour of titanium samples (OT4-O grade) with a dark yellow oxide film (first-order spectrum) in solutions of HCl, H_2SO_4, HNO_3, H_3PO_4, and CH_3COOH of various concentrations[74]. The samples were immersed in the solutions and monitored visually and gravimetrically.

The behaviour of the interference colours and of the metal in these solutions was somewhat unexpected: as long as a coloured film remained on the metal, the weight of the sample did not change. In these reactions the colour of the film can be used as an accurate indicator of the onset of dissolution.

The beginning of corrosive attack on titanium covered with a yellow oxide film is marked by the appearance of gas bubbles on the metal surface and by the loss of integrity and of uniform coloration of the film: these conclusions are made from visual and gravimetric observations.

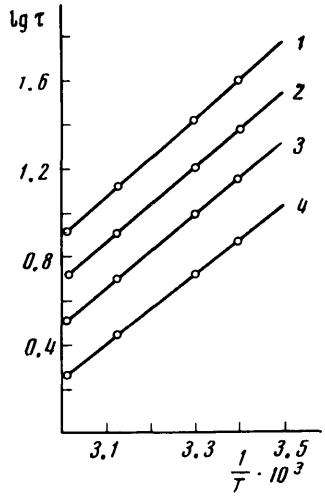


Figure 5. Plots of $\lg\tau = \varphi(1/T)$ for etching in hydrochloric acid solutions of different concentrations: *1*) 0.1 *N*, *2*) 0.25 *N*, *3*) 0.5 *N*, *4*) 1.0 *N*.

The presence of a yellow film on titanium ensures a relatively high corrosion resistance. Thus, in 22% HCl the weight loss of titanium was 2.395 g m^{-2} in 4 h without the yellow film, whereas in the filmed samples the loss was not measurable after 400 h.

In H_2SO_4 solutions of 20–45% concentration the corrosion of samples of the polished metal is slow at first, but it becomes quite fast after an induction period. At 55–96.5% concentrations corrosive attack begins as soon as the sample is immersed in the solution. A peculiar behaviour is observed when Ti is immersed in 75% H_2SO_4: a yellow film is formed on the surface in 20–25 h, and protects the sample for a further 200 h.

The yellow film is highly protective also towards solutions of H_2SO_4. Thus, in 60% H_2SO_4 the loss of unprotected Ti during 4 h is 3.25 g m^{-2}, whereas in the presence of the yellow film the loss is immeasurably small over 320 h.

When samples covered with a yellow interference film are stored in H_2SO_4 solutions of the concentrations used in this work (except 90 and 96.5%) a colour change is observed (Table 7), no doubt due to further oxidation of the metal.

In nitric acid solutions titanium exhibits self-passivation, and hence it is very resistant to corrosion in this medium[99]. Nevertheless, we have detected weight losses with samples of the polished metal in 5–55 wt.% solutions of HNO_3 after 720 h. For example, the loss amounted to 1.026 g m^{-2} in a 25% solution, and to 0.513 g m^{-2} in a 40% solution. In similar experiments with filmed samples, weight losses could be detected only after 1500–1700 h, and amounted to 0.171 and 0.342 g m^{-2} respectively.

Hence, the yellow interference film on titanium offers increased corrosion resistance even in solutions of nitric acid. This conclusion is confirmed by the observation that on storage in HNO_3 solutions of various concentrations the colour of the film changes from yellow towards blue in the same sequence as during the thermal oxidation of titanium to produce films showing a first-order interference spectrum.

Table 7. Colour changes of an oxide film on Ti exposed to H_2SO_4 solutions. (The film was initially yellow.)

Concentration of acid, %	Time of exposure, h	Colour of film after exposure
10	792	Yellow-violet
	960	Violet-blue
	1056	Light blue
25	168	Yellow-violet
	216	Violet-blue
	336	Blue
	480	Light blue
30	144	Yellow-violet
	168	Violet-blue
	216	Blue
	480	Light blue
40	408	Violet-blue
	960	Blue
	1056	Light blue
45	168	Violet
	216	Blue
	240	Light blue

Our experiments with H_3PO_4 showed that in this medium the titanium samples covered with a yellow film are least stable in the concentration range 55–75%, corrosive attack beginning after 365–412 h in these solutions. At concentrations above 75% the corrosion resistance increases appreciably, reaching 892 h in 85% H_3PO_4. Even greater stability, in excess of 1000 h, was found in H_3PO_4 solutions of concentration below 40%.

For comparison, we studied the chemical behaviour of polished titanium (free from interference colours) in H_3PO_4 solutions of the same concentrations. In 35–85% solutions of H_3PO_4 the reaction between the metal and the acid was quite rapid: thus, in a 60% solution the weight loss of titanium in 19 h was 1.539 g m^{-2}. In solutions below 30% concentration the attack on the titanium was very slight at first, and this initial stage was followed by an increase in weight and by the formation of a yellow film, indicating self-passivation of the metal under these conditions.

In acetic acid solutions of 5–45% concentration, titanium covered with a yellow film is extremely stable. Zero weight loss was recorded after 4800 h in acetic acid. On the other hand, samples of polished titanium gave measurable losses after 450–500 h in the same solutions. Thus, oxidised titanium is much more resistant to corrosion than the bright metal even in acetic acid.

The enhanced corrosion resistance of titanium covered with a yellow film, and the mechanism of its corrosion in solutions of HCl, H_2SO_4, and H_3PO_4, may be explained as follows.

During the induction period, when the colour of the film remains unchanged and no gas bubbles are evolved, defects in the film are being slowly eroded. Ultimately the film is punctured at the defective sites, and a "metal–solution" contact is established, leading to the formation of micro-corrosion galvanic couples of the "film–pore" type [13]. Evolution of gas bubbles can then begin, accompanied by disruption of the film, which is lifted from its metallic substrate and loses its protective properties.

V. REACTIONS IN THE METAL–OXIDE–SOLID SYSTEM. CARBO-THERMIC REDUCTION

We have recently extended our study of the possible applications of the "interference indicator method" to reactions between solid phases by investigating the iron–iron oxide–solid carbon system [101,102]. An analysis of this system offers particular interest from the standpoint of metallothermic and carbo-thermic reduction processes.

In order to stress the importance of these results, and the role of interference colours as reaction indicators in this work, we shall dwell briefly on some details of the mechanism of carbothermic reduction reactions, which is discussed in detail in a number of monographs [82,83,103].

In accordance with Baikov's principle of consecutive reactions [82], the final step in the carbo-thermic reduction of iron is usually expressed in the form

$$FeO_{(s)} + C_{(gr.)} = Fe_{(s)} + CO_{(g)}\,. \qquad (45)$$

By combining this equation with the equation for the gasification reaction

$$C_{(gr.)} + CO_{2(g)} = 2CO_{(g)} \qquad (46)$$

we conclude that iron is thermodynamically stable in this system only at temperatures of at least 700°. [82]

Current views on the mechanism of the carbo-thermal reduction of metals from their oxides, depending on the properties of the oxide {stability, volatility [dissociation pressure? (Ed. of Translation)]} and on the experimental conditions (temperature and pressure), are summarised in the following schemes [104]:

Scheme 1
$$MO_{(s)} = M_{(s)} + \tfrac{1}{2}O_{2(g)} \qquad (47)$$
$$\tfrac{1}{2}O_{2(g)} + C_{(gr.)} = CO_{(g)} \qquad (48)$$
$$MO_{(s)} + C_{(gr.)} = M_{(s)} + CO_{(g)} \qquad (49)$$

Scheme 2
$$MO_{(s)} + CO_{(g)} = M_{(s)} + CO_{2(g)} \qquad (50)$$
$$C_{(gr.)} + CO_{2(g)} = 2CO_{(g)} \qquad (51)$$
$$MO_{(s)} + C_{(gr.)} = M_{(s)} + CO_{(g)} \qquad (49)$$

Scheme 3
$$MO_{(s)} = MO_{(g)} \qquad (52)$$
$$MO_{(g)} + C_{(gr.)} = M_{(soln.\ in\ C)} + CO_{(g)} \qquad (53)$$
$$MO_{(s)} + C_{(gr.)} = M_{(soln.\ in\ C)} + CO_{(g)} \qquad (54)$$

All three schemes have one feature in common: gasification of the solid reducing agent. This highlights their common weakness, since it is well known that many different products can be formed when carbon is heated in air: gaseous monoxide and dioxide, and surface oxygen complexes. For example, it has been shown that oxygen becomes chemisorbed on purified carbon at temperatures below 300°, when the formation of gaseous products is negligibly small [105]. Nor should the absorption or occlusion of oxygen by the carbon be ignored.

Thus, there are reasons to suggest that at relatively low temperatures ($t < 500°$) the initial stage of the reaction between metal oxides and carbon does not involve the gasification of the solid reducing agent. But in this case a thermodynamic analysis of the M–O–C system based on Eqn. (45) cannot give a meaningful answer since it does not reflect the real nature of the reaction.

If the reduction gives rise to a metallic phase without the intervention of a gaseous product (CO or CO_2), the process can be tentatively expressed in the form

$$MO_{(s)} + C_{(gr.)} = M_{(s)} + CO_{(s)} \qquad (55)$$

where $CO_{(s)}$ denotes a solid solution of oxygen in graphite, or oxygen chemisorbed on the carbon.

Clearly, the thermodynamic driving force of reaction (55) is not determined by the quantity p_{CO}, but by the activity of oxygen in carbon, in accordance with the reaction isotherm

$$\Delta G = RT\,(\ln a_0' - \ln K_a) \qquad (56)$$

where ΔG is the change in Gibbs free energy of the system attending reaction (55), T is the absolute temperature, a_0' is the non-equilibrium (initial) activity of the oxygen sorbed by the carbon, and K_a is the equilibrium constant of reaction (55): $K_a = a_0$, where a_0 is the equilibrium activity of oxygen.

These considerations raise two important questions:

1. What is the practical importance of reaction (55)?
2. By what method can the reality of reaction (55) be demonstrated?

We shall try to answer both questions.

1. Reaction (55) is undoubtedly vitally important from the viewpoint of the theory of metallurgical processes, but it also has definite practical connotations.

Non-equilibrium structures of the metal–oxide–semiconductor (MOS) type are widely used in modern semiconductor technology. Chemical reactions at the interfacial boundaries of these structures can occur at low temperatures (and, even more so, at high temperatures), and they produce a very undesirable drift in the electrical characteristics of the semiconductor devices made from these structures [2].

In view of the very rapid development of semiconductor technology, the possibility of contact interaction between a conductor (graphite) and a semiconductor (the oxide) is a highly topical problem.

2. Experimental demonstration of the reality of the contact reaction (55) is a very difficult problem, which is the subject of continuing debate (see, for example, Ref. 103).

The very sensitive radioactive indicator method [106], used to detect the temperature at which direct reduction sets in, is inappropriate in this case because it relies on the gasification of "labelled" solid carbon.

We have used the "interference indicator method" to demonstrate the reality of reaction (55). [102] Reduction of a coloured oxide layer should be accompanied by a change in colour, and therefore the chemical interaction should be detectable from the colour change even if the reduction proceeds by the contact mechanism.

A few experiments were made to test this proposition. Samples of Armco-iron were heated in air after being polished and de-greased. When the surface had attained a stable temperature (measured by a Chromel–Alumel thermocouple), and a blue oxide film had appeared, the samples were placed in contact with a pellet of activated charcoal of "Karbolen" grade.

The pellets were pushed aside after various time intervals, and changes in interference colours in the reverse sequence to those corresponding to film growth were observed on the contact surface.

In another series of experiments the pellets were fixed to the specimens with special clamps, and the whole assembly was quenched in water to preserve the colour change. Contact reduction was again observed (see Table 8).

The phenomenon can be observed repeatedly, indicating that the contact reduction is satisfactorily reproducible.

In subsequent experiments by the interference indicator method we observed the contact reduction by carbon of oxide films on Ni at temperatures up to 250°, and on Cu up to 150°.

Table 8. Change of interference colour with time during the contact reduction of oxide films by graphite.

$t = 250°$		$t = 350°$	
Reaction time, s	Film colour	Reaction time, s	Film colour
0	Blue	0	Blue
180	Violet	30	Blue-violet
360	Yellow	60	Brown
630	Colour disappears	90	Yellow

Our results can be interpreted as follows. Oxide films on iron showing the colours of the first-order spectrum consist mainly of the phase α-Fe_2O_3. The temperature at which Fe_2O_3 begins to react with graphite is stated[104] to be 490°, but in our experiments with "interference indicators" chemical reaction between iron oxide and graphite was unmistakably detected at much lower temperature (up to 250°).

All the experiments were carried out in air. It is evident from our results that the presence of an oxidising atmosphere does not inhibit the contact reduction of the oxide film. This may be because the samples had been carefully polished and gave a good contact to the graphite pellet, which also had been polished. Under these conditions the access of air to the contact region was practically excluded.

Low-temperature chemical reactions between solid phases are usually thought to be hindered by the low diffusion rates under these conditions. This view is probably correct for the final stages of a reaction, striving to go to completion, but it cannot be applied to the initial stages. The oxide film on most technical metals (except the noble metals) is formed in the air, at room temperature, in a fraction of a second[6]. The main achievement of the theory of Cabrera and Mott[15] was to provide an explanation of this phenomenon.

In our experiments, too, the contact reaction between solids (oxide and carbon) takes place at an appreciable rate at relatively low temperatures. These results are inexplicable in terms of the standard reaction mechanisms quoted above. They can be explained, however, by the following scheme (Fig. 6). If the contact between the sample and the graphite surface is sufficiently perfect, many points and areas of contact are produced. Carbon, being a reducing agent and therefore an electron donor, can transfer electrons to the metal (an acceptor) through the oxide layer, which is a mixed (electronic–ionic) but predominantly electronic conductor.

This electron transfer generates an electric field across the metal–oxide–graphite system, which produces a kind of electrolysis in the oxide layer: cations migrate towards the metal–oxide interface, and cause the metallic substrate to grow, and oxygen anions migrate towards the graphite, where they are absorbed by the active solid. This process leads to a decrease in thickness of the oxide film, and therefore to a colour change.

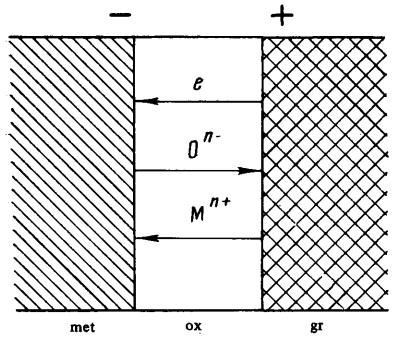


Figure 6. Mechanism of reduction to the metal by contact reaction between an oxide film and graphite.

Thus, by using the interference colour of oxide films on Fe, Ni, and Cu as an indicator of their contact reduction by graphite we have been able to demonstrate a low-temperature chemical reaction between solids and qualify the mechanism of this reaction.

VI. LIMITATIONS, ADVANTAGES, AND DISADVANTAGES OF THE METHOD

It may be concluded from the previous sections that a new method of studying the thermodynamics, kinetics, catalysis, mechanism, and other physicochemical aspects of heterogeneous reactions now exists: the use of the interference colours of thin films as indicators of the extent of reaction. In some cases the colour results from the formation of a thin layer of condensed products, in other cases the coloured layer itself is one of the reactants.

Of course, any method of experimental investigation has a limited region of applications. What are the limitations of interference colour as a reaction indicator?

Firstly (and in contrast to many of the organic indicators used for homogeneous reactions in aqueous solutions) interference colours can be used as indicators of heterogeneous reactions only. The temperature range over which they can be applied extends from room temperature or below to a few hundred degrees: the upper limit of temperature is determined by the stability of the coloured layer itself or by the stability of the underlying substrate.

In principle, the method can be applied whenever a condensed phase is present as a thin film showing interference colours which vary in the course of the reaction.

In this review we have relied mainly on metal–oxide systems to provide illustrations of the interference indicator method. This is partly because these systems are among the commonest and most easily accessible, and partly because of their extreme importance in industrial processes involving the oxidation and reduction of metals (metallurgy, machine construction, micro-electronics, chemical technology). However, the results obtained so

far justify the belief that the method should be equally applicable to systems in which the metal is replaced by a semiconductor and the oxygen by any other non-metal (e.g. S, Se, Te, F, Cl, Br, I). It is well known [3,14] that interference colours can appear on semiconductors as well as on metals, and that many gaseous or liquid reagents can be used instead of oxygen as the film-forming agent.

In summary, the interference indicator method can be recommended for the following specific investigations:

1. Comparing the rates of the initial stage of oxidation of a metal, semiconductor, or alloy at different temperatures with a single oxidising agent, or at a given temperature with different oxidising agents, and also the initial rates of oxidation of different metals and alloys with a given oxidising agent and at a fixed temperature.
2. Determining the rates of reduction of various oxidised metals, and comparing them under different sets of conditions. Quantifying the reducing power of various reagents, i.e. comparing their effectiveness.
3. Studies of heterogeneous catalysis, and comparing the effectiveness of different catalysts.
4. Studies of the solubility of oxides, sulphides, halides, and other compounds which can be prepared as interference-coloured films, in different solvents. Characterisation of the dissolution process, and of its dependence on the nature of the solvent, on temperature, convection, ultra-sonic irradiation, and electric field. In particular, we could study the dissolution of oxygen in a metal, a problem of fundamental importance in the theory and practice of welding, since oxide films are invariably present on the surface of metals being welded.
5. Studies of electrochemical processes in the metal–oxide–electrolyte system, and further investigation of the nature of metal passivity.
6. The contact interaction of solid phases, a problem of over-riding urgency in the rapidly developing technology of micro-electronic devices. The method seems particularly adapted to the very systems of interest in microelectronics.

The range of applications of the method is not, of course, limited to the above recommendations, and is likely to be further extended by the results of future work.

We shall now discuss the advantages and disadvantages of interference colour as an indicator of chemical reactions.

In the present review, certain aspects of the method have been specially stressed in order to demonstrate its simplicity and attractiveness. It requires no specialised or dedicated equipment, such as is used in the isotopic and radioactive indicator methods. In most cases the experiment can be easily arranged for convenient observation of the colour of the film. The temperature and pressure regions over which the method can be applied are sufficiently wide.

The method is entirely free from hazards, and does not require the special safety precautions and apparatus screening arrangements inherent in the use of radioactive indicators.

The main shortcoming of interference indicators is the fact that coloured films cannot be obtained in all systems. The method is not suitable for heterogeneous reactions in which the condensed phase is in a finely divided state.

Of course, any experimental method must have some weaknesses. However, new procedures should always be welcomed because they offer new possibilities to the experimenter. The present review aims to bring to the attention of its readers a new and (we believe) powerful method of studying heterogeneous reactions.

In conclusion, we offer some additional comments on the concept of a reaction indicator. The use of interference colour as an indicator of heterogeneous chemical reactions is an extension of the concept, and gives a new slant to the theory of chemical reaction indicators.

In contrast to homogeneous reactions in solutions, for which whole systems of special indicators have been developed, heterogeneous reactions have lacked special indicators of the extent of reaction. In some systems, stable or radioactive isotopes have been used as heterogeneous reaction indicators, but their complexity, limitations, and practical disadvantages are well known, and are mentioned in this review.

Our experiments with various interference indicators of heterogeneous reactions have shown that, as in the case of homogeneous reactions in aqueous solutions, the indicator produces a definite colour in the medium, varying with the extent of reaction or at a predetermined stage in the reaction. This clear analogy justifies the use of interference colour as a chemical reaction indicator, and we propose the term "interference indicator method" for the use of interference colours in this context.

As commonly used, the term indicator denotes a substance specially added to the reaction system to make visible the progress of the reaction. The increasing use of interference colours and of other criteria and properties of the reactants as indicators in heterogeneous reactions creates a need to reconsider and to extend the concept and the definition of a chemical indicator [2].

We propose the following comprehensive definition: a chemical reaction indicator is any easily observed criterion or property of the reaction system, or of the reactants, which changes during the course of the reaction, thus allowing the course of the reaction and its extent to be monitored. The property may be inherent in one of the reacting phases, or it may be contributed by a specially added substance.

In accordance with this definition, all indicators can be divided into two classes.

1. Intrinsic indicators. These include the criteria and properties which are fundamental to the reaction system or to the reactants. If they are easily observable, and if they change during the reaction, they allow the course of the reaction to be monitored: for example, changes in weight, volume, or pressure of the reactants. Other indicators belonging to this class are the varying e.m.f. of the system during a potentiometric titration, and the angle of rotation of plane polarised light during the inversion of cane sugar. Films showing interference colours can also be classified as intrinsic indicators.

2. Impurity indicators. These include all organic and inorganic substances added to reaction mixtures to produce a colour, luminescence, or other physical property varying during the reaction. Isotopic indicators belong to this class.

Alternatively, indicators could be classified according to the type of chemical reaction as *homogeneous* or *heterogeneous*.

REFERENCES

1. "Physics of Thin Films" (Translated into Russian), Izd. Mir, Moscow, Vol. 1, 1967; Vol. 2, 1967; Vol. 3, 1968; Vol. 4, 1970; Vol. 5, 1972.

2. B. F. Ormont, "Vvedenie v Fizicheskuyu i Kristallokhimiyu Poluprovodnikov" (Introduction to the Physical Chemistry and Crystal Chemistry of Semiconductors), Izd. Vysshaya Shkola, Moscow, 1968.
3. R. Burger and R. Donovan (Editors), "Oxidation, Diffusion, and Epitaxy" (Translated into Russian), Izd. Mir, Moscow, 1969.
4. K. H. Zaininger and C. C. Wang, Proceedings of the Institute of Radio and Electrical Engineers (Translated into Russian), Izd. Mir, Moscow, 57, 111 (1969).
5. N. P. Zhuk, "Kurs Korrozii i Zashchity Metallov" (Textbook of Metal Corrosion and Protection), Izd. Metallurgiya, Moscow, 1968.
6. V. I. Lainer and N. T. Kudryavtsev, "Osnovy Gal'vanostegii" (Fundamentals of Electroplating), Parts I and II, Metallurgizdat, Moscow, 1953.
7. A. Petzold, "Enamel" (Translated into Russian), Inostr. Lit., Moscow, 1958.
8. E. S. Vorontsov, "Sbornik Nauchnykh Trudov Chelyabinskogo Politekhnicheskogo Instituta" (Scientific Proceedings of the Chelyabinsk Polytechnic Institute), Chelyabinsk, 1970, No. 78, p. 31.
9. E. S. Vorontsov and V. D. Suikovskaya, Izv. Akad. Nauk SSSR, Metally, 227 (1970).
10. E. S. Vorontsov and K. A. Koshkina, Kinetika i Kataliz, 11, 246 (1970).
11. F. Todt, "Korroziya i Zashchita ot Korrozii" (Corrosion and Protection from Corrosion), Izd. Khimiya, Moscow, 1967.
12. "Anodnoe Okislenie Metallov" (Anodic Oxidation of Metals), Proceedings of the Second Intercollegiate Conference, Kazan', 1968, pp. 182 and 301.
13. N. D. Tomashov, "Teoriya Korrozii i Zashchity Metallov" (Theory of Metal Corrosion and Protection), Izd. Akad. Nauk SSSR, Moscow, 1959.
14. U. R. Evans, "The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications" (Translated into Russian), Mashgiz, 1962.
15. K. Hauffe, "Reaktionen in und an festen Stoffen" (Translated into Russian), Inostr. Lit., Moscow, 1963; Band II of "Chemie, anorganische und allgemeine, in Einzeldarstellungen" (Edited by M. Becke-Goehring).
16. O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys" (Translated into Russian), Inostr. Lit., Moscow, 1965.
17. J. Benard (Editor), "L'oxydation des Metaux", Gauthier-Villars, Paris, 1964 (Translated into Russian), Vol. 1, Izd. Metallurgiya, Moscow, 1968.
18. A. S. Bai, D. I. Lainer, E. N. Slesareva, and M. I. Tsipin, "Okislenie Titana i Ego Splavov" (Oxidation of Titanium and Its Alloys), Izd. Metallurgiya, Moscow, 1970.
19. J. R. Ligenza, J. Electrochem. Soc., 109, 73 (1962).
20. J. R. Ligenza, J. Phys. Chem., 65, 2011 (1961).
21. P. J. Jorgensen, J. Chem. Phys., 37, 874 (1962).
22. J. Edagawa. Y. Morita, S. Maekawa, and Y. Inushi, Japan. J. Appl. Phys., 2, 765 (1963).
23. P. F. Schmidt and W. Michel, J. Electrochem. Soc., 104, 230 (1957).
24. E. A. Efimov and I. G. Erusalimchik, "Elektrokhimiya Germaniya i Kremniya" (Eelectrochemistry of Germanium and Silicon), Goskhimizdat, Moscow, 1963.
25. E. S. Vorontsov and D. I. Tikhomirova, Zashchita Metallov, 345 (1972).
26. D. I. Tikhomirova and E. S. Vorontsov, Zhur. Prikl. Khim., 45, 658 (1972).
27. D. I. Tikhomirova and E. S. Vorontsov, Zashchita Metallov, 506 (1972).
28. H. M. Manasevit and W. I. Simpson, J. Appl. Phys., 35, 1394 (1964).
29. C. Muller and P. Robinson, TIIER, 52, 1613 (1964).
30. H. M. Manasevit, Trans. Met. Soc. AIME, 242, 465 (1968).
31. J. D. Filby and S. Nielson, Brit. J. Appl. Phys., 18, 1357 (1967).
32. H. M. Manasevit and D. H. Forbes, Brit. J. Appl. Phys., 37, 734 (1966).
33. H. Seiter and C. Zaminer, Angew. Phys., 20, 158 (1966).
34. T. A. Zeveke, L. N. Kornev, and V. A. Tolmasov, Kristallografiya, 13, 579 (1968).
35. J. D. Filby, J. Electrochem. Soc., 113, 1085 (1966).
36. R. W. Bickness, B. A. Joyce, J. H. Neave, and G. V. Smith, Phil. Mag., 14, 31 (1967).
37. D. J. Dumin and P. H. Robinson, J. Crystal Growth, 3, 214 (1968).
38. E. S. Vorontsov, S. P. Kaz'min, A. M. Mikulin, and G. F. Mikhina, Zashchita Metallov, 621 (1972).
39. S. M. Hu, J. Electrochem. Soc., 113, 692 (1966).
40. F. K. Herimann and D. M. Brown, J. Electrochem. Soc., 115, 99 (1968).
41. T. L. Chu, C. H. Lee, and G. A. Cruber, J. Electrochem. Soc., 114, 717 (1967).
42. R. E. Deal, P. J. Fleming, and P. L. Castro, J. Electrochem. Soc., 115, 300 (1968).
43. D. M. Brown, P. V. Gray, F. K. Herimann, H. R. Philipp, and E. A. Taft, J. Electrochem. Soc., 115, 311 (1968).
44. H. F. Sterling, Solid State Electronics, 8, 653 (1965).
45. T. L. Chu, J. R. Szedon, and C. H. Lee, Solid State Electronics, 10, 897 (1967).
46. R. C. G. Swann, R. R. Metha, and T. P. Cange, J. Electrochem. Soc., 114, 713 (1967).
47. V. Y. Doo, Trans. IEEE, Electron Devices, ED-13, 561 (1966).
48. A. E. Feuersanger, TIIER, 52, 1587 (1964).
49. F. Z. Keister, Trans. IEEE Component Parts, CP-12, 16 (1965).
50. R. T. Takemoto, Japan. J. Appl. Phys., 5, 844 (1966).
51. M. T. Duffy, C. C. Wang, A. Waxman, and K. H. Zaininger, J. Electrochem. Soc., 116, 234 (1969).
52. J. A. Aboaf, J. Electrochem. Soc., 114, 948 (1967).
53. A. Waxman and K. H. Zaininger, Appl. Phys. Letters, 12, 109 (1968).
54. M. Matsushita and Y. Koya, Abstracts, Electrochemical Society Meeting, 1968.
55. H. Nigh, Abstracts, Electrochemical Society Meeting, 1968.
56. S. K. Tung and R. E. Caffrey, Abstracts, Electrochemical Society Meeting, 1968.
57. K. H. Zaininger and A. Waxman, IEEE Trans. Electron Devices, ED-16, 333 (1969).
58. P. Gross and D. L. Levi, Symp. Extraction Metallurgy Some Less Common Metals, Inst. Mining Met., London, Paper 19, 1956.
59. E. S. Wajda, B. W. Kippenham, and W. H. White, IBM J. Res. Development, 4, 288 (1960).
60. F. B. Litton and H. C. Andersen, J. Electrochem. Soc., 101, 287 (1954).
61. G. Szekely, J. Electrochem. Soc., 104, 663 (1957).

62. C.S.Herrick and J.G.Krieble, J.Electrochem.Soc., 107, 111 (1960).
63. H.Schaefer, H.Jacob, and K.Etzel, Z.anorg. Chem., 286, 42 (1956).
64. F.Jona and G.Mandel, J.Phys.Chem.Solids, 25, 187 (1964).
65. H.Schaefer, "Chemical Transport Reactions" (Translated into Russian), Izd.Mir, Moscow, 1964.
66. F.Jona and G.Mandel, J.Chem.Phys., 38, 346 (1963).
67. K.Powell, J.H.Oxley, and J.M.Blocher, Jnr., "Deposition from the Gas Phase" (Translated into Russian), Atomizdat, Moscow, 1970.
68. N.V.Suikovskaya, "Poluchenie Tonkikh Prozrachnykh Plenok" (Preparation of Thin Transparent Films), Izd.Khimiya, Leningrad, 1971.
69. I.V.Alekhin and F.N.Petrov (Editors), "Slovar' Inostrannykh Slov" (Dictionary of Foreign Words), Izd.Inostr.Nats.Slovarei, Moscow, 1949, p.250.
70. "Kratkaya Khimicheskaya Entsiklopediya" (Short Chemical Encyclopaedia), Vol.2, Moscow, 1963, pp.181 and 247.
71. M.von Ardenne, "Physical Principles of the Use of Radioactive and Stable Isotopes as Indicators" (Translated into Russian), Inostr.Lit., 1948.
72. G.Hevesy, "Radioactive Indicators" (New York, Interscience, 1948) (Translated into Russian), Inostr.Lit., 1950.
73. Proceedings of the All-Union Conference on the Application of Radioactive and Stable Isotopes and Radiations in Soviet Industry and Science, Izd.Akad. Nauk SSSR, Moscow, 1958.
74. N.P.Peksheva and E.S.Vorontsov, Zashchita Metallov, 708 (1972).
75. H.von Wartenberg and S.Aoyama, Z.Elektrochem., 33, 144 (1937).
76. E.S.Vorontsov and A.A.Agapova, Izv.Vys.Ucheb. Zaved., Chernaya Metallurgiya, 8, 15 (1967).
77. N.F.Mott, Trans.Faraday Soc., 35, 1175 (1939).
78. N.Cabrera and N.F.Mott, Reports Progr.Phys., 12, 163 (1949).
79. E.S.Vorontsov and V.D.Suikovskaya, Izv.Vys. Ucheb.Zaved., Chernaya Metallurgiya, 11, 5 (1969).
80. F.Richardson and E.Dancy, Discuss.Faraday Soc., 229 (1948).
81. E.S.Vorontsov, Izv.Akad.Nauk SSSR, Metally, No.3, 51 (1968).
82. O.A.Esin and P.V.Gel'd, "Fizicheskaya Khimiya Pirometallurgicheskikh Protsessov" (Physical Chemistry of Pyrometallurgical Processes), Pt.1, Metallurgizdat, 1962, p.598.
83. S.T.Rostovtsev, "Teoriya Metallurgicheskikh Protsessov" (Theory of Metallurgical Processes), Metallurgizdat, Moscow, 1956, p.417.
84. E.S.Vorontsov, "Mekhanizm i Kinetika Vosstanovleniya Metallov" (Mechanism and Kinetics of the Reduction of Metals), Izd.Nauka, Moscow, 1970, p.56.
85. G.I.Chufarov and E.S.Vorontsov, Izv.Vys.Ucheb. Zaved., Chernaya Metallurgiya, No.9, 5 (1969).
86. E.S.Vorontsov, Izv.Akad.Nauk SSSR, Metally, No.1, 92 (1967).
87. E.S.Vorontsov and V.A.Kozheurov, Izv.Akad. Nauk SSSR, Metally, No.1, 230 (1971).
88. G.Tamman and W.Köster, Z.anorg.Chem., 123, 196 (1922).
89. E.S.Vorontsov and V.D.Suikoskaya, "Sbornik Nauchnykh Trudov Chelyabinskogo Politekhnicheskogo Instituta" (Scientific Proceedings of the Chelyabinsk Polytechnic Institute), No.78, Chelyabinsk, 1970, p.48.
90. E.S.Vorontsov, Uspekhi Khim., 34, 2020 (1965) [Russ.Chem.Rev., No.11 (1965)].
91. E.S.Vorontsov, Uspekhi Khim., 37, 167 (1968) [Russ.Chem.Rev., No.1 (1968)].
92. V.V.Boldyrev, Kinetika i Kataliz, 5, 571 (1964).
92. A.S.Tumarev and V.A.Pushkarev, Zhur.Prikl. Khim., 38, 267 (1965).
94. "Kratkaya Khimicheskaya Entsiklopediya" (Short Chemical Encyclopaedia), Vol.4, Izd.Sovetskaya Entsiklopediya, Moscow, 1965, p.76.
95. K.A.Koshkina and E.S.Vorontsov, Zhur.Prikl. Khim., 44, 209 (1971).
96. E.S.Vorontsov and A.N.Korneeva, Izv.Vys. Ucheb.Zaved., Chernaya Metallurgiya, No.7, 8 (1971).
97. A.N.Korneeva and E.S.Vorontsov, Zhur.Prikl. Khim., 45, 969 (1972).
98. A.N.Korneeva and E.S.Vorontsov, Zashchita Metallov, 629 (1972).
99. N.D.Tomashov and R.M.Al'tovskii, "Korroziya i Zashchita Titana" (Corrosion and Protection of Titanium), Mashgiz, Moscow, 1963.
100. H.Remy, "Lehrbuch det anorganischen Chemie" (Translated into Russian), Vol.1, Inostr.Lit., Moscow, 1966.
101. A.N.Korneeva and E.S.Vorontsov, Zhur.Fiz. Khim., 46, 1551 (1972) [Russ.J.Phys.Chem., No.6 (1972)].
102. A.N.Korneeva and E.S.Vorontsov, Izv.Vys.Ucheb. Zaved., Chernaya Metallurgiya, No.10, 18 (1971).
103. P.V.Gel'd and O.A.Esin, "Protsessy Vysokotemperaturnogo Vosstanovleniya" (High-temperature Reduction Processes), Metallurgizdat, Sverdlovsk, 1957, pp.137–188.
104. O.P.Kolchin, "Mekhanizm i Kinetika Vosstanovleniya Metallov" (Mechanism and Kinetics of the Reduction of Metals), Izd.Nauka, Moscow, 1970, p.40.
105. F.Walker (Editor), "Chemical and Physical Properties of Carbon" [sic] (Translated into Russian), Izd.Mir, Moscow, 1969, p.329.
106. V.P.Elyutin, Yu.A.Pavlov, and R.F.Merkulov, Symposium, "Primenenie Radioaktivnykh Izotopov v Metallurgii" (Use of Radioactive Isotopes in Metallurgy), Metallurgizdat, Moscow, 1955, p.48.

Voronezh Polytechnic
Institute, Physical
Chemistry Department