THE FORMATION OF DISCONTINUOUS OXIDE
FILMS ON TITANIUM DURING ANODIC
POLARIZATION IN ELECTROLYTE SOLUTIONS

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ABSTRACT

The anodic polarization of titanium in most electrolyte solutions results in the formation of thin uniform di-electric oxide films of titanium dioxide. Titanium dioxide is unattacked by most electrolytes and the thickness of the anodic film produced depends on the nature of the electrolyte, temperature, current density etc. At a constant current, provided the film is completely homogeneous, the potential will rise at a uniform rate as the thickness (and hence resistance) increases. Any deviations from the linearity of the potential/time curve at constant current will therefore denote a change in the nature of the di-electric oxide.

In the present study, such a deviation from the linearity of the potential/time curve was found in the region 7-12 V. The change in the nature of the oxide resulting in the deviation from linearity, has been studied using the various techniques described in the text. The change in structure of the oxide is considered to be physical and the nature of anodic films of titanium dioxide at formation voltages above 12 V is influenced by this phenomenon. The oxide in the region 7-12 V has been shown to be highly stressed and as a result fissured. At a critical voltage of 12 V the oxide blisters. The formation of a blistered anodic oxide film at such a low formation voltage is unusual and the unique anodic polarization characteristics of titanium in formic acid is shown to be related to this effect.

The anodic behaviour of titanium in formic acid has been studied in some detail and a theory for the phenomenon of "micropitting" discovered by Piggott and Shreir (1) has been put forward.
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INTRODUCTION

1.1. Growth of Oxide Films by Anodic Polarization

All anodic reactions involving a metal and an aqueous solution (in the absence of complex formation or formation of compounds other than hydroxides) follow one of the following overall processes:

\[ M^{z+} \rightarrow M_{aq}^{z+} + Z \epsilon \] ........................ (1)

\[ M + ZH_2O = M(OH)_z + ZH^+ + Z \epsilon \] ........................ (2)

\[ M + ZOH^- = M(OH)_z + Z \epsilon \] ........................ (3)

When certain metals covered with an air-formed oxide film, are made anodic in solution, the applied potential causes further growth of the film. An electrostatic field is set up in the oxide and this causes metal or oxygen ions to be pulled through the film and reactions at the metal/metal oxide or metal oxide/solution interface result in formation of oxide. With metals such as titanium, niobium or tantalum, oxides rather than hydroxides are produced during the anodic process. Thickening of the film is brought about by ionic conduction under very high field strengths. The process is almost one hundred per cent efficient with tantalum, but with other metals secondary anodic reactions such as oxygen evolution lower the efficiency of film growth.

If the oxide is a good electronic conductor and the anode potential is allowed to rise, anodic oxidation of the solution to oxygen occurs. This process may account for almost all the charge passing while the metal remains passive. If, however, the film is a poor electronic conductor, or if no electron producing discharge process is possible at the anode/solution interface, then more metal is changed into compound. Anodic oxidation or film growth then occurs and the metal cannot be said to be passive.

In all cases the anodic oxide film reaches a limiting thickness when
film breakdown occurs - this is frequently accompanied by spark discharge. Breakdown results from defects in the anodic film, e.g. cracks, blisters etc. Healing of these defects with simultaneous breakdown at other points may occur during anodizing at high potentials. If the film substance is attacked by the electrolyte solution it may be rendered porous and so more easily thickened by electrolyte penetration. Chemical stability of the oxide as regards hydration may also affect film stability. Combinations of the above phenomena are almost always found in practice.

1.2. Theory of Film Growth

The formation of insulating anodic oxide films on aluminium and titanium under conditions of ionic movement under a high electrostatic field was first systematically studied by Guntherschulze and Betz (3,4) who showed experimentally the relationship between current "i" and field strength in the oxide "F" could be related by an equation of the form:

\[ i = A \exp(BF) \] ............. (4)

Where A and B are constant and F is given by V/x, V being the potential across the film and x the film thickness.

For aluminium the following values for A and B were obtained:

\[ A = 3.6 \times 10^{-23} \text{ A/cm}^2 \]
\[ B = 4.25 \times 10^{-6} \text{ cm/volt}. \]

Equation 4 has been found to hold good at least to a first approximation. The field during formation was of the order \(10^7\) volts/cm and the growth rate \(10^0\) \(\text{A/V}\).

Films of this type may act as the dielectric of a capacitor. Application of the formula for a parallel plate capacitor shows that the capacity may be used to measure the thickness of the film, providing the permittivity is known.

Ionic conduction in crystalline solids occurs through the
movement of lattice defects\textsuperscript{(5, 6)}. These defects may be either vacancies or interstitials. Further complications arise, however, due to the existence of the metal/oxide and oxide/solution interfaces at which transfer processes must occur. The metal/oxide interface was taken into account by Mott\textsuperscript{(7)} and by Cabrera and Mott\textsuperscript{(8)}. A theory was presented to account for the formation kinetics of thin oxide films during low temperature oxidation of aluminium.

The above authors assume that a strong field is set up in the oxide layer by electrons which leave the metal and penetrate the oxide by the tunnel effect to enter vacant energy levels in oxygen atoms adsorbed at the oxide/air interface. They then show that if the oxide layer is sufficiently thin, the field change across it is very small and current is controlled by rate of entry of ions into the oxide, this being no longer proportional to the field strength $F$.

The current over the entrance barrier of the metal/oxide interface is assumed to be given by an expression of the same algebraic form as that for ionic movement within the oxide and the final expression obtained for the oxidation rate is identical in form to equation 4. In principle, for a thin film the above case of Cabrera and Mott should apply, but in practice there is clearly a physical limitation on the minimum thickness of an oxide film.

The anodic oxidation of a number of metals has been studied experimentally in recent years. In particular, aluminium, titanium, zirconium and niobium, all of which give stable non-conducting films. Charlesby\textsuperscript{(9)} has shown that in addition to ionic current flow which results in film formation, an electronic current also flows so that the complete relationship between current and field becomes:

$$i = i_+ + i_- = A \exp BF + C \sinh DF \quad \ldots \ldots \ldots \quad (5)$$

where $i$ = total current; $i_+$ = ionic current; $i_-$ = electronic current and $C$ and $D$ are constants.

The efficiency of film formation is then given by $i_+/i$. The validity of this relationship has been shown by Charlesby over a wide range of current densities for both aluminium and zirconium.
The current that does not form oxide may be expected to cause oxygen evolution - other reactions may occur however in particular solutions, e.g. persulphate, chlorine, iodine etc. Vermilyea has examined the anodic oxidation of tantalum in detail and has shown that the relation \( \frac{dF}{d \log i} \) should be proportional to the absolute temperature if the theory of Mott and Cabrera is to apply. In fact, the results to emerge were that the Tafel slope \( \frac{dF}{d \log i} \) was found to be independent of the absolute temperature. Dewald put forward a theory to account for this observed temperature independence of the Tafel slope found by Vermilyea. Dewald's theory takes into account the action of space charge formation due to a potential barrier within the oxide itself, in addition to the single barrier at the metal/oxide interface considered by Mott and Cabrera which may oppose the flow of ions.

The theory of Dewald explains the temperature independence of the relation \( \frac{dF}{d \log i} \) for films of a finite thickness (thousands of Angstroms) whereas, the Mott and Cabrera theory applies only in principle for a very thin film. However, as a film cannot be less than one cell thick, this means that the Mott and Cabrera theory can never reach the true limiting conditions. In the case of very thin films, where the space charge is negligible \( \frac{dF}{d \log i} \) shows temperature dependence to a close approximation.

1.3. Methods of Film Formation and Measurement

There are two simple techniques for studying the formation of anodic oxide films. These are: (1) constant ionic current and (2) constant voltage.

1.3.1. Formation at Constant Ionic Current

Each new layer of oxide of thickness \( dx \) formed at constant current requires an extra potential \( dV \) to maintain the field across the oxide film and \( dV/dx \) is called the differential field strength. As the film thickens so the resistance increases and in order to maintain a constant current the potential across the film must rise. The increase in voltage is proportional to the
increase in film thickness which in turn is proportional to the resistance for a uniform di-electric film.

\[ i = \text{const} = A \exp(BF) \]

therefore \( F = \text{const} = \frac{V}{x} \)  \( \ldots \ldots \) \( \ldots \ldots \) (6)

also, since the film thickness \( x \) is proportional to the charge passed,

\[ V \propto t \]  \( \ldots \ldots \) \( \ldots \ldots \) (7)

At constant current, therefore, voltage and film thickness are both linear functions of time.

The particular advantages of film formation at constant current are:

(a) formation takes place at a constant rate up to the maximum voltage, and any departure from linearity of the voltage and thickness/time curves owing to changes in efficiency, or in film composition are readily observed.

(b) The voltage drop across the electrolyte is constant.

However, the range of current densities which can be used is limited to about 100 : 1, by heating effects in the film at high constant currents, and low ionic efficiencies at low currents.

1.3.2. Formation at Constant Voltage

The application of a constant voltage to the thin air-formed film would produce initially a surge of high current. The usual procedure is to form the film at constant current to a preselected voltage, hold the voltage constant and allow the current to decay. Then

\[ i = A \exp \left( \frac{BV}{x} \right) \]  \( \ldots \ldots \) \( \ldots \ldots \) (8)

The advantage of this method is that a wider range of formation currents can be
obtained. Charlesby in his study of aluminium covered a current range of 1000 : 1 and was able to verify equation 4 by determining the decay of current, and the decrease in film capacitance with time. This method suffers from the disadvantage that the film is not formed under steady conditions; the total increase in film thickness during formation at constant voltage is only about 15% and a correction is necessary for the varying voltage drop across the anodizing cell.

1.4. Anodic Oxidation of Titanium

The present study originated from the use of anodic films on titanium as a means of preventing galling during wire drawing. A survey of the literature showed that Richaud\textsuperscript{(14)} formed anodic films on titanium in 20\% $H_2SO_4$ at 20\(^\circ\)C and 18 V and considered these to be porous or fissured as they had the ability to absorb lanoline. Miller, Jeffery and Pray\textsuperscript{(15)} found that the oxide film with the best anti-galling properties was obtained using 5\% NaOH at 205\(^\circ\)F. The use of a phosphoric/sulphuric solution at room temperature for anodizing titanium is a subject of a patent claiming that the oxide film prevents galling. It should be observed that claims for porosity have been based largely on the ability of the films to absorb oil.

The anodic behaviour of titanium in various solutions has been the subject of numerous studies concerned with the dielectric properties of the film, passivity of the metal, breakdown of the oxide etc. Böhm\textsuperscript{(16)} determined the i/t relationship at constant voltage (60V) in potassium hydroxide, borax, sulphuric acid and in chromic acid solutions and showed the oxide to behave as a typical valve electrode. However, when purer metal is used (Van Arkel process), oxygen evolution appears to occur more readily than film formation and the behaviour is far less like a valve electrode than is that of zirconium. The dependence of valve metal behaviour on purity of the metal is a problem on which almost no data has been obtained.

The majority of work in the literature refers to the formation of a barrier type oxide film. Hall and Hackerman\textsuperscript{(17)} have studied the anodic and
cathodic behaviour of titanium in neutral chloride solutions under galvanostatic conditions. At low current densities the potential was shown to increase linearly with time until the oxygen evolution value was reached, the potential then remained constant. They consider that their data does not permit an unequivocal choice between chemisorption or oxide film formation as a first step prior to oxygen evolution. These authors also studied film breakdown in chloride solutions and showed that breakdown and consequent pitting occurred at 12V. Haring's mechanism was used to explain pitting of titanium by chlorides. Cotton showed that pitting of this type can be prevented by having platinum in contact with the metal surface. Johansen, Adams and Van Rysselberghe studied the anodic oxidation of titanium at low current densities using boric acid and ammonia at pH 8 and 25°C and report the formation of anodic oxide films below the oxygen evolution potential. Tajima and Mori have claimed that films can be formed to 1300V in borate solutions.

The anodic protection of titanium in non-oxidizing acids has been studied by Inglis and Cotton and they have shown that in 40% sulphuric acid at 60°C a slight increase of potential results in a marked reduction in the corrosion rate.

The anodic behaviour of titanium in formic acid was first studied by Piggott and Shreir and the effects appear to be unique. The present work provides a more detailed study of the above system. The corrosion behaviour of titanium in formic acid has been studied by Lane, Golden and Ackerman who have shown that titanium is passive provided oxygen is present. In oxygen free solutions, the metal exhibits the phenomenon of "border line" passivity and the behaviour depends on the thickness and continuity of the air formed film, smoothness of surface etc. It would appear that either corrosion or passivity could result when apparently identical specimens were immersed in the same solution of formic acid. Examples of "border line" passivity have also been reported by Hutchinson and Permar.

By analogy with aluminium, it was considered that the electrolyte solution should be such that film growth and localised film dissolution could
proceed simultaneously during anodizing in order to produce porous or fissured films. In an attempt to produce such films, Piggott and Shreir decided to use formic acid because of its corrosiveness and its manifestation of the phenomenon of "border line" passivity.

1.5. Anodic Oxidation of Aluminium

The work discussed above refers to the formation of barrier films only. In the case of aluminium, however, thick porous films may be produced under certain conditions. The electrolyte solution determines whether a barrier film or thick porous film will be produced. The latter type is produced in solutions of sulphuric, phosphoric, oxalic, or chromic acid and is distinguished from the barrier type by the fact that it will grow at almost constant voltage to a thickness of many microns. It now appears to be apparent that porous films are formed in electrolytes which dissolve the oxide at an appreciable rate. The excellent corrosion resistance of titanium due to the refractory nature of the oxide, means that a barrier film would be produced under conditions where a porous film would be produced on aluminium.

Pore formation in anodic aluminium films has been explained by Hunter and Fowle\(^{(25)}\) by simultaneous formation and dissolution of the film. The concentration of pores has been estimated at $4 \times 10^8 \text{ cm}^{-2}$ by Rummel\(^{(25)}\). The pores are believed not to penetrate the film completely, the thickness of unpenetrated films being called the "barrier layer thickness". Booker, Wood and Walsh\(^{(27)}\) showed that the pores formed on aluminium are in regular arrays with hexagonal packing of the pore channels.

Keller\(^{(28)}\) suggested that once a pore has started due to some locally high rate of dissolution, an increased current flows at this point. This causes a local increase in temperature which in turn causes the local rate of dissolution to increase. It is considered that oxygen is the mobile species rather than the metal. Metal movement would lead to production of oxide at the oxide/solution interface and would tend to block the pores. Hoar and Mott\(^{(29)}\) have suggested that extra dissolution at the base of the pores is a field enhanced process. These
workers also postulate that OH\(^-\) ions (not O\(^-\) ions) move through the oxide to the metal where they react with metal ions releasing H\(^+\) ions which move back through the oxide. The mechanism of growth of the porous films still remains an open question however.

Franklin\(^{30}\) has shown that non-porous films also have a pronounced cellular structure. Barrier films up to 5000V have been produced in boiling borate solutions. In general, thin films on aluminium are amorphous and the thick anodic films are crystalline.

1.6. Chemistry and Properties of Titanium

Titanium is widely distributed in the earth's crust (0.6%) and also throughout the universe, being almost always associated with oxygen in the natural state. In the Periodic Table of Elements, titanium is situated in the first Long Period and in Group IV A. The metal exists in two allotropic forms. At low temperatures, below 882\(^\circ\)C, the structure is hexagonal close packed with a c/a ratio of 1.663. Above the transition temperature the structure is body-centred cubic.

The density of titanium is 4.505 g/cm\(^3\) and the melting point approximately 1750\(^\circ\)C. This gives the metal good properties under conditions of high stress at elevated temperatures.

1.7. Corrosion Resistance of Titanium

The corrosion behaviour of titanium in aqueous solutions is characterised by a marked tendency of the metal to exhibit passivity. Stern and Wissenberg\(^{31}\) have shown that although the exchange current for the hydrogen reaction and other electrochemical reactions is low (a condition which is not conducive for the establishment of passivity), this is offset by the unusually electronegative critical potential (approximately -0.23V with reference to the saturated calomel electrode) required for passivity. The metal thus exhibits passivity in solutions of redox potentials no higher than that of the
2H⁺ + 2 = H₂ equilibrium, so that passivity can be achieved by alloying or coupling the metal with platinum or palladium.

Titanium exhibits excellent corrosion resistance to most chemicals when corrosion is of a uniform type. The resistance of titanium to direct chemical attack is due to the protective oxide film on the surface. Thus oxidising acids or salts have less effect than reducing agents. Titanium has been shown to be corroded to any appreciable extent only by the four mineral acids, hydrofluoric, hydrochloric, sulphuric and orthophosphoric; by four organic acids, formic, oxalic, trichloracetic and trifluoracetic and also by the inorganic salt ammonium chloride.

It has been shown by Inglis and Cotton (22) that anodic polarization of titanium increases the corrosion resistance in non-oxidizing acids.

1.8. The Oxides of Titanium

Titanium forms oxides having oxidation stakes of + 2, + 3 and + 4. Titanium monoxide, TiO, is prepared by the high temperature reduction of the dioxide by carbon, magnesium or titanium. Titanium Sesquioxide, Ti₂O₃, is formed from the reaction:

\[ 2\text{TiO}_2 + \text{H}_2 = \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \quad \ldots \ldots \ldots \quad (9) \]

Both TiO and Ti₂O₃ are basic oxides. The dioxide TiO₂ occurs in nature in three mineral forms, rutile, anatase and brookite. Rutile and anatase have tetragonal forms, while brookite is rhombic (32). Titanium has been shown to be an n-type semi-conductor (metal excess) (33, 34). The addition of WO₃ dissolved in TiO₂ raised the electrical conductivity, while Ga₂O₃, Al₂O₃ and NiO, ions of lower valency, reduced the conductivity. The affinity of TiO₂ for acids is very small and the ignited oxide has been formed to dissolve only in hydrofluoric acid. TiO₂ is an amphoteric oxide.

Further less common intermediate oxides of titanium have also been reported; these include Ti₃O₄, Ti₅Oₐ and Ti₇O₁₂. Salts of the dioxide are
known as titanic salts; salts of the divalent and trivalent metal are known as
titanous salts. Hydroxides corresponding with many of the above oxides are
known.

1.9. Nature of the Anodic Film on Titanium

Some studies have been made of the structure of the anodic oxide on
titanium. Yamaguchi\(^{(35)}\) has examined stripped films and found brookite to be
present. Anatase was found to be the structure of the anodic oxide produced on
titanium by Harrington and Nelson\(^{(36)}\). The nature of the oxide layers produced
in a wide variety of electrolytes was investigated by Rivolta\(^{(37,38)}\). Both rutile
and anatase as well as hydrated oxides were detected under the various conditions.
Titanium hydride was also detected by electron diffraction, presumably as a
result of etching in hydrofluoric acid. Using optical microscopy, Rivolta showed
that the interference colour varied with the orientation of the grains. He
considered that this was due to different thicknesses of oxide on different grains.
There is a possibility, however, that this is an indirect effect due to variations
in the pre-existing films. The structure of the anodic film has also been studied
by other workers\(^{(39-43)}\) using electron diffraction.

1.10. Discontinuous Anodic Oxide Films

Discontinuous oxide films are frequently formed during the high
temperature oxidation of "valve" metals\(^{(44,45)}\).

Vermilyea\(^{(46)}\) has reported the formation of such films during anodic
oxidation in the case of tantalum and Lakhiani and Shreir in the case of niobium\(^{(47)}\).

Under the effect of a constant field strength at constant current, the
increase in thickness with time \(\frac{dx}{dt}\) and the increase in voltage with time \(\frac{dV}{dt}\)
are linear functions. Any change in the nature of the oxide, breakdown or
dissolution of the film will therefore result in a departure from linearity.
Vermilyea considers that in the case of tantalum, an amorphous film first forms
on the metal surface; nucleation and crystal growth then occurs underneath this
amorphous film at the oxide/metal interface. Rupture of the amorphous film occurs as the crystalline areas grow from underneath and both crystalline and amorphous oxide may then be seen on the surface using electron microscopy. This type of crystallisation under the influence of high field strengths is known as "field crystallisation".

The recrystallisation process depends on (a) the metal, (b) the method of surface preparation, (c) the formation procedure, (d) the temperature, (e) the field strength and (f) the nature of the solution.

A similar phenomenon of field crystallisation was observed by Lakhiani and Shreir in the case of niobium in acetic acid solutions. In sulphuric acid of comparable concentration, field crystallisation did not occur and then amorphous films were formed. Lakhiani and Shreir produced thick grey absorbing films by allowing the crystallised films to grow. A weight gain of $0.6 \text{ mg/cm}^2$ was obtained and such a film was thus considerably thicker than the uniform barrier film which exhibits interference colours.

In the present work discontinuities have been found in the voltage/time curve produced during the anodic oxidation of titanium in various electrolytes.

Surface roughness may also affect the linearity of the voltage/time curve. Vermilyea (11) reported that $\frac{dV}{dx}$ increased with increasing voltage during formation at constant current when the surface was prepared in various ways, the common factor being roughness. It was suggested that the increase in $\frac{dV}{dx}$ was due to an increase in the current density. Part of the surface is insulated by oxygen bubbles which form where electrical breakdown occurs at rough surfaces. The effect is therefore most pronounced with rougher surfaces.

Young (48) reports the occurrence of microfissures in barrier films on tantalum and zirconium. These discontinuities in the films were detected by impedance measurements. Young concluded that with tantalum, microfissures were responsible for the phenomenon of electrolytic rectification. The irreproducibility of the anodic leakage current from specimen to specimen serves as an indication of the presence of microfissures.

Discontinuities may also be formed due to either compressive or
tensional stresses in the oxide. A discussion of the formation and effects of such discontinuities in anodic films on titanium will constitute a later part of this thesis.

1.11. **Object of the Research**

The object of the present research has been to study the factors affecting the nature and mechanisms of formation of anodic oxide films on titanium. In particular the effect of discontinuities in the film as regards its properties has been studied.

It was considered that the work done by Piggott and Shreir\(^{(1)}\) on the titanium/formic acid system and in particular their experimental techniques for studying the phenomenon of micropitting did not give conclusive results. A more accurate study has therefore been made of the above system and further developments made as regards the mechanism of micropitting breakdown using electron microscopy, and incorporating more delicate recording equipment for the electrical studies.
2. **EXPERIMENTAL PROCEDURE**

2.1. **Materials**

The titanium was supplied by I.C.I. Ltd. in the form of sheet 0.035 cm. thick. In the initial experiments unmounted specimens were used as anodes and two sheets of platinum foil (1 cm x 1 cm) were used as cathodes. The purity of the metal was commercial grade (I.C.I. 130A). A typical analysis was 0.03% C, 0.05% Fe, 0.015% N, 0.005% H and 0.1% O. Large crystals of titanium (iodide process) were obtained from Watertown Arsenal, Cambridge, Massachusetts; however, these were found to have inclusions and proved unsuitable for single crystal studies.

Reagents used were AnalaR grade and all solutions prepared from doubly distilled water. Concentrations of solutions of formic acid are expressed as vol%.

2.2. **Surface Preparation**

The effect of surface preparation is most important as regards the behaviour of titanium during anodizing. The various methods used are as follows:-

(a) mechanical polishing
(b) electrolytic polishing
(c) chemical polishing.

(a) **Mechanical Polishing**

The production of a well polished surface on a metallographic specimen of titanium or a titanium base alloy is made more difficult by the tendency of the metal to pit and flow during polishing. Flow of the metal may be avoided in two ways: (a) careful hand polishing using a good lubricant, or (b) removing the flowed layer as fast as it is produced by polishing on a high speed wheel, using a coarse cloth dampened with a dilute etchant and applying heavy pressures.

In the present work method (a) was used although this can be an
extremely laborious and time consuming process. The specimens were mechanically polished to 3/0 emery paper and then on one micron diamond dust. All specimens were degreased in trichlorethylene and washed in distilled water after each buffing operation. The specimens were finally washed using ethyl alcohol and dried using a hot air dryer to avoid staining of the metal surface.

(b) Electrolytic Polishing

This method has the great advantage of avoiding surface flow, and is used in routine work on a large scale. The method used is largely dependent, however, on the nature and chemical composition of the specimen. Perchloric acid is a common reagent used for the electrolytic polishing of titanium; however, there is always the danger of explosion if the bath is allowed to become warm. Probably the most satisfactory solution is that recommended by Rem-Cru Titanium Inc. and has the following composition:

90 ml ethyl alcohol
10 ml n-butyl alcohol
6 g anhydrous AlCl₃
28 g anhydrous ZnCl₂

This solution may be used for polishing specimens mounted in plastic materials. The above solution is extremely corrosive, however, and should be stored in glass or polythene containers. It is stable for about one week after preparation.

(c) Chemical Polishing

As titanium and its alloys are extremely resistant to attack by dilute solutions of the common acids and alkalis at room temperature, the solutions used for etching or chemical polishing must invariably contain hydrofluoric acid. The composition of the solution used in the following study was:

1 part 97% Sulphuric Acid
1 part 75% Nitric Acid
1 part 44% Hydrofluoric Acid
1 part water.

The time of immersion in this solution was two minutes. This period was assumed to remove almost all particles of diamond dust or emery which
became embedded in the metal during mechanical polishing.

Experiments carried out on weight losses during etching suggest that the decrease in thickness during etching is approximately 1 micron/minute.

The surface preparation used as standard in the present study consisted of mechanical polishing as described above, followed by chemical polishing for two minutes in the above polishing solution. This method was found to give the best reproducibility.

2.3. **Mounting of Specimens**

For most of the voltage/time studies sheet specimens were used. However, for the more exact studies such as current decay, leakage current measurements and rectification studies, mounted specimens were considered more desirable. Mounting the specimens permitted more exact surface preparation and the use of the same specimen more than once. Unmounted specimens were used only once. However, mounting has several advantages over the thin foil specimens which are often used for studying anodic oxidation. Firstly, grinding and mechanical polishing is simplified and secondly the current distribution over the surface of a mounted specimen has been found to be more uniform than with an unmounted sheet, where current concentrates preferentially at the edges.

2.4. **Anodizing**

Voltage/time studies (at constant current) were made in a series of electrolytes under various conditions of concentration, temperature, current density etc. The following electrolytes were studied:

- Sulphuric acid, sodium sulphate, sodium chloride,
- sodium hydroxide, sodium formate, sodium oxalate,
- oxalic acid, formic acid, acetic acid, ammonium formate
- ammonium chloride and formaldehyde.

Current/time studies (at constant voltage) were made in many of the above electrolytes with temperature and concentrations as variables. For
constant voltage anodizing the film was first formed at constant current to a pre-determined voltage (thickness) and when this was reached anodizing was continued at constant voltage.

2.5. **Design of Cell**

The following characteristics were considered important in designing a cell for the present study.

(a) An anode, so mounted that its relative position to the cathodes could be altered if necessary. Space for either mounted or unmounted specimens was allowed for.

(b) Two cathodes, arranged at right angles to the anode in order to give the most uniform current distribution. In the case of mounted specimens, one cathode could be used. The cathodes were fitted on interchangeable syringes in order to permit variation of the cathode/anode distance.

(c) Provision for the use of a reference electrode. This was necessary under those conditions where the absolute potential of the anode was required.

(d) Facilities for agitation of the electrolyte near the anode by means of a high velocity gas stream (nitrogen or argon)

(e) Avoidance of all other materials other than glass and polytetrafluorethylene p.t.f.e. in order to minimise the effect of impurities.

(f) Variation in the temperature of electrolyte was required. This was brought about by the introduction of an immersion heater and thermoregulator. Control of temperature by this means (in conjunction with agitation) was ± 0.2°C.

A photograph of the electrolytic cell is shown in Fig. 2B and a diagram of the same cell in Fig. 2A.
The cell was approximately 250 ml capacity. The final arrangement of the cell is shown in the diagram. The anode was mounted in a syringe (A) by means of a p.t.f.e. gland, slightly tapered on the outer diameter so as to give a tight fit. The cathodes (1 x 1 cm) were platinum sheet and held in the syringes C.

The method of entry of the heater (H) and thermoregulator (T) are shown. The upper part of the cell was fitted to the lower by means of a Quickfit socket (B.55) and all joints fitted with p.t.f.e. sleeves. These prevented seizing up of the joints, particularly after experiments at high temperatures.

When the reference electrode was in use it was inserted by means of Quickfit sockets and cones into the syringe (R). The capillary could then be rotated so as to permit a variation in distance from the tip to the surface of the anode.

The cell was kept at as small a volume as possible owing to the cost of formic acid, the main electrolyte used in this study. For this reason it was found that the nitrogen agitator (N) had to be directed on to the anode face at a slight angle. This in fact proved to be an advantage as the direction of flow of gas could be arranged to be in any direction over an arc of about 1 cm.

2.6. Electrical Circuits
2.6.1. Power Supply

The electrical circuit used for anodizing is shown in Fig. 2C. A constant current and constant voltage unit (fully stabilised d.c. up to 100 mA and 350-400V) was developed, based on a design by A. Stebbings (49).

**Constant Current Supply Specification**

Ranges: 0 - 1 mA; 0 - 5 mA;
0 - 20 mA; 0 - 50 mA.

Maximum Voltage: 300V
Output impedance (with compensation) 300 Mohms
Maximum negative output impedance: approx. -50 Kohms
Output ripple: less than 7 mV r.m.s. at all settings.
Regulation (when fed via stabilising transformer): $\pm 0.2\%$ in
input current for $\pm 12\%$ input voltage variation.

**Constant Voltage Supply Specification**

- **Range:** 0 - 300 V.
- Maximum current: 50 mA (100 mA for short periods)
- Output impedance: Approx. 6 ohms.
- Output ripple: Less than 1 mV r.m.s. at all settings.

### 2.6.2. Instruments

**Valve Voltmeter**

The valve voltmeter used (Mullard, Type E 7555/2) had an
extremely wide range scale (0.5V - 15,000V). This was used as a visual
guide to cell voltage during anodizing. This instrument was also used for low
current density experiments and open circuit potential studies.

**Recorder**

A pen recorder (Leeds Northrup, Speedomax H) was used to give
permanent recordings during the voltage/time studies. The full scale
deflection of the recorder was 5mV, and therefore the cell voltage was reduced
through an attenuator to give the corresponding full scale deflection on the
recorder. By means of a switch in the attenuator the full scale deflection on the
recorder could be adjusted to give 30, 60, 100 or 200V. Voltage/time
relationships at constant current were obtained as direct plots on the recorder
chart, and all curves in the present work are shown as tracings of the recorder
curve.

**Milliammeter**

In order to give exact values of the current produced from the
constant current apparatus, an Avometer (Mark 8) was connected in series with
the main output supply.
CELL USED FOR ANODIZING

LEGEND

A. Anode Holder
B. Cathode Holders
H. Heater
T. Thermoregulator
R. Reference Electrode Holder
N. Nitrogen gas agitator
Capacitance Bridge

The capacity of the oxide coated electrode, in series with a subsidiary electrode of platinum sheet was measured by a Universal bridge (Wayne Kerr Ltd. Type B.221) with the following specifications:

- Capacitance Range: 0.1 pF to 11 pF
- Accuracy better than \( \pm 0.25\% \)
- Conductance Range: \( 10^{-1} \) to \( 10^{-8} \) mhos
- Frequency: 1592 cps.

The capacity of the subsidiary electrode was much greater than that of the oxide electrode so that the impedance measured was that of the latter. The equation for the value of the capacitance of a uniform di-electric is as follows:

\[
C = \frac{K \varepsilon}{x} \quad \ldots \ldots \ldots (10)
\]

A small error is introduced by the presence of an electrical double layer in the solution near the specimen. The electrical double layer on a film free metal electrode consists of a layer of charge on the metal facing a layer of opposite charge sign due to an excess of ions of one sign in the adjacent solution and thus produces a high capacity per unity area. The capacity measured was slightly less therefore than would be obtained with a double layer of infinite capacity and the estimated thickness of the oxide is therefore greater by a constant amount \( 50 \). However, the error is negligible for films thicker than \( 200 \).
high as $^{\pm} 0.02$ mg. Other factors which might influence the accuracy of weighing are as follows:

(a) The area of the specimen used for weight determinations was larger than that for other experiments. The area of the specimens used in the present studies were 32 cm.$^2$ and typical weight gain values were 0.5 mg. The error in area was assumed to be correct to 1%.

(b) As titanium oxidises only slowly in the air, any film which formed during the period between etching and anodizing was so negligible as to be neglected.

(c) The effect of adsorption of moisture from the electrolyte during anodizing was found to have no effect. Anodized specimens were thoroughly dried at $105^\circ$C but there was no decrease in weight as compared with specimens dried at room temperature. Moisture was therefore not assumed to be adsorbed.

(d) Colorimetric analysis has shown that when barrier films form the amount of titanium entering into solution is negligible.

The error in weighing was therefore a combination of inaccuracies in weighing and surface area. Thus for a weight gain of 0.5 mg:

\[
\text{Error due to weighing } = ^{\pm} 0.02 \text{ mg.} \\
\text{Error due to surface area } = ^{\pm} 0.02 \text{ mg.} \\
\text{Total error } = ^{\pm} 0.04 \text{ mg.}
\]

Thus the total error for a weight gain of 0.5 mg adds up to 0.04 mg (i.e. 8%) but this will decrease as the weight gain increases.

2.8. Experimental Measurements and Techniques

Various techniques were used to study the nature of the film growth.
FIG. 23.
These include:

(a) Voltage/time studies at constant current
(b) Current/time studies at constant voltage
(c) Resistance measurements
(d) Capacity measurements
(e) A.C. Rectification studies
(f) Stress measurements in the oxide
(g) Optical Microscopy
(h) Electron Microscopy
(i) Weight change studies

(a) **Voltage/Time Studies**

With the current kept constant the change in potential between the titanium anode and platinum cathode was measured. Any change in linearity of the voltage/time curve would indicate either a change in efficiency, a change in structure, or the formation of discontinuities or cracks due to stresses in the oxide film. In the majority of the studies here, the cell voltage and not the absolute potential of the anode was measured, as the electrolyte resistance in most cases was negligible in comparison with the overall resistance of the circuit.

(b) **Current/Time Studies**

The cell voltage was first allowed to rise under the influence of a constant current. When the required voltage was reached it was held constant and the current allowed to decay. This type of study was used for the measurement of leakage currents under various conditions. The technique was also useful in rectification studies.

(c) **Resistance Measurements**

Measurement of the resistance of the oxide in the "normal" direction is considered to be the direction of current flow when the titanium was made the cathode, and the "reverse" direction with titanium as the anode. The resistance/thickness curve for the oxide should be linear under ideal conditions,
and any deviations should therefore tend to show the presence of micro-cracks etc.. Such cracks would allow electrolyte penetration with a corresponding decrease in oxide resistance.

(d) Capacity Measurements

This technique was again used as a means for detecting the presence of discontinuities in the oxide. The relationship between V and 1/C should be linear for a uniform dielectric, the value of 1/C increasing as the film thickens. Change in capacitance with time was studied. If the capacity increases with time it would suggest that the oxide film is porous and discontinuous (51-54).

(e) A.C. Rectification Studies

"Normal" and "reverse" flow of current was measured at various constant voltages and rectification ratios calculated. Values of rectification ratio were then plotted against further variables such as input voltage, film thickness, temperature etc.. It was considered that the results obtained would give some insight into the effects of discontinuities in the oxide on the rectification characteristics. In certain experiments, the anodic oxide film was used to study full wave rectification of 50 c.p.s. mains voltage.

(f) Stress Measurements

The measurement of stress in the anodic film on titanium was carried out using the method of MacNaughton and Hothersall (55). The high ratio of the molecular volume of oxide to atomic volume of titanium indicates that high stresses in the film may exist and may affect the anodizing characteristics.

(g) Optical Microscopy

Optical microscopy proved to be an invaluable tool both for the study of titanium surfaces before anodizing and the oxide surface after anodizing. The colour variations across the various oxide grains could be studied particularly well using optical microscopy (examples are shown later).

(h) Electron Microscopy

The use of the electron microscope has shown the existence of
minute discontinuities on the oxide surface. The initiation of such
discontinuities leading to eventual breakdown could be followed only by using the
electron microscope.

(i) Weight Change Studies

Weight change/voltage curves was calculated in order to give the
"growth rate" of the oxide in \( \frac{\Delta}{V} \). Weight gain/voltage curves should be
linear (at least in the initial stages of anodizing and therefore once again, any
deviations would tend to indicate faults in the structure of the oxide).

The experimental procedure used in the above techniques have been
described in their respective sections. The techniques described above for
anodizing and studying the kinetics of film growth permitted a systematic and
exact study of the anodic oxidation of titanium.

2.9. Formation of Anodic Oxide Films on Titanium

Oxide was formed by polarizing the titanium positively at constant
current density against either one or two platinum electrodes. In order to keep
a constant current density, a constant electrostatic field strength in the oxide
is required. With a constant electrostatic field the voltage across the cell should
rise linearly with time. The rate of increase in voltage across the cell depends on
the nature of the electrolyte, current density, temperature and surface preparation
and in the case of 95% formic acid, may rise rapidly to approximately 400V.
Any departure from linearity over the voltage/time curve owing to change in the
nature or composition of the film was readily observed on the pen recorder
chart. The oxide films formed were further studied using the techniques
outlined above to elucidate their more precise mechanisms of formation.
3. PRELIMINARY EXPERIMENTS

3.1. Introduction

The fundamental factors influencing the nature of anodic films on metals are:

(a) nature of the electrolyte solution
(b) concentration of electrolyte solution
(c) current density
(d) temperature
(e) surface preparation.

Hunter and Fowle\(^{(25)}\) have shown that in the case of aluminium the nature of the films formed depends mainly on the nature of the solution. For any particular solution, the temperature and concentration appear to control the rate of dissolution at the base of pores in thick porous films.

The effect of the above variables was considered to be an essential feature as a preliminary study of the nature of anodic films on titanium. It was borne in mind, however, that the effect of these variables on porous films on aluminium would not necessarily have the same effect on barrier films on titanium.

The first of these variables to be studied, both as regards the nature of the films produced and as a means of acquiring reproducibility, was the effect of surface preparation. As a continuation of the work of Piggott and Shreir on the titanium/formic acid system, formic acid was chosen as the main electrolyte for a study of concentration, current density and temperature effects. Various other electrolytes have also been studied.

3.2. Effect of Surface Preparation

Preliminary investigations showed that variations in the nature of the metal surface greatly affected the form of the voltage/time curve. Before determining the final voltage/time curves, therefore, it was necessary to both standardise the method of surface treatment and study the more detailed effects
of different surface preparations.

All other variations were kept constant and the effect of surface preparation on the anodic oxidation of titanium was studied using 20% formic acid at a c.d. of 2 mA/cm$^2$ and at a temperature of 25°C. The specimens were subjected to the various surface treatments shown in Table 3.2.1. The effect of surface preparation on the voltage/time curve is shown in Fig. 3A.

In order to give good reproducibility it was found necessary to completely remove any mechanically polished surface layer. It was, however, necessary to remove this work-hardened layer under carefully controlled conditions and to remove surface contamination, e.g. emery or diamond particles. Although the pick up of such particles is not as great in the case of titanium as with softer metals such as niobium, Piggott$^{(56)}$ has found that titanium will retain diamond particles even after very prolonged etching, as shown by electron diffraction patterns.

The specimens, which were chemically etched for ten to thirty seconds (2 and 3) after mechanical polishing, did not give good reproducibility. This was probably due to insufficient time for etching and hence incomplete removal of both the mechanically polished surface layer and impurities such as emery and diamond. Specimen No. 6 which was chemically cleaned for 120 s gave reproducible voltage/time curves and more prolonged times of etching did not appear to affect the results significantly. It would therefore appear that an immersion time of 120 s was sufficient to remove any surface irregularities, whether due to the work hardened layer or impurities.

The voltage/time characteristics of specimens 1 and 4 were of some interest. These specimens having slightly rough surfaces, showed an increase in the rate of oxidation even at the relatively low oxide formation voltage of 15V.

It is also of particular interest to note that the maximum formation voltage appears to be affected by the amount of highly conducting impurity left embedded in the oxide after mechanical polishing. Fig. 3B shows the effect of diamond particles left after polishing to 1 micron diamond and shows that the
maximum formation voltage on a mechanically polished surface is less than when the surface is chemically polished owing to highly conducting impurities in the former.

**TABLE 3.2.1.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Mechanical treatment</th>
<th>Etching time</th>
<th>Nature of Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/0 emery</td>
<td>Nil</td>
<td>Rough</td>
</tr>
<tr>
<td>2</td>
<td>3/0 emery</td>
<td>10s.</td>
<td>Rough</td>
</tr>
<tr>
<td>3</td>
<td>3/0 emery</td>
<td>30s.</td>
<td>Etched</td>
</tr>
<tr>
<td>4</td>
<td>Nil</td>
<td>Nil</td>
<td>Rough</td>
</tr>
<tr>
<td>5</td>
<td>3/0 emery</td>
<td>1 min.</td>
<td>Etched</td>
</tr>
<tr>
<td>6</td>
<td>3/0 emery</td>
<td>2 min.</td>
<td>Etched</td>
</tr>
</tbody>
</table>

The following theory is proposed to account for the low maximum voltage obtained when impurities such as emery and diamond are present on the titanium surface. This effect is particularly pronounced with solutions which give thin films e.g. sodium sulphate.

Initially, a thin oxide film will form on the anode in those areas free from impurity. This oxide film resists the flow of current by virtue of its high resistance and most of the current then passes through the highly conducting silicon carbide or diamond (e.g. for silicon carbide, the electrical resistivity is only approximately 0.5 ohm/cm at 20°C). The oxide never becomes thick enough to detach the particles from the surface and so for the same specimen under the same conditions of anodizing, the maximum formation voltage will be less for that containing embedded highly conducting particles.
FIG. 3A

EFFECT OF SURFACE PREPARATION ON V/t CURVE.
The effect of increased conductivity of the oxide due to embedded particles results in a much higher electronic (leakage current) and hence a lower maximum formation voltage.

In the case of electrolytes which form thicker films (e.g. 90% formic acid) no difference in maximum formation voltage was observed after different surface treatments. This is probably due to the fact that the highly conducting particles become detached before the maximum formation voltage is reached. The high field in the vicinity of the emery or diamond particles may result in rapid growth of the oxide film around these particles until they become detached. Alternatively, gas evolution at these particles may cause them to become detached.

The "as received" material was in the form of rolled sheet and it can therefore be assumed that the surface contained many rolling defects (as inclusions or mecanical defects). No two specimens were therefore alike.

It is evident from Fig. 3A, that the rougher the surface, the greater is the slope of the voltage/time curve. This appears to be contrary to observations made on other metals e.g. tantalum and with leaky specimens (e.g. abraded) the current efficiency was found to be low during anodic polarization.

In the case of titanium, however, stresses are produced in the oxide and breakdown occurs while it is still relatively thin. Where breakdown of the oxide occurs, Young\(^{(57)}\), has shown that progressively less charge is required to form oxide to a given potential at a fixed current density and proposes the following theory for the increasing value of $dV/dt$ with rough surfaces. If the original surface discontinuities are large enough, the stresses in the film will reach a value at which breakdown occurs. It follows that failure may occur in several ways but irrespective of the method of failure it will result in a leakage channel across the oxide. The resultant high current then evolves oxygen which becomes trapped in the fault, pushing out electrolyte and so insulating the leakage channel. The local rise in temperature may then cause a local thickening of the oxide. The effect of the failure of the oxide, by whatever theory, is that $dV/dt$ increases with increasing voltage.
FIG. 3B
EFFECT OF CONDUCTING PARTICLES ON THE "MAXIMUM FORMATION" VOLTAGE IN 0.1M SODIUM SULPHATE SOLUTION.
With titanium, owing to the low voltage at which faults occur, the increase in \( \frac{dV}{dt} \) occurs at a lower voltage and the apparent effect is that the rougher surfaces give steeper slopes of \( \frac{dV}{dt} \), very soon after the onset of polarization.

From the above studies it appears fairly evident that the course of anodizing depends to a large extent on the production of a reproducible surface. The electrical properties of the films may be quite different depending on the nature of the surface. Chemical treatment after polishing is considered very necessary in obtaining a uniform surface and the following treatment was carried out as a standard method of preparation in all the following studies: polishing to 1 micron diamond, followed by etching for 120 s in the acid solution previously mentioned.

3.3. The Effect of Various Electrolytes

The anodic oxidation of titanium in various electrolytes has been the study of previous investigations by Rivolta \(^{(37)}\). The preliminary experiments carried out here permitted a study of the effect of the nature of the electrolyte and electrolyte concentration on the voltage/time characteristics. In addition to studying a selection of electrolytes at random, a particular study of the voltage/time characteristics of the titanium/formic acid system was made.

The electrolytes studied could be classified as corrosive and non-corrosive and voltage/time studies were carried out at low and high temperatures in both types of electrolyte.

3.3.1. Anodic Oxidation of Titanium at 25°C

The results of a study made of the anodic oxidation of titanium in various electrolytes is shown in Fig. 3C. In sodium hydroxide and sulphuric acid solutions (5%), the thickness of the films was limited and the maximum thickness decreased with increasing concentration of electrolyte. Film breakdown occurred easily, as shown by a sudden drop in cell voltage followed
FIG. 3C

EFFECT OF VARIOUS ELECTROLYTES ON THE V/t CURVE

- Oxalic Acid
- Sulfuric Acid
- Sodium Sulfate
- Acetic Acid
- Sodium Formate

Time (min)

Potential (V)
by voltage oscillations. This effect was particularly noticeable in sodium hydroxide solution, where after breakdown, the cell voltage never rose above approximately 15V.

With the higher concentrations of these electrolytes larger quantities of titanium were dissolved as shown by a yellow coloration of the electrolyte. It was therefore concluded that any thin anodic oxide films which were formed in these high concentrations of corrosive electrolytes were quickly attacked, after which attack of the metal becomes the predominant process, with no appreciable film formation.

Studies were also carried out using these electrolytes which were not corrosive towards titanium. These included sodium sulphate, sodium acetate, sodium phosphate, ammonium phosphate etc.

In all cases the voltage rose steadily with time until a final constant value was reached, this being the "maximum formation voltage" for a given electrolyte under given conditions. However, in all cases a plateau on the voltage/time curve over the range 7-12V was observed. This plateau was most evident with corrosive electrolytes although its existence also depended on current density, concentration of electrolyte, temperature and surface preparation. The nature of the plateau will be discussed further in a later section.

In the case of slightly corrosive electrolytes (e.g. acetic acid) no breakdown in voltage was observed; however, violent oscillations in cell voltage were observed at the maximum formation voltage showing that pronounced dissolution of the oxide was taking place.

The results obtained from the above studies show that with the electrolytes under consideration only barrier films were produced. It will be shown later that these films are non-porous as the leakage currents were very low even at high potentials.

With sodium hydroxide and sulphuric acid in higher concentrations, dissolution of the metal occurred.
3.3.2. Anodic Oxidation of Titanium at 90°C

At high temperatures only barrier films were produced with all electrolytes. However, the thickness of the barrier films produced at higher temperatures were always thinner than for exactly similar conditions at low temperatures. The maximum formation voltage decreased with temperature in the case of all electrolytes studied. In most cases the maximum formation voltage at 90°C was only 15-20V after which the current was predominantly electronic and gas evolution was the primary electrode process. The effect of decreasing maximum formation voltage with increase in anodizing temperature has been previously observed in the case of aluminium (25).

The effect of temperature on the voltage/time curve for concentrated formic acid is shown in Fig. 3D. This electrolyte was chosen here as the variation in maximum formation voltage between 90°C and room temperature was greater than for any other electrolyte studied.

An interesting curve showing the decrease in potential of titanium in 0.1 M sodium hydroxide, while maintaining a constant current source throughout and with continually increasing temperature is shown in Fig. 3E and it can be seen that there is a linear decrease in the formation voltage. The effects of temperature on other characteristics (e.g. leakage currents) will also be discussed later.

The corrosiveness of the electrolyte appeared to be unimportant during high temperature anodizing as the barrier thickness never became great enough for breakdown and chemical attack. The low formation voltages in all electrolytes was not unusual since the electronic conductivity of titanium dioxide increases with temperature. This is true in the case of other semi-conductors and the general relationship is given by an equation of the form:-

$$ K = A \exp \left( -\frac{\mathcal{Q}}{RT} \right) $$

At temperatures around 90°C, it would appear from the voltage/time curves that the ionic current (or film producing current) is negligible. It is
Fig. 3D.

EFFECT OF TEMPERATURE ON \( V/t \) CURVE in 90\% HCOOH
FIG. 3E

EFFECT OF TEMPERATURE ON THE "MAXIMUM FORMATION VOLTAGE"

IN 5% SODIUM HYDROXIDE SOLUTION.
evident from these studies that films formed at high temperature are not porous.

The effect of field crystallisation observed by Vermilyea for tantalum and by Lakhiani and Shreir for niobium at elevated temperatures, was not observed in the case of titanium. With tantalum and niobium the maximum formation voltages at elevated temperatures are much higher than with titanium and this is probably due to the fact that the semi-conducting nature of the oxides on these metals is not so pronounced as that of titanium dioxide.

3.4. **Effect of Concentration of Electrolyte**

The effect of electrolyte concentration was studied in various electrolytes including: formic acid, sulphuric acid, sodium hydroxide, sodium sulphate and sodium formate. The results obtained have shown that a variation in concentration of the electrolyte has a marked effect on the voltage/time characteristics and hence the nature of the oxide films formed. With corrosive electrolytes, the variation has been considered to be due to a change in corrosiveness of the electrolyte with a change in the concentration.

With non-corrosive electrolytes, variations in concentration have only slight effects on the nature of the voltage/time curves. In all but the very high concentrations of non-corrosive electrolytes (e.g. sodium sulphate), the formation of a plateau occurred in the region 7-12V. The following results may be deduced from the voltage/time characteristics in non-corrosive electrolytes.

1. The charge passed to attain a given potential is greatest with very dilute solutions. However, with increasing concentration the amount of charge required decreases for the attainment of any particular potential and eventually approaches a constant value.

2. The maximum voltage increased slightly with increase in concentration.

3. In dilute solutions the extent of the plateau at 7-12V is increased and the increase in dV/dt at 12V is not so pronounced.
4. High concentrations reduce the extent of the plateau.

Fig. 3F shows the effect of sodium sulphate concentration on the voltage/time curves.

With the more corrosive electrolytes, however, the effect of concentration of electrolyte on the anodizing characteristics was much more pronounced. The effect of concentration of sulphuric acid on its corrosion behaviour towards titanium is shown in Fig. 3G. It is clear that concentration of sulphuric acid will therefore be most important as regards the anodizing characteristics of titanium.

The voltage/time curves for the anodic oxidation of titanium in sodium hydroxide at two different concentrations is shown in Fig. 3H. The points which should be observed from Fig. 3H are:

1. The maximum formation voltage decreases with increase in concentration
2. The existence of the plateau at 7-12 V is most pronounced at the higher concentrations
3. The charge required to reach potentials above the plateau is less at lower concentrations. (It should be noted that this does not apply to very low concentrations when the electrolyte then behaves as a non-corrosive electrolyte.

The formation of a low maximum formation voltage at high concentrations is regarded as a direct consequence of increased rates of dissolution of the anodic film at these high concentrations. The reason for the more pronounced plateau will be discussed under the section dealing with the plateau phenomenon. However, at this stage it can be suggested that if the plateau is due to stresses in the oxide, then an increase in dissolution rate would be expected to take place under conditions of high stress (c.f. preferential attack of stressed areas on metals etc.).

Effect 3 can also quite easily be explained in terms of reduction in anodizing efficiency due to the high rate of oxide dissolution during anodizing at
FIG. 31

EFFECT OF SODIUM SULPHATE CONCENTRATION ON V/f CURVE

(EFFECTIVE VOLTS)

TIME (MIN.)
FIG. 3G

CORROSION BEHAVIOUR OF TITANIUM IN SULPHURIC ACID

(AFTER LANE GOLDEN AND ACKIRMAN)
FIG. III

V/t CURVES FOR TITANIUM IN VARYING CONCENTRATIONS
OF SODIUM HYDROXIDE.
high concentrations.

The above results, particularly those determined in corrosive electrolytes are as would be expected and in general show that the concentration of electrolyte has a noticeable effect on the anodizing characteristics of titanium. The concentration effects in formic acid are unique and will be studied in detail under the appropriate section.

3.5. Effect of Current Density

Experiments were carried out keeping all other variables (e.g. electrolyte, temperature, concentration etc.) constant and varying only the current density. The effect of varying the current density on the voltage/time curve is shown in Fig. 31. The experiments were carried out in 30% formic acid solutions at 25°C. A secondary purpose in carrying out these experiments was to find an intermediate current density suitable as a standard for future experiments. As a result of these investigations 2mA/cm² was chosen as the most suitable current density for future work.

The results obtained are as expected and the following points should be noted from the graphs:

1. The maximum voltage obtained was almost independent of current density. Higher current densities gave only slightly higher maximum formation voltages.
2. The slope of the curve dV/dt was greater with higher current densities.
3. The formation of the plateau was eliminated at high current densities and the change in slope at 12V almost eliminated at low current densities.
4. The charge required to reach the maximum formation voltage was less at higher current densities.

The effect of increasing current density is very similar to increasing the concentration of a non-corrosive electrolyte, as regards the voltage/time
curves. As there is always a time lag before complete film formation at constant current (to fully form a film it is necessary to continue anodizing at constant voltage until the minimum leakage current has been reached) it can be assumed that formation of the films was closer to completion for any particular potential, at low rather than at high current densities.

3.5.1. Effect of Very Low Current Densities

Hall and Hackerman\(^{17}\), have studied the anodic polarization of titanium in aqueous solutions of sodium chloride at low current densities. These authors showed that the potential/time curve could be split into three parts:

(a) The anode potential increases with time at a rate proportional to current density.
(b) The anode potential remains constant with time and oxygen is evolved continuously.
(c) The anode potential increases rapidly to about 10 volts after several hours, for current densities in excess of 1 mA/cm\(^2\). Localised pitting of the oxide then occurred with no further oxygen evolution.

In the present work, these results were corroborated by studying the anodic polarization in chloride solutions at low current densities. The form of the potential time curve is shown in Fig. 3J. In these experiments a saturated calomel electrode was used, as the IR drop through the electrolyte was a fair percentage of the overall cell voltage.

It was found that the interval during which the potential did not rise with time (i.e. at the oxygen evolution potential) was negligible at current densities above 0.25 mA/cm\(^2\). This was well below the value claimed by the above authors. The effect of repolarization after allowing open circuit decay showed the rapid rise of potential back to the oxygen evolution value as shown by Hall and Hackerman.
FIG. 31

EFFECT OF CURRENT DENSITY ON V/t CURVE IN 30% FORMIC ACID.

![Graph showing the effect of current density on the voltage-time curve in 30% formic acid. The graph includes three curves for different current densities: 5 mA/cm², 2 mA/cm², and 1 mA/cm². The x-axis represents time (in minutes) and the y-axis represents potential (in volts). The graph illustrates how increasing current density affects the rate of voltage change.]
3.6. Open Circuit Potential Studies

In order to investigate the nature of the surface and its behaviour when immersed in an electrolyte, attempts were made to measure the electrode potential of titanium in various electrolytes. It was considered that such experiments might shed further light on the effect of surface preparation on reproducibility.

Adams et al. have used potential time measurements to study zirconium in aqueous solutions. These authors have shown that the potential of zirconium rapidly rises to a more noble value on immersion in an electrolyte. This is due to the formation of an oxide film.

Potentials of titanium were measured against a standard saturated calomel electrode with a valve voltmeter connected across the circuit. It was considered most important that no chloride should enter the electrolyte (unless intended) and so all water was double distilled. After the varying surface treatments the specimens were rinsed and immersed in the electrolyte within 30 s; this ensured the minimum formation of oxide in the air.

Nitrogen agitation of the electrolyte was used and the effect was to increase the rate of change of potential initially. Eventually, however, both agitated and non-agitated solutions gave the same final potential, particularly in oxidizing solutions where formation of a protective oxide is more rapid.

The electrode potential depends on the surface condition of the metal and e.m.f. measurements of this kind can therefore be used to observe differences and changes in the metal surface caused, for example, by different methods of surface preparation. Immersion of titanium in a sodium chloride solution will initially produce a negative potential provided no oxide has been allowed to grow on the metal in the interval between preparing the surface and immersion. Once the potential has risen to give a positive value (with respect to the standard hydrogen electrode), the corrosion resistance is much greater and the metal is said to be passive. This increase to a positive potential is due to the formation of the protective oxide.

Studies were made of the change in electrode potential with time in
both solutions which produced protective films and solutions which caused breakdown of the oxide film. The effect of surface preparation on electrode potential in both these types of solutions was studied.

Fig. 3K shows the effect of surface preparation on the variation of electrode potential with time in 5\% sodium chloride solution exposed to the air. Fig. 3L shows the same study carried out in 20\% sulphuric acid.

In the case of immersion in sodium chloride solution, the potentials in all cases were initially negative and all eventually reached positive values. The abraded specimen exhibited the most negative electrode potential as this specimen has not had time for previous passivation in the air. It is interesting to observe that even those specimens which had been allowed to stand in the air for several hours before immersion, still exhibited negative electrode potentials initially. This would suggest that the growth rate of oxide on titanium at room temperature is very slow.

Uhlig and Geary\(^{(59)}\) have studied the passivation reactions brought about by the addition of cupric and ferric ions to a 2N solution of sulphuric acid. Pronounced passivation was shown to occur even in solutions which would normally breakdown any protective oxide film.

The results obtained from the present study may be summarised as follows:

(a) In all cases the open circuit potential was initially negative, rising to a positive, passive value after several hours. The maximum value obtained in the present work was +0.38V after a period of about five hours.

(b) The most active surfaces (giving the most negative potentials initially) were those which had been freshly abraded on the 3/0 emery paper.

(c) Oxidizing in air at room temperature for three hours was not sufficient to raise the initial open circuit potential to a positive value.
EFFECT OF VERY LOW CURRENT DENSITIES ON V/t CURVES
(5% NaCl)

0.1 mA/cm$^2$

0.05 mA/cm$^2$
FIG. 3K

EFFECT OF SURFACE PREPARATION ON OPEN CIRCUIT POTENTIAL IN 5% SODIUM CHLORIDE.

- Abraded to 3/0 emery
- 1 polish and 2 min. etch in standard soln.
FIG. 34
EFFECT OF SURFACE PREPARATION ON OPEN CIRCUIT
POTENTIAL IN 20% SULPHURIC ACID.

1. Polish and 2 min. etch in standard soln.

-0.2 0 0.2
POTENTIAL (V)

0 1 2 3 4 5 6
TIME (MIN)
(d) Chemical etching was found to reduce the activity of the surface as compared with an abraded specimen, giving an intermediate electrode potential. This was probably due to the formation of a hydride layer on the metal surface.

The above studies on open circuit potentials gave a definite insight into the effect of the nature of the metal surface with respect to its electrochemical behaviour.

3.7. Plateau Formation

During initial preliminary experiments a plateau was evident on the voltage/time curve at 7-12V. It was considered that the formation of such a plateau may have been due to one of the following:

(a) A physical change in the oxide structure during anodizing.
(b) A chemical change in the oxide composition.
(c) Some dissolution of the oxide in the electrolyte.

Fig. 3M shows the effect obtained in 5% sodium hydroxide solution.

The plateau was found to be present under standard anodizing conditions in almost all electrolytes. Only electrolytes such as concentrated formic acid which gave a very rapid rise in anode potential with time, did not show the effect. The plateau was further found to be affected by concentration of electrolyte, temperature, current density and surface preparation.

It was decided to carry out more detailed studies to shed more light on the reason for a plateau on the V-t curve and electron microscopy, leakage currents, capacity measurements, stress measurements and rectification have been used for this purpose.
FIG. 31

PLATEAU FORMATION IN 5% SODIUM HYDROXIDE SOLUTION.
3.8. Anodic Oxidation of Titanium in Chloride Electrolytes

The anodic oxidation of titanium in sodium chloride solution, at chloride compositions above about 0.5%, produce breakdown of the film by localised pitting at \( \sim 10-12 \text{V} \). This phenomenon has been observed by other workers \(^{(17)}\). The effect is due to the nature of the chloride ion itself and a review of the theories of chloride pitting has been given by Greene \(^{(60)}\).

Pitting was observed to occur initially at the edges of the specimen and in the case of partially immersed specimens, at the air/solution interface. It is of interest to note that the 10-12 V region where breakdown occurs, corresponds approximately to the upper limit of the plateau on the voltage/time curve. This suggests some inherent weakness in the oxide structure in this region and a connection between film breakdown in chloride solutions and plateau formation in other solutions.

Breakdown in chloride solutions is characterised by oscillations in the voltage/time plot; these are more pronounced than say those caused during breakdown in sulphuric acid at more elevated potentials. These pronounced oscillations appear to be related to the rapid film breakdown and localised penetration that occurs in chloride solutions. During pitting, corrosion product can be seen streaming away from the pits into the solution. It could be postulated that initially a soluble complex is formed within the pit which hydrolyses on reaching the bulk solution. Under these conditions, stifling of the attack is prevented and extremely deep pitting of the metal occurs. An example of pitting produced in this way on a titanium bar is shown in Fig. 3N.

3.9. Discussion

The above investigations have shown that titanium forms barrier films when anodized in the majority of electrolytes and that in corrosive electrolytes porous oxides, similar to those produced on aluminium, do not appear to form on titanium. It has been shown, however, that the exact nature of the barrier films formed depends to some extent on anodizing conditions. Chloride
electrolytes were unique as they produce breakdown of the film by localised pitting in the region 10-12V.

The barrier films produced may be divided into two main classes:

(a) Those produced in non-corrosive electrolytes
(b) Those produced in corrosive electrolytes.

Weak, non-corrosive electrolytes produced a maximum formation voltage of the oxide of less than 100V.

The more corrosive electrolytes produced breakdown at much lower potentials and in such electrolytes the potential was observed to drop suddenly (from, say, 25 to 10 volts). This breakdown was considered to be due to the effect of chemical reaction between the anodic oxide and electrolyte and large amounts of titanium were observed to go into solution under these conditions.

The formation of highly soluble complexes between titanium and sulphuric acid of the form \((\text{Ti} (\text{SO}_4)^{2-} + x^{2x})\) have been suggested by Chuk-Ching Ma and Peres. The formation of these complexes is said to be a maximum in the region of 40% sulphuric acid; this to some extent explains the decreasing breakdown voltage with increasing acid concentrations up to this value. The large voltage oscillations observed here are probably due to the oxide breaking down almost to the bare metal surface followed by localised high current densities being thus produced in these areas and the resulting rapid growth of the film.

The concentration of electrolyte affects the nature of the film to a negligible extent in non-corrosive electrolyte but markedly in corrosive electrolytes. The case of formic acid will be discussed later. It is therefore most probable that any variations in the nature of the oxide film is due solely to an increased or decreased corrosion rate brought about by a change in electrolyte concentration.

The effect of surface preparation was studied in some detail. During the growth of anodic oxide films, surface irregularities of the scale of the oxide films are believed to be flattened and, neglecting any change in the surface area of the oxide due to smoothing, the electrode potential increases linearly with time. Vermilyea showed, however, that with rough surfaces (etched,
"as received" rolled, mechanically abraded or surfaces made rough in other ways) the rate of rise of potential increased with time above a certain potential. It was considered that this effect was due to the reduction of the effective surface area by adherent oxygen bubbles. Electron microscopy showed "spherical pits" on the metal surface of the metal, indicating the adherence of oxygen bubbles.

The above phenomenon is explained in the following way. The original layer of oxide is constrained to cover a progressively thinner area. The resultant stresses, however they may be produced, will themselves produce breakdown of the film and consequent gas evolution. The shielding effect then results in an effective area decrease and hence an apparent increase in efficiency due to increase in current density.

Only barrier films of a limited thickness were produced when the temperature was raised to 90°C. From the voltage/time plots and leakage current studies made later, it would appear that the electron current increases very markedly even over the relatively small temperature range of 25-90°C. Thick porous oxide films were not produced on titanium by raising the temperature to 90°C, c.f. niobium where thick films were produced at elevated temperatures owing to crystallization of the anodic oxide. With titanium at 90°C the ionic current was negligible and oxygen evolution was the predominant electrode process. This pronounced increase in conductivity of titanium oxide with temperature appears to be unusual and it may be possible that this is associated with a change in the stoichiometry or nature of the oxide at elevated temperatures. An increase in the number of oxygen defects would increase the conductivity. Since passivity at elevated temperatures occurred in the majority of electrolytes, it is evident that this phenomenon is due to the properties of the oxide film and is not a specific property of the solution.
4. THE ANODIC OXIDATION OF TITANIUM IN FORMIC ACID AND ALKALI FORMATES

4.1. Introduction

Piggott and Shreir investigated the anodic behaviour of titanium in formic acid\(^{(1)}\). It was considered worthwhile to investigate this unique system in more detail using more refined techniques of measurement, in order to elucidate the complex effects produced. The effect of acid concentration and temperature is summarized in Fig. 4A on the basis of the different effects produced during anodic polarization and it is possible to distinguish the following zones:

(a) Micropitting zone: 0.1 - 60\% formic acid
   : below 50\(^{0}\)C

(b) Barrier film formation to high potentials:
   70-96.5\% formic acid
   : below 50\(^{0}\)C

(c) Barrier film formation to low potentials:
   0.1-96.5\% formic acid
   : above 50\(^{0}\)C

(d) Uniform corrosion with the formation of a loose non-adherent precipitate:
   96.5 - 100\% formic acid
   : 0-100\(^{0}\)C

The transition from one zone to another usually occurred over a range of temperature as indicated by the cross-hatched areas of Fig. 4A. The transition from barrier film formation to the formation of non-adherent deposits at 96.5\% formic acid was, however, quite well defined. The most interesting facet of this study was the formation of uniform micropits over the oxide surface, quite unlike the localised gross pitting observed in chloride solutions. The term "micropitting" is used in the present context to denote the formation of microscopic pits, uniformly and densely distributed over the metal surface.

In zone (a) uniform barrier films are produced initially, but at a
FIG. 4A
EFFECT OF CONCENTRATION AND TEMPERATURE.
FIG. 14B

EFFECT OF FORMIC ACID CONCENTRATION ON V/t CURVES.
critical potential the surface of the initially formed oxide becomes pitted; initiation of pitting was accompanied by precipitation of titanium hydroxide from solution.

In zone (b) titanium behaves as a typical "valve" metal and dielectric oxide films could be formed to high potentials before spark breakdown occurred.

In zone (c), film formation at temperatures above 40-50°C proceeded only to a limiting potential of 20-30V when film growth ceased and further passage of charge resulted in the oxidation of the solution at constant potential.

Zone (d) produced a uniform corrosion product of titanium hydroxide which formed as a loosely adherent yellowish deposit on the metal surface.

Fig. 4B shows the effect of these various zones on the voltage/time characteristics. It is interesting to note the formation of very thick barrier films (up to 400V) in the region 70-96.5% formic acid. This value was the highest formation voltage for films formed in any electrolyte in the present study. In the case of such films, the maximum formation voltage was followed by spark breakdown, resulting in a sudden voltage drop. The term "maximum formation voltage" has no real scientific significance under conditions where spark breakdown does not occur; theoretically, the film should grow to an infinite thickness after an infinite time. Where no spark breakdown occurs, the maximum formation voltage is taken as that where dV/dt appears to be zero on the voltage/time curve e.g. in Na₂SO₄.

4.2. Anodic Polarisation of Titanium in the Region 0.1-60% Formic Acid

Micropitting of the surface occurs throughout this whole range of formic acid concentration. The potential at which breakdown occurs varies with the concentration, however, and shows a minimum at 30%. This effect is shown in Fig. 4C. It is interesting to note that the conductivity of formic acid shows a maximum at approximately 30%. There may be some special significance in this which will be discussed later. The breakdown potential in 30% formic acid
Fig. 19.

Effect of formic acid concentration on the breakdown potential in microspitting region.
was a minimum at 42V whereas at the extreme ends of this concentration range (0.1 and 60%) the breakdown potential increased to 60V.

After micropitting has been taking place for some time, the interference colours were replaced by a rough, dull-grey film. The onset of micropitting was manifested by voltage oscillations, which became larger as micropitting continued, and also by the formation of fine particles of titanium hydroxide streaming into the bulk solution.

In one experiment a thick barrier film was formed on the specimen to 150V in 90% formic acid; the specimen was then anodically polarized in 30% formic acid. This effect is shown in Fig. 4D. On repolarising the potential rose rapidly to 60V when it suddenly stopped and micropitting of the very thick film took place. From this experiment it was apparent that micro pitting breakdown was independent of the film thickness.

4.3. Anodiz Polarization of Titanium in the region 70-96.5% Formic Acid

The anodic polarization characteristics in the region 60-70% formic acid will not be discussed as this zone proved to be a transition from one type of behaviour to another. The mechanism of anodic polarization in this region varied from one specimen to another. It was therefore concluded that this "border line" phenomenon was very dependent on the surface nature of the specimen. Using the most careful specimen preparation techniques it was still impossible to obtain a precise concentration of formic acid where the transition in oxidation mechanism from micropitting to anodizing occurred. The work of Lane, Golden and Ackerman (23) on the corrosion behaviour of titanium in formic acid shows a similar "border line" phenomenon in that either corrosion or passivity may take place on apparently identical specimens at a particular formic acid concentration.

Thick barrier films were produced on titanium throughout this concentration range (70-96.5%). The maximum formation voltage depended on the concentration of acid; the higher the acid concentration, the greater the
FIG. 4.D

EFFECT ON THE V/t CURVE IN MICROPITTING REGION AFTER PRE-POLARISING SPECIMEN TO 150V IN 90% FORMIC ACID.

90% FORMIC ACID (TO 150V)

MICROPITTING

30% FORMIC ACID

TIME (MIN)
FIG. 4d.

EFFECT OF CONCENTRATION ON V/t CURVE IN 70 - 96.5%
FORMIC ACID.
maximum formation voltage. This effect is shown in Fig. 4E. Interference colours were produced in all cases, but thick grey absorbing films resulted at greater thickness. The rise of potential with time was extremely rapid in this concentration range and plateau formation at 7-12V was not observed. In these high concentration ranges, breakdown often occurred by sparking across the electrodes.

Owing to the thick barrier films produced in this region, it was considered a suitable concentration range in which to carry out weight gain experiments and thus to determine the increase in barrier thickness with voltage (expressed as Angstroms/volt).

4.3.1. Estimation of Growth Rate of Barrier Films on Titanium (in Å/Volt)

As the weight gain produced by the formation of titanium dioxide from the metal was extremely small, specimens were made of large surface area. For the present work the specimen surface area chosen was 32 cm$^2$.

It has been shown by Siebert$^{(62)}$ that the growth rate of the anodic oxide on titanium depended on the thickness of the oxide. Using capacity measurements as a guide to growth rate, Siebert obtained a mean value of approximately 20 Å/Volt. Knowing the density of the oxide and the weight gain, it is possible to calculate the volume of oxide produced. The surface area of the specimen then being known it is therefore possible to calculate the thickness of oxide for any particular voltage. The errors in such a gravimetric study have already been outlined. The weight gain/voltage curve is shown in Fig. 4F for a 90% formic acid solution.

I.C.I.$^{(63)}$ have shown that the anodic oxide produced up to 45 Å consisted of brookite; from 45 Å to 170 Å both brookite and anatase were present and from 170 Å to 330 Å only anatase was present. The density of the oxide produced to a thickness of above 330 Å was therefore taken as that of anatase. The values obtained were as follows:
FIG. 4F

WEIGHT GAIN IN 50% FORMIC ACID.
Increase in weight of specimen at 130 V = 42\mu g/cm^2

and taking the density of the oxide as that of anatase
i.e. 4.16 gm/cm^3

Thus thickness in \( \frac{\mu\text{m}}{\text{Volt}} \) = 20.6 \( \frac{\mu\text{m}}{\text{Volt}} \).

The value obtained is in close agreement with that obtained by other workers.

4.4. Anodic Polarization of Titanium in the Region 96.5-100\% Formic Acid

The transition at 96.5\% formic acid from the formation of very high voltage barrier films to a loose non-adherent oxide was very sharp. Studies carried out at 96\% and 97\% gave the two different phenomena.

Once the non-adherent oxide had completely covered the surface (at a potential of around 25V), exfoliation took place revealing the almost bare metal surface on which further oxidation then took place. A graph of weight gain/voltage for this region is shown in Fig. 4G. It will be observed that after a certain potential has been reached, the weight gain/unit time decreases due to exfoliation of the oxide.

A sample of this oxide was taken, dried in air at room temperature and weighed. It was then ignited for four hours at 750°C and reweighed. The weighings were almost identical showing that the oxide contained no water or crystallisation.

4.4.1. Anodic Polarization of Titanium in Formaldehyde.

The anodic decomposition of formaldehyde results in the formation of formic acid\(^{(64)}\). It was considered therefore that at the anode a zone of highly concentrated formic acid would be produced on anodising in formaldehyde. The polarization characteristics should therefore be similar to those obtained in 100\% formic acid. This was confirmed and a loose non-adherent oxide was produced on the titanium surface in formaldehyde. However, if anodizing was continued too long the anodic products appeared to polymerise into a honey coloured gelatinous mass.
**FIG. 4G**

WEIGHT GAIN / TIME CURVE IN 100% FORMIC ACID.
Agitation of the solution appeared to reduce the concentration of formic acid at the anode surface as barrier films were produced instead of the thick non-adherent films formed in unagitated solutions. It was not possible to arrange conditions, however, to give an effective concentration of formic acid around the electrode which produced micropitting.

4.5. **Anodic Polarization of Titanium in Alkali Formates**

Voltage/time studies were carried out using sodium formate and ammonium formate solutions. In all cases involving anodizing with the formate ion present, micropitting occurred. Owing to the limiting solubility of these salts in water, however, it was not possible to reach concentrations high enough to give either thick barrier films or non-adherent oxides. From these results it can therefore be concluded that the formate ion and not formic acid is responsible for the phenomenon of micropitting.

The voltage/time curves for equivalent molar concentrations of formate ion, produced in formic acid and sodium formate are very similar. Formate solutions also exhibit the plateau at 7-10V. It was noted, however, that the nature of the pits was slightly different when produced in the two solutions; formic acid gave deeper pits and the effect of pitting therefore appears to be enhanced by acidity. An acid theory for chloride pitting has been proposed by Hoar (65) but this theory does not appear to be applicable to the system under consideration.

4.5.1. **Effect of pH on Micropitting**

From the above results it was considered important to investigate the effect of pH on the formation of micropits. Sodium formate /sodium hydroxide solutions were made to give pH values ranging from 8-13. It was found that micropitting occurred even at pH 13. However, the pits were neither as deep nor as pronounced as those obtained in acid formate solutions.
The high hydroxyl content in alkaline solutions has a solvent action on the titanium and slight etching of the metal surface as well as pitting occurred. This tended to lower the effective intensity of the pits.

Dissociated formate ions in the presence of hydrogen ions (acidity) appears to give the optimum conditions for micropitting. It may be possible that above a certain concentration of formic acid dimerisation occurs, and the activity of the formate ions is reduced, resulting in barrier films rather than micropitting. This topic will be discussed in more detail later.

4.6. Effect of Chloride Additions to Formic Acid

The effect of controlled additions of chloride ion to low and high concentrations of formic acid was studied. The aim of these experiments was two fold: -

(a) To investigate the effect of chloride additions on micropitting.
(b) To investigate the possibility of breakdown of very thick barrier films (as produced in 90% formic acid) by chlorides.

The effects on the voltage/time curves in the two concentration regions are shown in Figs. 4H and 4I. Owing to the complexity of the voltage oscillations, the graphs were traced as accurately as possible from the pen recorder chart.

Chloride additions varying from zero to 0.5% were made to 30% formic acid. This concentration of formic acid was chosen as it represented the mean concentration for the zone of micropitting. The breakdown with pure formic acid (30%) occurred at 45V and with pure chloride (0.5%) at 12V. Intermediate additions of chloride gave breakdown potentials between these two extremes. The addition of only 0.1% sodium chloride prevented micropitting by causing breakdown at around 30V, below the breakdown voltage required for micropitting. 0.05% sodium chloride had no apparent effect and the electrolyte
V/t curves for chloride additions to 10% formic acid.

No chloride

0.1% chloride

0.3% chloride

0.5% chloride
FIG. 41

EFFECT OF CHLORIDE ADDITIONS TO 90% FORMIC ACID.

No Cl
(36 CV)

0.05% (Breakdown at 190V)

0.1% NaCl

0.2% NaCl

0.5% NaCl

TIME (MIN.)
behaved as pure formic acid. The addition of 0.5% chloride, however, completely dominated the nature of the electrolyte and the voltage/time curve was identical with that for pure chloride. As can be seen from the curves, intermediate chloride additions gave very violent voltage oscillations. Under these conditions the system was in an unstable state with both chloride and formate ions trying to exert their influence on the electrode behaviour.

When titanium was anodized in 90% formic acid with similar additions of chloride, it is interesting to note that 0.1% chloride caused breakdown of even the very thick barrier films. Thus, even when present in very small amounts the chloride ion may completely change the anodizing characteristics. It was evident from these experiments that extreme care was necessary when preparing solutions to obtain complete freedom from chloride.

The existence of pre-formed localised pits as formed in chlorides did not affect subsequent micropitting in formic acid. Micropitting still took place in a uniform manner and the pits produced in chlorides did not serve as sites for subsequent attack.

Whenever anodizing was carried out in one of the three concentration zones in formic acid and subsequently repolarized in another zone, the anodizing characteristics assumed those of the latter zone. For example a non-adherent oxide surface, when repolarized in 90% formic acid was removed by the growth of a thick barrier film from beneath and around it. Similarly, barrier films could be grown on a surface which had been previously micropitted and micropitting produced on surfaces having a thick barrier film.

4.7. Discussion

The results obtained in the present work have shown that the anodic behaviour of titanium in formic acid is markedly dependent on the concentration and temperature of the acid and that these factors will determine the nature of the electrode reactions. The system appears to be unique in several respects. For example although zirconium is very similar in many ways to titanium, the
anodic behaviour in formic acid is such that only barrier films are produced. The above effects were not obtained with titanium in any other electrolyte studied.

It is evident therefore that the effects described resulted from some unique property of the system titanium/formate ion. In particular, the following aspects of the subject are relevant:

(a) Corrosion behaviour of titanium in formic acid.
(b) Nature of formate ion at different concentrations of acid.
(c) Complex formation.
(d) Nature of the anodic oxide.
(e) Reaction on various crystal faces.
(f) Adsorption of formate ions.

The relationship between the nature of the electrolyte solution and the anodic behaviour of a metal is most complex and so any discussion must be partly speculative. The different effects observed are dependent on changes in the nature of formic acid solutions in water at different concentrations of acid. As the concentrations of acid increase, the concentration of undissociated molecules will increase and in addition, there will be a pronounced tendency of the molecules to form dimers. The formation of dimers could reduce the reactivity or adsorption power, etc. of the ion.

Not only does the corrosion rate of a given metal vary with electrolyte concentration, but many examples can be quoted which show that the corrosion rate may show maxima and minima in certain ranges of concentrations. Ma and Peres showed a maximum corrosion rate for titanium in sulphuric acid at 40%, a minimum at 65%, which is then followed by a further rapid rise. These authors suggest that corrosion in the low concentration region is probably due to the formation of complex ions \( \text{Ti(SO}_4\text{)}_{2+x}^{2x} \) and that the rate of formation of these complexes increases with acid concentration reaching a maximum at 40%. In the range 40-65% the complex anions are considered to decompose giving titanium dioxide, which passivates the titanium, and sulphuric acid. The increase in rate
at concentrations greater than 65% is explained by the formation of another complex \( (\text{TlO}_2\text{(SO}_4\text{)}_x)^{-2x} \). There is no definite evidence to support complex formation although it should be noted that the detection of complexes in solutions of this nature is extremely difficult.

In the micropitting range, the formation of complexes is highly probable. However titanium hydroxide could be seen to stream away from the metal surface into the bulk electrolyte; if complex formation is to be postulated therefore, it must be assumed that a transient soluble complex is first formed within the pit which decomposes to the hydroxide in the bulk electrolyte. If this were not true, pit propagation would probably not take place owing to the stifling of the reaction within the pits by hydroxide precipitate.

Lane, Golden and Ackerman (23) have studied the corrosion behaviour of titanium in various concentrations of formic acid 15, 35, 60 and 100°C in aerated and non-aerated solutions. They have shown that at 35°C, the rates in aerated solutions are negligible and at higher temperatures the rates are negligible in oxygenated solutions. From their results it would appear that the rate increases with concentration to a maximum at 50%, falling rapidly with concentration to a very low value at 90% formic acid. Corrosion rates at higher concentrations were not studied. In many cases "border-line passivity" occurred and the corrosion behaviour then appeared to depend on the nature of the metal surface.

These results agree fairly well with the phenomena found during anodic polarization in the titanium/formate system. In the lower concentrations up to 50% the corrosiveness of the acid may help to break down the oxide giving pitting by transient complex formation; above 50% the acid is not so corrosive and cannot break down the oxide to give the initial step in pit formation.

Formic acid shows a pronounced maximum in conductivity at approximately 30% v.v.; it is interesting to observe that this figure corresponds to the composition leading to micropitting breakdown at the lowest potential (42V). A maximum conductivity would suggest maximum dissociation into hydrogen and formate ions. This may account for the maximum corrosion activity observed at this concentration. It would appear, therefore, that there is a relationship
between conductivity, corrosion rate and breakdown of oxide leading to micropitting.

In the higher concentrations of formic acid dimerisation occurs and the formate ion does not play so great a part in the electrode reactions. Under these circumstances pitting is precluded and anodic oxidation occurs.

In order to take an active part in the electrode reactions it is reasonable to assume that adsorption of formate to the metal surface will take place to a certain extent. Formic acid gas is adsorbed onto certain metals and their oxides including titanium dioxide, platinum, rhodium etc.. Muller and Herasymenko have studied the anodic oxidation of formic acid on platinum and rhodium and showed that oscillations of the polarizing voltage took place. These authors considered that such oscillations indicated the adsorption of formic acid at certain active sites in the metal surface. Such active centres could be vacant lattice sites, areas of high dislocation density etc..

The adsorption of formic acid on titanium may be represented by a Muller type of adsorption. The H-H distance for formic acid was calculated graphically from standard data and found to be 2.7 Å. These geometric distances might favour the two-point adsorption envisaged below.
Furthermore, it has been shown\(^{(69)}\) that the decomposition of formic acid on copper is influenced by the orientation of the copper substrate. As will be shown later, the anodic oxidation of titanium is particularly influenced by the orientation of the substrate and it may therefore be tentatively proposed that the decomposition or adsorption of formic acid on titanium will also be influenced by the orientation of the substrate. Adsorption of formic acid in the high concentration regions would tend to be far less pronounced owing to dimerisation. It would therefore appear that adsorption of formic acid, which is dependent on concentration, is also related to the phenomena of micropitting and passivity found during the anodic polarization of titanium in formic acid.

Thus at low concentrations, complex formation rather than oxide formation may be the energetically and kinetically favourable process; it is highly probable that this is preceded by adsorption of formate on to the metal or oxide surface so that the adsorption of water (the oxide favouring species) is prevented. These complexes diffuse away from the metal/solution interface and then react with water giving a precipitate of titanium hydroxide in the bulk solution. The formate ion appears to be the species that is active in the complex formation as it has been shown that micropitting occurs over a range of pH and can occur even in alkaline formate/solutions. It should also be noted that the minimum breakdown potential occurs at 30% formic acid - a concentration which had the highest conductivity. At 50% formic acid, the acid may be predominantly in the form of dimers which do not adsorb so readily on the metal surface so that adsorption of water and the subsequent direct transfer of metal ions onto the lattice of the oxide (anodizing) is the preferred process.

Above the breakdown potential in the micropitting region, oscillations in potential were observed. As the pits propagated into the metal, the amplitude of oscillations increased. Although the oxidation of formic acid on platinum is accompanied by oscillations in potential, this is unlikely to be a major cause of the oscillations observed in the present study. Oscillations of potential have been observed to occur during the anodic polarization of titanium
in chloride solutions and it is considered therefore that these result from the
gometry of the pit rather than from the specific nature of the anion. The fact
that the magnitude of the oscillations of potential increased as the pits propagated
into the metal gives support to this view.

The ohmic potential of the solution permeating the pit will be
markedly increased by the presence of gas bubbles (carbon dioxide from the
oxidation of formic acid) and by the presence of precipitated titanium hydroxide
resulting from the hydrolysis of complexes; dispersal of these species into the
bulk solution will result in a fall in potential. In addition, fluctuations of
concentration polarization are likely under conditions prevailing within the pit.
It is apparent that as the pit length increases, the effect of these factors will
become more pronounced with a consequent increase in the magnitude of the
oscillations. It should be noted that actual oscillations recorded must be regarded
as a statistical integration of the changes of the ohmic potential and concentration
polarization occurring at the individual pits.

At very high concentrations of acid (general attack) the activity of
water is so low that preferential adsorption of dimers of formic acid may now be
possible. In this case it would appear that the complex is stabilised as soon as
it is formed, giving a loosely adherent precipitate on the metal surface.
5. A STUDY OF THE CHARACTERISTICS OF ANODIC OXIDE FILMS OBTAINED ON TITANIUM

5.1. Introduction

More detailed studies were carried out in order to investigate the nature of the anodic oxide obtained on titanium. In particular the change in slope of the voltage/time curve was considered of interest.

A change in the slope or a plateau in the voltage/time curve at constant current density represents a change in the magnitude of the ionic current, which results from some physical or chemical transformation of the oxide. Thus in the case of niobium there is a slight change of slope at 20V (probably due to a change in the chemical nature) and a pronounced plateau at 75V which is due to the field crystallisation of the initially formed amorphous oxide\(^{(70)}\). Plateau formation has also been observed in the voltage/time curves during anodizing of uranium\(^{(71)}\). Plateaux are fairly common on the weight gain/time curves obtained during the thermal oxidation of many metals.

It has been shown that providing the rate of formation of the oxide is slow, the voltage/time curves for titanium are characterised by a sudden decrease in the rate of oxide formation, and that this persists over the range 7-12V. This phenomenon is not confined to formic acid, and is shown in Fig. 3C, for various electrolytes. The thickness of the oxide is so small in this region that identification of the oxide above and below the plateau was not possible.

Techniques employed to study the nature of all titanium oxide films included:

(a) Voltage/time curves.
(b) Current/time curves.
(c) Stress measurement.
(d) Capacity studies.
(e) Optical microscopy.
(f) Electron microscopy.
(g) Rectification measurements.
Techniques (e), (f) and (g) will be discussed separately later.

The study of ionic currents in thin films of titanium was considered to be of particular importance. It has been shown by Charlesby (9) that the total current passing through films of aluminium oxide is partly ionic and partly electronic. Owing to the observed non-stoichiometry of titanium anodic oxide films, it was considered that structural changes in the film (whether chemical or physical) would manifest themselves by changes in the "leakage" current. Any change in the surface of the film, producing microfissures or cracks would allow penetration of the electrolyte. This in turn would vary the capacity across the oxide and therefore changes in capacity with time for a constant thickness would indicate the presence of defects. Any change in the nature of the oxide should result in a change in the nature of the stress in the film; this was considered particularly possible in the case of titanium, where the oxide/metal volume ratio is large. A simple method for the qualitative value of stresses in the oxide at different thickness was devised - a procedure which has been subsequently described by Vermilyea.

5.2. Current/Time Studies

Films were formed to various potentials at constant current, formation then being completed by holding at the required constant potential and noting the current decay with time. The current/time curves at high constant voltages in 90% formic acid are shown in Fig. 5A. It is apparent from this graph that both the rate of decay in current and the final leakage current depend on the formation voltage.

Fig. 5B shows the effect of temperature on the leakage current in 30% formic acid. These results show that the leakage current is greater at higher temperatures. This result is in general agreement with the fact that increase in temperature increases the electronic conductivity of the oxide.

Current/time curves were also plotted in 20% formic acid. Of
FIG. 5A
CURRENT/ TIME CURVES AT CONSTANT VOLTAGE IN 96% FORMIC ACID
(ANODISING REGION)
EFFECT OF TEMPERATURE ON LEAKAGE CURRENT (IN 30% HCOOH).

LEAKAGE CURRENT (mA/cm²).
FIG. 58
CURRENT/ TIME CURVES IN 2O% FORMIC ACID.
FIG 5D

EFFECT OF FORMATION VOLTAGE ON LEAKAGE CURRENT AT THE PLATEAU REGION.
particular interest in this study was the effect of the 7-12V plateau and the onset of micropitting on the leakage current. Fig. 5C shows the current/time curves for various formation voltages in 20% formic acid and Fig. 5D shows the effect of formation voltage on the leakage current in the region of the plateau. Leakage current measurements are very dependent on the nature of the surface and quantitative reproducibility was difficult to achieve. However, the values obtained here, using carefully prepared surfaces were in fair agreement.

The maximum leakage current at 10V is in good agreement with the reduced film formation efficiency observed in the 7-12V plateau on the voltage/time curves. Film growth in the micropitting region is extremely slow as seen from the fact that almost all of the current flowing is leakage current. In the present work, the term "leakage current" has been defined as the current flowing under the application of a constant voltage after an arbitrary time; the time adopted was 300 s which is in accord with the recommendations made by Meserve (72).

5.3. Measurement of Stresses in the Oxide

It was considered that at the 7-12V region where the plateau occurred on the voltage/time curve, the applied voltage was insufficient to produce a chemical change in the oxide by field crystallisation. On this assumption, it was considered that physical defects produced in the film were probably producing this change in formation efficiency. The formation of defects should lead to an increased stress in the oxide, possibly therefore showing a maximum in stress at the plateau voltage.

There are several methods for measuring stress in electro-deposits (73-75) but very little work appears to have been done on measuring stress in anodized films. Owing to the fact that anodic oxide films are very thin in comparison with most electro deposits, the method used for measurement must be much more sensitive. Methods used for stress measurements in electrodeposits generally depend on the movement of a strip of metal during plating on one side only.
In the Hoar-Arrowsmith method movement of the strip is prevented by means of an electro-magnetic field. In order, however, to obtain deflection of a strip of metal due to stresses in an anodic film, the strip must be very much thinner. A very thin strip of metal was made by etching titanium sheet for three hours in the etching solution used for surface preparation. The exact thickness of the metal was not measured as it was decided to carry out only a qualitative study of the magnitude of stress.

The thickness of the strip precluded the use of most conventional methods of measuring stress with the exception of the method devised by MacNaughton and Hothersall\(^{(55)}\). This technique is extremely simple and consists in measuring the change in distance between the ends of two metal strips by means of a travelling microscope. The upper ends of the two strips are clamped together (Fig. 5.3.1.).
FIG 5E

STRESS (AS DEFLECTION OF STRIP) / FORMATION VOLTAGE

AT THE PLATEAU REGION.
The titanium strips were coated on the inner sides by a thin layer of Lacomit. This prevented the formation of a film on this side of the strip but was suitable only for films formed to low formation voltages - at high voltages it was found that film formation occurred to some extent under the Lacomit. However, in the low voltage region studied in the present work, this did not occur and film formation took place only on the uncoated side.

After forming films to each successive voltage, the distance "d" between the tips of the two strips was measured using a travelling microscope. Before measurement of "d" all adhering drops of electrolyte were removed using a hot air drier. Any increase in stress in the anodic films on the outer uncoated sides resulted in a separation of the two strips. Using this method, relatively large deflections of the strips were obtained.

Fig. 5E shows the deflection of the strips (as a variation in the distance "d") as a function of the formation voltage in the region of the 7-12V plateau. The films were formed in 20% formic acid solution. It is interesting to observe that the oxide shows a maximum in stress at 10V. This agrees fairly well with the maximum in leakage current and the change in slope of the voltage/time curve at 7-12V.

5.4. Capacity Measurement in the Oxide Film

Measurement of capacity of the oxide film was carried out in the region of the 7-12V plateau in order to determine whether there were any structural changes in the oxide.

When a metal is anodized in a suitable electrolyte to form an insulating film, a large capacity is found to exist between the metal and the electrolyte. Guntherschulze and Betz (76) made an analogy between a metal/metal oxide/electrolyte and a parallel plate condenser, the di-electric of which is the thickness of the oxide and the conductors being the metal and electrolyte. Charlesby (77) has shown that for aluminium, while the formation voltage \( V \) increases uniformly with time, the reciprocal capacity \( \frac{1}{C} \) also increases uniformly
with time. Thus for an oxide-free surface the product $V_f \cdot C$ is a constant, at a
given current density and temperature, irrespective of film thickness (where $V_f = 0$).

A linear relationship between $V_f$ and $\frac{1}{C}$ thus implies a uniform oxide.

Provided that the dielectric constant is known, capacity measurements may be
used to give the instantaneous film thickness and hence growth rate of the film.

Much work has been carried out on capacity measurements of various oxide films.
Young \cite{young} studied the dependence of film capacity on frequency in order to study
the non-stoichiometry of various films.

Anasbacher \cite{anasbacher} studied capacity measurements on discontinuous
oxide films and found that when adsorbed electrolyte was removed, the capacity of
a porous aluminium oxide condenser decreased considerably. Jason and Wood \cite{jason}
showed that the capacity of a porous aluminium oxide condenser was related to the
adsorption of the electrolyte at the surface of the pores. Pores filled with
electrolyte were considered to serve as conducting channels to the large capacity
of the "barrier" layer at the pore base. Wanklyn \cite{wanklyn} and Wanklyn & Sylvester \cite{wanklyn_sylvester}
have recently used a.c. impedance measurements to investigate the nature of the
protective film formed during the corrosion of zirconium alloys. These authors
observed a rise in the capacity of the films caused by the penetration of the
electrolyte into cracks in the oxide. Young \cite{young} found very large capacities in
oxide films anodized at the breakdown voltage for tantalum and niobium.

The overall conclusion is that cracked films have high capacities
owing to the electrolyte entering the cracks and reducing the effective thickness of
the dielectric.

In the present work it was decided to investigate changes in capacity
with time, below and above the 7-12V plateau in order to detect the presence of
micro-cracks. Titanium specimens were anodized in 20% formic acid to various
potentials around and on the plateau and on switching off the current, changes in
capacity with time were measured. The size of the platinum cathodes was
increased to 8 cm$^2$ to give as large an area as possible. The area of the anode
was 1 cm$^2$. Experiments were also carried out using a circular cathode of
FIG. 57

% CHANGE IN CAPACITY WITH FORMATION VOLTAGE
etched silver sheet (giving a large surface area) surrounding a double sided anode.

The percentage change in capacity with time in the plateau region is shown in Fig. 5F. On reaching the plateau region, as can be seen from Fig. 5F, the capacity increases quite markedly with time; below the plateau the film can be assumed to be fairly homogeneous owing to the unchanging value of capacity with time. Above the plateau discontinuities can still be seen to exist, but by a mechanism which will be discussed later, their effectiveness is reduced.

5.5. Discussion

The above results lead to the conclusion that the anodic oxide film on titanium is stressed and consequently fissured. Pilling and Bedworth\(^{80}\) pointed out that when an oxide grows on a convex surface, (e.g. a wire) and that when new layers of oxide appear on the inside of the existing oxide, (implying movement of oxygen rather than metal), the ratio of molar volumes of oxide and metal will determine the sign of the stresses. On a rough surface a similar argument holds. As the ratio of the molecular volume of oxide to that of titanium is large (1.78) stresses may be assumed to exist in the oxide. It will be assumed in the present work that oxide growth on titanium is brought about by the inward movement of oxygen as shown by the work of Hass\(^{81}\). This inward movement of oxygen will result in the oxide being in a state of strain; parallel to the metal surface the atoms will be closer together than in an unstrained oxide and further apart in a direction normal to the surface. Furthermore, if the metal itself is in a state of internal stress before the oxidation then these stresses would be reproduced in the metal oxide. Even the most careful surface preparation will produce stresses (tensile or compressive) at the interfaces which will be balanced by stresses of opposite sign in the bulk material. The oxide near the surface of titanium will tend to be in a state of compressive stress owing to the volume ratio being greater than 1. Expansion of the oxide parallel to the metal surface will be constrained so that the oxide will be forced in a direction normal to the metal surface resulting in blistering. This has been confirmed, as will be shown later, by electron
microscopy. Such an arrangement would lead to breakdown occurring at a certain critical thickness which, in the case of anodic oxide films on titanium, corresponds with a potential of 12V.

This effect of breakdown of oxide at a certain critical thickness has been found previously during dry oxidation of titanium, Jenkins$^82$. When the oxygen ions passing through the oxide (probably by vacant anion sites in the lattice) reach the metal surface, part enters the metal in solid solution and part reacts with the metal to form fresh oxide. At low temperatures, (e.g. anodizing at room temperature) very little of the oxygen would enter the metal as solid solution. Jenkins has observed that the thin dense slate-grey oxide formed on titanium during heating at low temperatures is replaced by a thick porous yellow brown scale at high temperatures. This latter scale is composed of layers of oxide which are twisted and shattered and is believed to result from the breakdown of the thin dense scale when it reaches a critical thickness. It is thought that growth stresses within the thin layers cause shattering of the outer layers of oxide at this critical thickness.

Thus films formed on titanium at low temperatures are more protective than those at high temperatures. Kofstad and Hauffe$^{83}$ have provided further proof of the inward movement of oxygen in the oxidation of titanium by the use of radioactive tracers. During low temperature oxidation the compressional stresses at the metal/oxide interface may tend to close up fissures and thus give a protective oxide film. At the critical thickness for breakdown, however, the strain energy per unit volume becomes greater than the energy required to detach the oxide from the metal and spalling, or other mechanical failure, occurs resulting in the films becoming non-protective.

Thus, at this critical thickness, fissures and blistering will appear in the oxide when the stresses in the oxide become sufficiently large to detach the oxide from the metal surface.

The production of fissures would give oxidation characteristics completely different from that of a crack-free oxide (e.g. in dry oxidation the
mechanism changes from parabolic to linear) and a change in oxidation characteristics as shown by the change in slope of the voltage/time curve at 7-12V. The increase in slope which occurs at 12V may be due to the complete detachment of the oxide from the metal surface resulting in blistering of the outer surface. A detachment from the metal would result in a decrease in stress and an oxidation characteristic differing from either the fissure-free oxide (below 7V) or the fissured highly strained oxide in the region 7-12V.

The anodic oxidation characteristics of titanium around the 7-12V plateau may be summarised as follows:

1. Growth of a uniform homogeneous oxide film below 7V. Any stresses which may be present below 7V are not large enough to cause micro fissures.

2. Microfissures form in the oxide in the 7-12V region. These fissures form at the surface of the oxide only as compressional stresses at the oxide/metal interface close up any microcracks which have propagated this far down. Electrolyte entering these cracks produces leakage channels and so increases the electronic current. The oxidation efficiency therefore decreases.

3. Detachment of the oxide from the metal surface owing to the limitation of lateral expansion, results in blister formation on the outer surface of the oxide above 12V. Visual support for this postulate will be given in a later section. Blistering relieves the stresses in the oxide and also tends to close up (at least partially) fissures on the outer surface of the oxide. This latter effect is due to the extra volume of oxide being displaced from the inner to the outer region of the oxide.
The increase in leakage current at the plateau may again be explained in terms of fissures forming in the oxide. The current takes the easiest conduction path along the electrolyte filled fissures and so does not contribute to the growth of oxide. The sites for the initiation of fissures may result from impurities in the metal surface e.g. diamond, carborundum or impurities within the metal which would conduct and thus inhibit film growth and healing at the base of the crack. Premature breakdown would then occur in these regions. Conduction through a pore would continue only as long as the impurity remains. It should be noted that owing to the nature of the stresses in titanium oxide the fissures would tend to run vertically to the metal surface. Fortunately, however, leakage current is minimised by the minute oxygen bubbles formed within the pores by anodic action.

The capacity increase with time observed with films formed at the plateau also provides evidence that the oxide structure in this region is fissured. It is evident from the results that the capacity of the oxide films formed up to 7V (e.g. below the plateau on the voltage/time curve) remains constant with time. The capacity of the oxide films formed at and above the plateau, however, gradually increase with time. This is most marked for those films formed at the plateau (i.e. between 7-12V) where leakage channels (vertical fissures) are assumed to exist.

It is considered from measurement of stresses, leakage currents and capacities that discontinuities in the surface of the oxide occur initially at the commencement of the plateau and are caused by stresses set up within the oxide. These discontinuities have the form of vertical cracks and allow penetration of electrolyte. Cracks formed at the plateau under stressed conditions may be initiated by conducting impurities in the oxide which themselves are surrounded by a stress field. Above the plateau, the oxide breaks away from the metal surface and in doing so tends to close up the cracks formed on the plateau.

Stresses in the oxide will be further increased by the differential oxidation rates of the various crystal faces on different grains. This will be discussed in a later section dealing with differential oxidation.
6. RECTIFICATION BY ANODIC OXIDE FILMS ON TITANIUM

6.1. Introduction

The exact mechanism of rectification by valve metal electrodes is still not fully understood. A number of explanations have been given but none of them appears to have been generally accepted. Rose\(^{(84)}\) and Lampert\(^{(85)}\) studied the rectification properties of cadmium sulphide and the behaviour of this dielectric with metallic contacts appears to be fairly well understood. With anodic oxide films on valve metals, however, the situation is further complicated by the following facts:

1. An electrochemical reaction must occur for charge to cross the oxide/solution interface.
2. The film material itself may be modified by applying large cathodic current.
3. The films are so thin that as a first approximation space charge effects may be neglected.
4. Most of the observed current through such films is usually due to the presence of flaws.

It is interesting to note, however, that Haring\(^{(16)}\) suggests that leakage currents through flaws in the oxide have no direct bearing on the phenomenon of rectification. It has also been shown that there is a change in properties of an anodic film after continued cathodic polarization; both the anodic and cathodic resistances have been found to decrease. This effect is known as "deformation".

Several of the theories for rectification proposed, rely on the existence of flaws in the oxide, either fissures or conducting impurities. It was considered therefore of interest to study rectification phenomena through titanium oxide films as these films have previously been shown in this work to be stressed and contain fissures. Young\(^{(86)}\) suggests that fissures are responsible for the low cathodic resistance and also for the observed leakage current during anodic polarization. Vermilyea\(^{(87)}\) obtained evidence to show that "weak spots" were
FIG. 6A
CIRCUIT FOR FULL WAVE RECTIFICATION.

(first half cycle)

(second half cycle)

Variable A.C.
responsible for the high cathodic current. Evidence that weak spots produce the anodic leakage current and high cathodic current is obtained from the fact that the anodic leakage current increases with increase in thickness of the film at a given field.

The effect of hydrogen and oxygen evolution during cathodic and anodic polarization also have an influence on rectification as these processes serve to carry charge across the interfaces. These effects will be dealt with more fully in the discussion.

6.2. Experimental

Using the circuit shown in Fig. 6A it is possible to obtain a pulsating d.c. current from an a.c. input along the arm AB. The titanium specimens were pre-anodized to a given potential in 2% sulphuric acid.

A variable input a.c. voltage was then applied to the films using a "Variac" transformer connected directly to the mains supply. The pulsating d.c. output was fed into a 500 ohms load and the output voltage read on a Vibron valve voltmeter. The nature of the output d.c. was observed visually on a Nagard oscilloscope. This gave a visual indication of the percentage rectification. Output d.c. voltage was then noted with varying input a.c. for films of different thicknesses.

For the measurement of "forward" and "reverse" currents, (i.e. cathodic and anodic respectively) the cell shown in Fig. 2A was used. The anodic and cathodic currents for a particular constant voltage was taken as the current after an arbitrary period of five minutes at this constant voltage. The forward and reverse currents were noted for varying input voltages for different film thicknesses. The effect of temperature on the anodic and cathodic currents was also studied. By modifying the Guntherschulze-Betz relationship to a first approximation, thus giving Ohms law, the anodic and cathodic resistances of the oxide may be calculated. This is considered to be a legitimate approximation for thin films. The current taken for calculation of resistance was that passing
after five minutes at constant voltage, as after five minutes the anodic leakage current was found to be fairly constant.

The majority of the rectification studies were carried out in the 7-12V plateau region. It was thought that highly stressed oxides would affect the rectification characteristics as a result of the increased number of fissures produced by such stresses. The term "recification ratio" used in this section is defined as follows:

\[
\text{Rectification ratio} = \frac{\text{current in forward direction}}{\text{current in reverse direction}}
\]

6.3. Effect of Input Voltage on Rectification Ratio

Fig. 6B shows how the rectification ratio varies with input voltage for films formed at 7V, 10V and 15V. These values correspond to formation voltages just below, on and above the plateau. In order to give comparative results, the input voltage has been expressed as a percentage of the formation voltage.

It was found that owing to the small resistance in the forward direction (i.e. titanium as the cathode), large currents could be passed through the film, (50 mA/cm\(^2\)) for long periods without any noticeable heating effects. Such currents passing through the film in the reverse direction, however, (titanium as the anode) produced a fairly rapid rise in electrolyte temperature.

With normal anodic leakage currents a maximum in the leakage current has previously been shown to exist at approximately 10V. However, observing the anodic leakage currents after cathodic polarization it was found that the plateau region produced low anodic leakage currents resulting in high rectification ratios. It would therefore appear that cathodic polarization changes the nature of the film and this in turn changes the magnitude of the anodic leakage current.

The rectification ratio was found to decrease under standard conditions, with increase in film thickness. This is probably due to the increased heating effect (owing to the higher resistance of thick films. A more exact
FIG. 8B.

EFFECT OF INPUT VOLTAGE ON RECTIFICATION RATIO (20% HCOOH).

INPUT VOLTAGE (VOLTS)

RECTIFICATION RATIO

7V FILM

10V FILM

15V FILM
discussion on the effect of temperature on the rectification ratio is given later.

The rectification ratio was also found to decrease with increase in input voltage for a particular film. This phenomenon may also be explained in terms of a heating effect. It was found, however, that with films formed at the plateau voltage, the rectification ratio increased slightly with input voltage. It is considered that the heating effect at the plateau is not so pronounced owing to the presence of electrolyte filled fissures. This effect is only true, however, when the input voltage is expressed as a percentage of the formation voltage.

6.4. Effect of Temperature on the Rectification Ratio

Anodic oxide films were formed on titanium to formation voltages of 7V, 10V and 15V in 15% formic acid solution. An input of 6V was applied across the films in both directions and the rectification ratio calculated at various temperatures from 20° to 90°C. The effect of temperature on the rectification ratio for these films is shown in Fig. 6C. It was found that both the forward and reverse currents increased (for a given voltage) with increase in temperature. This was due to the increase in electronic conductivity. However, the anodic leakage current increased at a more rapid rate than the cathodic current and so the resultant effect in all cases was a reduction of the rectification ratio with increase in temperature. In theory, therefore, at a certain elevated temperature the rectification ratio would reach unity; the temperature required, however, would be far above the boiling point of the electrolyte. Pulse techniques (passing high currents through the electrode for fractions of a second) have been used to determine this temperature. It should be noted in Fig. 6C that the input voltage in both cases is 6V and is not expressed as a percentage of the formation voltage.

6.5. Effect of Temperature on Anodic and Cathodic Resistances

The effect of increased temperature is to reduce the resistance of the oxide in both the anodic and cathodic directions. Resistances have been calculated using Ohms law as a first approximation to the Guntherschulze-Betz...
relationship between current and field strength.

Applying a constant voltage, both the anodic and cathodic currents passing after a period of five minutes were noted and resistances were calculated at various temperatures. Table 6.5.1. shows the effect of increase in temperature on resistance for various anodic films.

It was particularly interesting to compare the changes in anodic resistance with temperature for films formed below the plateau (7V), on the plateau (10V) and in the micropitting zone (50V) in 15% formic acid. The resistances were obtained without previous cathodic polarization. The resistance of films formed in the micropitting zone were extremely low as the solution in the micropits themselves served as conducting channels.

6.6. **Effect of Input Voltage and Temperature on the Anodic Leakage Current in Anodic Oxide Films on Titanium**

FILMS were formed on titanium in 5% sodium sulphate to potentials of 15V and 20V. Having formed these films to 15V and 20V, the leakage current was noted for various input voltages (below the formation voltage) at 25°C and 90°C. The input voltages are given as a percentage of the formation voltage. Fig. 6D shows the effects of these variables on the leakage current.

For a given input voltage with a particular film, the leakage current increases considerably with temperature. The leakage current has also been shown to be a function of the input voltage; the higher the input voltage the greater is the leakage current. The relationship is non-linear, however, and doubling the percentage input voltage more than doubles the leakage current.

6.7. **Discussion**

The phenomenon of rectification through anodic oxide films was first observed almost one hundred years ago using aluminium. If an alternating current is sent through a cell containing aluminium and carbon electrodes and if the a.c. input voltage is less than the formation voltage, only the negative portion
EFFECT OF TEMPERATURE ON RECTIFICATION RATIO.
<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Temperature</th>
<th>Anodic Resistance</th>
<th>Cathodic Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>7V</td>
<td>20°C</td>
<td>$1 \times 10^4$</td>
<td>~50 ~</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>$0.8 \times 10^4$</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>$0.5 \times 10^4$</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>$0.3 \times 10^4$</td>
<td>35</td>
</tr>
<tr>
<td>10V</td>
<td>20°C</td>
<td>$2.5 \times 10^4$</td>
<td>~58 ~</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>$1.2 \times 10^4$</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>$0.8 \times 10^4$</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>$0.5 \times 10^4$</td>
<td>41</td>
</tr>
<tr>
<td>15V</td>
<td>20°C</td>
<td>$6 \times 10^4$</td>
<td>~66 ~</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>$4.5 \times 10^4$</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>$3 \times 10^4$</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>$2 \times 10^4$</td>
<td>50</td>
</tr>
</tbody>
</table>
FIG. 6D.

EFFECT OF INPUT VOLTAGE AND TEMPERATURE ON
ANODIC LEAKAGE CURRENT.

LEAKAGE CURRENT (mA/cm²).

INPUT VOLTAGE (VOLTS).
of the current can pass (i.e. aluminium as the cathode).

Later work showed that a current always flowed in the direction where the aluminium acted as the anode, although the current was many times below that obtained with aluminium as the cathode. The aluminium was considered to behave as an electric valve and all metals exhibiting this effect have become known as "valve metals". The valve effect has been found with the following metals: tantalum, niobium, vanadium, antimony, bismuth, magnesium, iron copper, tin, titanium etc. The extent of the valve effect depends on the metal itself and the electrolyte used, some metals exhibiting the phenomenon to a far greater extent than others.

There have been several theories to explain the phenomenon of electrolytic rectification, but no theory completely explains the effect. One of the most interesting features of rectification studies was found to be the change in properties of the film after cathodic polarization; this included the decrease in both cathodic and anodic resistance. This effect, known as "deformation" possibly involves two processes:-

1. The breakdown of cathodic resistance due to conduction at fissures.
2. A change in stoichiometry which renders the film more conducting.

Young considers that protons and hydrogen atoms (produced during the cathodic cycle) increase the conductivity in the fissures in the oxide. Schmidt suggests that the cathodic current depends on the size of the cation (including its hydration shell); he suggests that the surface field of the ion controls the current which he believes to be uniform over the surface. Vermilyea showed that weak spots were responsible for most of the cathodic current but did not give an explanation of why these weak spots rectified. The presence of fissures in the film means that cathodic hydrogen may reach the metal and result in either removal of the film or hydrogen embrittlement. Young suggested that hydrogen ions may travel into the fissures and then discharge, the
resulting hydrogen atoms then escaping by outward diffusion. In anodic polarization, however, small ions (e.g. protons) migrate away from the metal surface whereas negatively charged anions migrate to the metal surface. The large size of the anions precludes entry into fissures. This theory of cationic size is in agreement with the work of Schmidt.

The effect of hydrogen evolution on the properties of the film may be twofold:

1. The fissures may be opened up by the pressure developed by hydrogen bubbles.
2. The oxide is partially reduced and becomes a better n-type conductor.

It seems likely that cathodic hydrogen evolved within the oxide will result in a combination of both the above factors. Other authors including Smith have concluded that defects in the film are responsible for the anodic and cathodic currents and hence rectification.

Haring has proposed a mechanism for electrolytic rectification on tantalum and considers that the barrier film functions alternatively as (a) an ionic space charge which exactly counter balances the applied voltage and so blocks the current and (b) as an electronic semi-conductor which permits the flow of current in the usual manner, (i.e. it rectifies).

The present studies have shown that the rectification characteristics depend on the nature of the oxide. Rectification is more pronounced in films having fissures, (i.e. at 10V). This is in general agreement with the work of most of the authors mentioned above that rectification is enhanced by defects in the film. Böhm found typical valve behaviour with titanium at 60V; however, the rectification ratio found by this author was only about 20:1.

To compare the rectification ratios for various films it was necessary to multiply by a factor input voltage/formation voltage.
At the higher cathodic constant voltages, the cathodic current rose more rapidly with time. This would suggest that cathodic hydrogen has some definite effect on the properties of the film. It is therefore proposed that hydrogen ions carrying the current through film defects result in a very low cathodic resistance. This mechanism as deduced from the above experiments is in general agreement with that proposed by Young.

It has been shown that in order to reduce the rectification ratio through aluminium oxide to unity, it is necessary to pass currents through the electrode of 40-50 A which results in heating of the oxide. The effect of higher input voltages (which are required to pass current through thicker films) is to produce higher currents which cause extreme heating of the electrode. Thus as a result the effect of increasing voltage is to reduce the rectification ratio. It has been shown that for a point electrode of aluminium the rectification ratio was reduced to unity at 62V. This voltage, above which an increase will result in destruction of the rectifying effect (by means of the large temperature increase) is called the "inversion point".

These results obtained show that titanium acts as a valve metal and that the rectification characteristics depend on the nature of the oxide and in particular the presence of defects.
7. **OPTICAL AND ELECTRON MICROSCOPY**

7.1. **Optical Microscopy Studies**

A characteristic feature of the anodic behaviour of titanium is the formation of different interference colours on different grains. This phenomenon has been studied by Rivolta\(^{(37,38)}\) who showed that different interference colours could be obtained in a variety of electrolyte solutions provided that the potential was greater than 10V. He concluded that the colours were due to different thicknesses of oxide on grains of different orientation. Beryllium gives interference colours when anodized in chromic + nitric acid and Young\(^{(91)}\) has suggested that this may be due to local variations in temperature owing to a variable ohmic p.d. at different parts of the surface. Cadmium behaved similarly when anodized in potassium hydroxide at low current densities, and it may be significant that close-packed hexagonal metals are particularly prone to show this behaviour.

Colour photo-micrography was therefore considered to be a particularly good method of studying this effect of different interference colours. It was further considered that this method would show to best advantage the nature of the breakdown leading to micropitting.

The photographs were taken using a normal metallurgical microscope, Leika camera and Agfa (36mm) film. For the higher magnifications oil immersion was used.

Visual observation showed that micropitting breakdown first occurred on those grains which were commencing to show the second-order yellow interference colour. By the time micropitting of any consequence had taken place, those parts of the micropitted grains which were unattacked had turned a definite second order yellow. Colour photographs (Fig. 7) were taken at:

1. 45V - showing onset of micropitting on particular crystal faces.
2. 50V - intermediate stage of micropitting.
3. 70V - micropitting almost completed throughout.
In Fig. 7A the yellow grains are the thicker (complete second order yellow) and micropits may be observed on the thinner yellow/green oxide. It should be noted that micropitting is confined to one type of grain only. The thick yellow grains remain completely unattacked at this stage.

Fig. 7B shows the effect of micropitting on the surface topography of 50V films. The yellow unattacked grains have now thickened to give a red interference colour and the grains on which pits initiated are now almost completely covered with pits. The oxide on the grains which remain unattacked, however, have thickened slightly to give the yellow colour shown by the unattacked grains in Fig. 7A.

Fig. 7C is the same as Fig. 7B but at a magnification of X1,000. It may now be seen that the thick red "unattacked" grains exhibit some evidence of cracking, as shown by the parallel lines in the oxide. More detailed examination shows that micropitting is, in fact, being initiated at some of these cracked areas.

Fig. 7D (X1,000) shows the state of the surface at 70V. The surface is completely micropitted save for one single grain in the centre of the picture. Comparing with Fig. 7C it can be seen that the micropits have become very much larger and are so deep as to be out of focus. It is interesting to note that even after micropitting has taken place for some considerable time, there are certain grains which still remain unattacked. This may be regarded as an example of the phenomenon of "border line passivity" on micro scale.

7.2. **Electron Microscopy**

7.2.1. **Electron Microscope**

Owing to the fact that two points cannot be resolved with normal light, when the distance between them is less than one half the wave length of light, it is necessary to use an electron beam to bring about resolution at high magnifications. The transmission electron microscope is similar in principle to the transmission optical microscope. The light beam, however, is replaced by a beam of electrons and focusing is brought about by magnetic "lenses". The
electrons are first focused by an electro-magnetic field to give a parallel path to
the beam, which is then directed along the axis of the microscope. The beam
then passes through the electro-magnetic objective and projector lens, finally
forming an enlarged image on the viewing screen or photographic plate. Any
object interrupting the flow of electrons will not allow transmission and thus show
up as a dark zone on the screen. Various degrees of darkness may be obtained
depending on the extent of transmission through the interrupting object.

7.2.2. Preparation of Specimens

Specimen preparation for electron microscopy is extremely critical. Specimens were carefully polished, degreased, washed and anodized in the
required electrolyte solution to various potentials. Owing to the difficulty of
stripping anodic films from titanium, it was necessary to use a replica technique.
The specimens were 1 cm² in area and from a replica this size it was possible by
careful cutting to obtain 16 specimens for electron microscopy.

7.2.3. Replica Preparation

After anodizing to the required potential the specimen was removed, rinsed and dried. In order to obtain a "negative" of the surface, before
depositing the carbon "positive", the surface was treated with "Bexfilm". Bexfilm resembles cellophane and dissolves in acetone. After immersion in
acetone for a period of five seconds, the Bexfilm was partially dissolved. When
this semi-dissolved film was placed on the oxide surface it dries rapidly and in
doing so contracts, taking up the exact shape of the surface. This initial film
was then stripped and by this means the surface was cleaned further. This
procedure was then repeated on the now clean surface to obtain a Bexfilm negative
replica of the surface.

It was not possible to obtain good replicas of the surface with the
standard procedure using a 1% solution of formvar in chloroform.
The replica was then mounted on a glass slide with "Sellotape".

7.2.4. Deposition of the Carbon Film

The carbon was deposited by evaporating carbon at an angle of incidence of $45^\circ$ onto the Bexfilm replica. Angle deposition was found to give better contrast than evaporation at normal incidence. This process was carried out in a vacuum chamber by passing a current of about 40A through 5mm diameter pointed carbon rods. The points of these rods were kept tightly pressed together by springs. The intense heat caused by the very high current evaporated the carbon which was deposited on the specimen. The extent of evaporation was judged visually by the intensity of the brown film formed on a piece of porcelain located in the same region as the specimen. A drop of "Apiezon" oil was put on the porcelain to emphasise the darkening effect. The thickness of carbon required to give a satisfactory replica was found by experience, but required about five 1 s bursts of carbon evaporation.

7.2.5. Final Preparation of the Carbon Replica

The complete replica consisting of Bexfilm plus carbon was removed from the glass slide. The Bexfilm was then removed by dissolution in acetone, leaving the carbon positive. It was found, however, that immersion of this composite replica in acetone caused the carbon to curl and break. In order to strengthen the film, therefore, while removing the Bexfilm, a layer of Vaseline was smeared over the carbon surface. On immersion in acetone, the Bexfilm dissolved leaving the carbon plus Vaseline layer intact. The time required for complete dissolution of the Bexfilm was about four hours, the acetone being changed from time to time using a hand pipette. All excess acetone was removed from the carbon (plus Vaseline) replica which was then placed in carbon tetrachloride solution which dissolved the Vaseline leaving the carbon replica. The replica was removed from the carbon tetrachloride solution using small copper grids;
FIG. 7E

15V Film
Mag. x 12,000

FIG. 7F

30V Film
Mag. x 12,000
FIG. 7G

50V Film
Mag. x 4,000

FIG. 7H

55V Film
Mag. x 12,000
FIG. 71

75V Film
(90% HCOOH)
Mag. x 12,000

FIG. 71

75V Film
(10% Na$_2$SO$_4$)
Mag. x 12,000
the specimens were now ready for examination under the electron microscope.

The replicas of various oxide surfaces were then examined by projecting the images on the viewing screen and in certain cases photographs were taken.

### 7.3. Results

Figs. 7E to 7J show the electron micrographs of the various oxide surfaces. Electron photo-micrographs taken of oxide films formed below 12V (which included the plateau at 7-12V) showed a uniform surface. It was considered therefore that the oxide formed up to this point was fairly homogeneous. Further film formation to 15V (Fig. 7E) showed blistering of the oxide surface and the extent of these blisters increased with further film formation as shown by Fig. 7F. The films shown in Figs. 7E-7J were formed in 10% formic acid solution (i.e. that range of concentration producing a micropitted surface). It can be seen by continuing the series to 55V films (Fig. 7G) that the blisters formed act as nuclei for breakdown leading to pitting. As can be seen from Fig. 7H, cracking of the blisters occurs in a characteristic manner such that four segments are produced.

It is apparent from the photographs that the postulate that blisters form above the plateau has been confirmed by electron microscopy. The formation of microcracks at right angles to the metal surface which was considered to exist in the region of the plateau, were not revealed at the magnification and resolution possible with the instrument used in this study. This does not preclude the possibility that microcracks actually exist in this region of potential.

It was found that cracking of the blisters at around 50-60V was limited to those conditions which resulted in micropitting. Fig. 7I shows a film formed to 75V in 90% formic acid. In this concentration region (where anodizing rather than micropitting occurs), the blisters have not cracked but have simply continued to grow in size. This fact shows quite conclusively that breakdown of the oxide by blisters cracking is a characteristic of Ti in low
concentrations of formic acid. Fig. 7J shows the surface of an oxide film formed to 75V in 10% sodium sulphate solution. The oxide is cracked throughout and the nature of the cracks is quite different from that shown in Fig. 7G for blister cracking in formic acid. It is considered that in sodium sulphate simultaneous cracking and healing takes place whereas in formic acid healing does not take place, perhaps owing to the formation of soluble complexes.

It would therefore appear that micropitting is initiated by the formation of blisters above the plateau and their subsequent rupture. Attempts were made to produce electron micrographs of the pits produced in chloride solutions at 12V. However, the large amount of corrosion product formed prevented the replica stripping off the oxide surface cleanly.

7.4. Discussion

The postulate that blisters form above the 7-12V plateau appears to be valid as blisters were in fact observed above 12V. As the strain energy of the oxide increases with increase in thickness so the amount of oxide becoming detached at the metal/oxide interface will increase resulting in an increase in size of the blisters formed at the oxide/solution interface. Breakaway of the oxide is greater than the adhesion energy of the oxide to the metal.

Blisters of this form would be expected to occur in all electrolyte solution followed by cracking and sparking, thermal breakdown etc. at a sufficiently high potential. In the case of 0.5-60% formic acid, however, the breakdown of the blisters appears to result from corrosion by the acid. From consideration of Fig. 7K, it would be reasonable to assume that the oxide at the apex of the blisters was under very high strain. The maximum corrosion rate in formic acid might therefore be initiated in these regions. As previously mentioned, formic acid itself shows a maximum in corrosion rate in the concentration range which gives micropitting. As will be discussed later, however, it is considered that this corrosion effect on the apex of the highly stressed blisters results only in the initiation of micropitting but once the oxide is broken, pitting
occurs by a different mechanism.

Fig. 7K shows the series of events leading up to the formation of blisters.

It is also considered, however, that stresses due to the differential oxidation of the various crystal faces will also produce stresses which will enhance the formation of blisters. As shown by the colour photo-micrographs, micropitting occurs on the thinner grains. Electron microscopy has shown that blistering occurs to some extent on all grains, though on some more than others. It was not possible to tell from electron microscopy whether the thin or thick oxide grains showed the greater amount of blistering. However, the fact that micropitting occurs on the thinner grains first would suggest that these are more highly stressed and would therefore show a greater amount of blistering.

It is suggested that blistering on the thinner grains is greater as stresses here are built up in two ways. These are:

1. Blistering from the stresses by the Pilling-Bedworth principle at a critical thickness as shown in Fig. 7K. This is common to all grains.

2. Blistering arising from stresses due to differential oxidation of the various crystal faces.

Fig. 7L (a) represents three grains of different orientation with a very thin air-formed film (this is not necessarily uniform) and Fig. 7L (b) shows the different thicknesses of oxide after anodizing to a potential where different interference colours become evident. Fig. 7L (c) shows that any expansion of the thinner oxide is constrained by the more rapidly growing surrounding oxide. Although the orientation of the grain will be the dominating factor in the initial growth of the film it will become of less significance as the film thickens owing to the higher ohmic p.d. across the thicker oxides. This will result in a higher ionic current through the thinner oxide which will now start to grow more rapidly. The combined effect of the concentration of the current on the thinner grain and the constraint produced by the surrounding thicker oxide will result in the development
STRESSING OF OXIDE LEADING TO BLISTERING.

(below 7V) Uniform growth

(7-12V) Conduction through fissures.

(above 15V) Breakaway at metal/oxide interface and blister formation.
of a high stress in the oxide on this thinner grain and eventual detachment of the oxide from the metal surface with the formation of a blister (Fig. 7L(c)). Fig. 7L(d) shows the corrosion attack on the metal beneath the ruptured blister.

The combined effect of blister formation by the two mechanisms above occurs only on the thinner grains. Blistering on the thicker grains occurs only by the Pilling-Bedworth mechanism. The higher stress at the apex of the blisters where the oxide is extremely thin, results in a much higher strain at the blister apex on these grains. Corrosion attack by the formic acid would therefore, by analogy with metals, be expected to occur preferentially on highly strained regions of oxide.

This theory agrees with the results obtained by optical and electron microscopy.

Cathcart, Campbell and Smith\(^{(45)}\) have observed blister formation during oxidation of niobium at 400\(^{\circ}\)C. At this temperature breakdown occurred after 300 min. and the rate changed from parabolic to linear. Marker studies showed that the oxide formed at the oxide/metal interface and it was concluded that oxygen ions diffused inwards. They considered that when a segment of the metal lattice at the interface was converted to oxide, a three dimensional expansion of the metal lattice was required to bring metal ions into the oxide lattice, and this was resisted by the overlying layers of previously formed oxide with consequent blister formation. Thus oxidation (particularly by the inward movement of oxygen) continually produces stresses in the oxide.

The presence of blisters on the surface of the oxide at potentials greater than 12V has thus been demonstrated by electron microscopy and it would appear that blister rupture occurs at a potential which corresponds with the initiation of micropitting. Presumably each ruptured blister is the site of an extremely small pit and with passage of charge these pits coalesce to give micropits.
8. GENERAL DISCUSSION

8.1. Introduction

The present investigations were concerned with the factors affecting the formation of discontinuous anodic films on titanium and in particular with the nature of the discontinuities themselves. The anodic behaviour of titanium in formic acid has been studied in some detail and theories proposed for the unique effects observed. Voltage/time studies have shown that under certain conditions a distinct plateau occurs at 7-12V and this is connected with a physical change in the oxide. The exact nature of this change has been elucidated using capacity measurements, current/time relationships, stress measurements, rectification studies and by studies of the surface topography of these discontinuous films using optical and electron microscopy.

The present discussion is therefore concerned with correlating the previous discussions at the end of each section and presenting an overall picture for the anodic behaviour of titanium and the nature of the anodic film on titanium under various anodizing conditions.

The effect of surface treatment, nature and temperature of electrolyte on the anodic behaviour of titanium will also be further reviewed in this section.

8.2. Surface Treatment

It is evident from the results given in Section 3.2. that slight variations in surface treatment may completely change the anodizing characteristics. The surface of the "as received" specimens vary considerably due to (a) surface defects encountered during metal fabrication, (b) impurities embedded in the surface during metal working, and (c) variations in chemical composition of the metal itself. The results were therefore non-reproducible with "as received" specimens. Mechanical polishing of this initial surface gives a more reproducible surface but only if the mechanical polishing is carried out under carefully controlled conditions. During polishing, however, it is possible for carborundum and diamond particles to become embedded in the surface layers.
As titanium is particularly prone to flow of surface layers during mechanical polishing, pick-up of these particles is therefore enhanced. These particles, which may not be completely removed by etching, may affect the anodizing process giving irreproducible results.

Particles of carborundum or diamond, being highly conducting, act as leakage channels through the oxide. These result in decreased ionic efficiency. It has been recognised for some time that abrasive may be forced into the surface of soft metals during industrial or metallographic polishing (92, 93, 94). It is considered that these conducting particles affect the leakage current in current/time studies so that reproducible results are difficult to achieve. Variations in the leakage current will also give rise to variations in the rectification ratio for a particular film and as suggested by Vermilyea "weak spots" or conducting impurities may enhance the rectifying effect.

As proposed in Section 5, conducting impurities in the film are surrounded by highly strained oxide and serve as initiation sites for the production of microfissures. Furthermore they serve to conduct away the charge so preventing healing of a fissure once it has formed.

From the present work it is clear that chemical treatment to remove as many of these conducting particles as possible must be carried out under carefully controlled conditions in order to obtain a uniform surface which would give reproducible results. The chemical treatment adopted as outlined in Section 3 produced such a surface and the results obtained were reproducible. It is considered, however, that some conducting impurities do remain in the film even after prolonged chemical treatment.

8.3. Nature and Temperature of Electrolytes

If the anodic film produced on metals such as titanium, zirconium, niobium and tantalum is a homogeneous dielectric, then the relationship between potential and time during its formation at constant current should be rectilinear.

In the present study, however, a survey of various electrolytes at
25°C showed a departure from the linearity of the voltage/time curve at 7-12V. The extent of this plateau depended on the corrosiveness of the electrolyte (e.g. sodium hydroxide gave a very pronounced plateau). The maximum formation voltage and slope of the voltage/time curve have also been shown to be dependent on the electrolyte used. Corrosive electrolytes produced low breakdown voltages, characterised by a sudden drop of potential (e.g. sulphuric acid). The less corrosive electrolytes produced higher maximum formation voltages (characterised only by oscillations in the anodizing voltage) but no sudden breakdown. The very slightly corrosive electrolytes produced the highest maximum formation voltages.

The effects produced by variations in concentration of electrolyte appear to be closely related to the change in corrosiveness produced by such a concentration variation.

An increase in electrolyte temperature produced a reduction in anodizing efficiency. The electronic current increased rapidly with increase in temperature resulting in oxygen evolution rather than film formation as the predominant electrode reaction. The 7-12V plateau was eliminated at higher temperatures owing to both the very slow rise in potential with time and the low maximum formation voltage. There may also be an annealing effect which relieves the stresses in the oxide to some extent which are considered to give rise to the plateau.

8.4. **Anodic Oxidation of Titanium in Formic Acid**

The changes in anodizing characteristics, on the anodic polarization of titanium in formic acid, with concentration have been attributed to both the change in corrosiveness with concentration and also to the complexes produced between titanium and formic acid. Formic acid appears to be the only electrolyte showing such pronounced concentration effects.

8.4.1. **Micropitting of Titanium in Formic Acid**

In the region 0.5 - 60% formic acid and at temperatures below 45°C,
titanium exhibits the phenomenon of micropitting. It is considered that this effect is primarily due to:

(1) The high stresses in anodic oxide films on titanium.

(2) The chemical nature of formic acid (i.e., as regards corrosion behaviour, adsorption effects and complex formation).

Anodic titanium dioxide films have been shown directly and indirectly to be stressed. These stresses have been shown to result in the formation of a blistered oxide at a critical thickness. Blistering is, however, produced in many other electrolytes and therefore once blistering has occurred, the process leading to micropitting is dependent mainly on the nature of the formic acid. It is considered that the breakdown of the oxide to produce micropitting occurs in three stages:

(1) Corrosion of the stressed, blistered oxide by formic acid.

(2) Adsorption of formate on to the metal.

(3) Formation of soluble titanium/formate complexes.

The weight loss versus concentration curve for titanium after anodic polarization in formic acid shows a maximum at 40% by volume of the acid. Formic acid also exhibits a maximum in conductivity at 30% v/v. This suggests a maximum ionization and thus a maximum reactivity of the acid at the concentration which is the optimum for micropitting. The minimum breakdown potential (42V) leading to micropitting has also been shown to occur at 30% formic acid. It is apparent therefore that the phenomenon of micropitting is directly related initially to the corrosion behaviour of formic acid in the above concentration region. The effect of formic acid on the micropitting of titanium has previously been discussed by Piggott (95). It is considered, however, that the present study has further elucidated the conditions leading to micropitting. The corrosiveness of formic acid is considered to result in the second step in the overall process leading to micropitting.
The fact that the anodic film on titanium is highly stressed at a very early stage renders it particularly prone to dissolution in the acid. When breakdown of this inherently weak oxide has occurred, continued dissolution is thought to occur by the formation of soluble complexes.

8.5. The Physical Nature of the Anodic Oxide Film on Titanium

The ratio of the molecular volume of titanium dioxide to the atomic volume of titanium is 1.75; this is a high value and signifies that the oxide produced is more voluminous than the metal consumed. Such a condition results in the oxide produced being under a highly compressive stress. Assuming that Ti ion pass inwards then this compressive stress will be greater near the oxide/metal interface and will become smaller at the oxide/solution interface.

The result of such a stress distribution within the oxide tends to produce vertical fissures when the oxide reaches a certain critical thickness. Such fissures act as conducting channels (as electrolyte may penetrate into them) and reduce the overall film formation efficiency. This effect is manifested by the change in slope of the voltage/time curve at 7-12V. A further increase in thickness causes detachment of the oxide from the metal with production of blisters at the outer surface. Blistering in this manner also tends to close up the microfissures produced at the plateau. The formation efficiency of the oxide increases slightly as shown by the second change in slope of the voltage/time curve at 12V. The new formation efficiency is still less than that below 7V, however, probably due to the effective increase in surface area caused by blistering. Blistering has been shown to take place in this region using electron microscopy.

Differential oxidation on the various grains increases the stress in the oxide in certain areas. The oxide produced on the less "active" grains is thinner and is further compressed by the thicker oxide on some of the surrounding grains. This effect enhances the detachment of the oxide from the
metal on these thinner grains as the oxide may only expand upwards, thus producing an increased amount of blistering. It has been shown by colour photomicrography that breakdown of the oxide occurs initially on these thinner grains (i.e. where the oxide is most highly stressed).

It is considered that micropitting breakdown is directly related to the blisters in the oxide being in a high state of stress. Breakdown occurs (as shown by electron microscopy) by direct corrosion on the apex of the blisters. This is followed by adsorption of formate onto the metal, current concentration and the formation of a transient soluble complex which does not allow healing to occur.

The presence of stresses in the oxide has been shown experimentally using the method of MacNaughton & Hothersall.

The nature of the oxide in the 7-12V region proposed above has been further studied using experiments involving measurements of capacity and anodic leakage currents. The percentage capacity change with time shows a maximum at approximately 10V. As an increase in film capacity with time suggests a penetration of electrolyte and reduction of the effective thickness of the oxide, these results would indicate that the oxide in this zone is highly fissured.

The maximum observed in the anodic leakage current also suggests a reduction in formation efficiency due to the presence of highly conducting electrolyte in the fissures.

The change in the physical nature of the oxide at 7-12V appears therefore to be fairly well accounted for by the experimental results. It is therefore proposed that:

1. The oxide becomes highly stressed in the region 7-12V according to the Pilling Bedworth principle.
2. Vertical fissures are produced in the oxide in this region which allow penetration of electrolytes.
3. Fissures are assumed to start at the highly stressed zones around conducting impurities. These impurities also serve to conduct the current and
prevent healing within the fissures.

(4) Blistering of the oxide occurs at 12V due to the stress in the oxide becoming greater than the adhesion energy of the oxide to metal at this critical thickness.

(5) Differential oxidation of the various crystal faces serves to increase the stress and thus the amount of blistering on those grains having the thinner oxide.

(6) The high stresses at the apex of the blisters results in breakdown at those areas in the presence of formic acid within a certain concentration region.

8.6. Rectification Properties

The rectification properties of the oxide have been shown to depend on its physical nature. The rectification ratio rose with input voltage in the 7-12V region. The rectification ratio is therefore apparently increased by defects in the oxide. This agrees fairly well with theories put forward for rectification by other workers and it should be noted that an increase in rectification ratio at 7-12V indirectly enhances the concept of a stressed oxide in this region if the defect theory for rectification is valid.

The rectification ratio decreases with increase in temperature and with increase in oxide film thickness. The anodic oxide film on titanium acts as a rectifier and titanium as a valve electrode.

8.7. Electron Microscopy Studies

These studies have backed up fairly conclusively the postulated breakdown by blistering and attack on the blisters. The blisters formed in the oxide outside the micropitting range of concentration merely continue to grow in size and are not ruptured in this range of acid concentration. Electron microscopy thus shows both the change in surface topography at 12V and also
the effect of formic acid concentration on the breakdown or otherwise of the blisters, leading to micropitting or continued anodizing.

8.8. Conclusion

Discontinuities in voltage/time curves during anodizing have previously been reported for tantalum and niobium. The discontinuity found in the voltage/time curve at 7-12V on anodizing titanium is considered to result from a physical change in the nature of the oxide rather than from a crystallographic change as is the case with tantalum and niobium.

The various experimental techniques employed, as outlined in the text lead to the conclusion that the highly stressed oxide on titanium cracks in the region 7-12V and becomes detached from the metal substrate above 12V to form blisters. The oxide therefore transforms from a homogeneous to a non-homogeneous film on reaching a thickness of approximately 200Å. This transformation also affects the electrical properties of the film and the extent of transformation is primarily affected by the nature and concentration of electrolyte.

It is further considered that the breakdown of the oxide film in low concentrations of formic acid to give micropitting is also in part due to this physical transformation at 7-12V.
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