Chapter 1

Literature review
1.1 General introduction

Due to the rapid increase in the use of metals for various industrial purposes, corrosion has gradually become a major problem in most countries. Recent studies on the cost of corrosion to Australia, Great Britain, Japan, USA, and other countries have revealed that the total economic losses due to corrosion amounts to approximately 4% of the Gross National Product [1-3]. Besides the identified losses, there are diverse hidden consequences of corrosion which are not always amenable to such economic estimation. Prominent among these are various incidences of environmental pollution, industrial accidents, depletion of natural resources, etc.

The considerable effort directed to metal corrosion studies has resulted in the development of different structural corrosion resistant materials, such as stainless steels. The ability of stainless steels to passivate in many corrosive environments is responsible for their high corrosion resistance in various media. Consequently, stainless steels have been found to be useful for many industrial applications. However, over the past few decades the problems of industrial application, corrosion resistance and protection of stainless steels have been extended to several new dimensions.

On the one hand, there is a problem of shortage and rising cost of the required stainless steel alloying elements [4, 5]. For this reason, there has been a growing interest in producing economically alloyed stainless steels. In this regard, the replacement of nickel with manganese as an austenite stabiliser in stainless steels is one of the outcomes of the endeavour. Although the Cr-Mn stainless steels exhibit lower corrosion resistance than
their Cr-Ni counterparts [5-7], their corrosion resistance is high enough in some environments. It has already been demonstrated that the Cr-Mn steels can be successfully used under atmospheric conditions or in some media in chemical industry, particularly under anodic protection [8, 9].

On the other hand, the applications of stainless steels have become far more extensive. In parallel with the increasing use of this metal as a basic structural material for various equipment employed in highly corrosive media in chemical industry, the amount of stainless steels used under atmospheric conditions has also increased considerably. A good example here is the use of stainless steels in offshore platform constructions for processes associated with the extraction of mineral resources such as oil and gas in the shelf zones [10], where the aggressivity of the atmosphere is due mainly to the chloride-containing aerosols. In addition, a substantial increase in atmospheric corrosivity has occurred due to the increasing pollution of the atmosphere with nitrogen and sulphur oxides, which have also been identified as the major cause of acid rain [11].

1.2 Principles of electrochemical corrosion of metals

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with an environment resulting in a deterioration of the metal and its properties. All metallic corrosion processes occur due to the thermodynamic instability of metals in corrosive environments. Thus, the essence of corrosion processes, as a whole, is the transformation of a metal into its thermodynamically stable products (such as oxides, hydroxides, basic salts, etc.), or into soluble ionic species.
It is customary to separate corrosion processes into two groups: (i) chemical corrosion; and (ii) electrochemical corrosion. The former refers to the reaction of a metal with an environment in which the oxidation of the metal and the reduction of the oxidising constituent of the corrosive medium proceed in a single whole act. This type of corrosion occurs when metals are in contact with dry gases (air, products of combustion, etc.) and liquid nonelectrolytes (oil, benzene, etc.). High temperature oxidation of iron in dry air is a typical example:

\[ 4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]  \hspace{1cm} (1.1)

The electrochemical nature of metal corrosion in electrolyte solutions was established by De La Rive [6, 12] in the middle of the last century and since then has been quoted everywhere in the corrosion literature. Subsequently Vernon [13] has shown that this applies also to atmospheric conditions, where corrosion becomes possible only if the surface of metal is moistened. Electrochemical corrosion, in contrast to chemical corrosion, involves the oxidation of a metal and reduction of an oxidising constituent of the corrosive medium, which proceed as two half-reactions and not in a single whole act. Furthermore the overall reaction does not necessarily result in the formation of a chemical compound of the metal with the oxidiser. For example, the overall electrochemical reaction of metal dissolution in an electrolyte solution is subdivided into two coupled half-reactions: (i) anodic (oxidation of the metal); and (ii) cathodic (reduction of the oxidiser). If we consider the iron-acid solution system on this basis, then the corrosion process in the system

\[ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2(\text{g}) \uparrow \]  \hspace{1cm} (1.2)
consists, in reality, of two separate electrode reactions:

(i) the anodic reaction of oxidation of the iron

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1.3) \]

and

(ii) the cathodic reaction of the reduction of hydrogen ions

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \uparrow \quad (1.4) \]

Since these reactions are electrochemical in nature, they depend not only on the temperature and the concentrations of the substances involved, but also on the value of the electrode potential.

In general, the reaction rates \( i_a \) (anodic reaction) and \( i_c \) (cathodic reaction) can be expressed by the following equations [14]:

\[ i_a = K_1 \exp \left( \frac{\beta n F}{RT} E \right) \quad (1.5) \]

and

\[ i_c = K_2 C_{\text{H}^+} \exp \left( -\frac{\alpha n F}{RT} E \right) \quad (1.6) \]

where \( K_1 \) and \( K_2 \) are constants; \( C_{\text{H}^+} \) is the concentration of hydrogen ions; \( R \) is the gas constant; \( T \) is the absolute temperature; \( \alpha \) and \( \beta \) are the transfer
coefficients; \( n \) is the number of electrons involved in the reactions; \( F \) is the Faraday constant; and \( E \) is the electrode potential.

From equations (1.5) and (1.6), it follows that the rate of the anodic reaction increases with an increase (ennobling) in the potential, while the rate of the cathodic reaction increases with a decrease in the potential. Since the reaction rates are exponential functions of the electrode potential, they are extremely sensitive to its magnitude. For instance, to change the reaction rate tenfold, assuming that \( T = 293K, n = 1 \) and \( \alpha = \beta = 0.5 \), there is a need to vary the potential \( (E) \) only by \( 116mV \) (Tafel slope).

The magnitude of the electrode potential \( (E) \) satisfying the equation

\[
K_1 \exp \left( \frac{\beta n F}{RT} E \right) = K_2 C_{H^+} \exp \left( -\frac{\alpha n F}{RT} E \right)
\]

(1.7)

is called steady-state potential, \( E_s \). The rate of anodic reaction exceeds that of cathodic reaction \( (i = i_a - i_c > 0) \) at \( E > E_s \) and the rate of cathodic reaction exceeds that of anodic reaction \( (i = i_a - i_c < 0) \) at \( E < E_s \). Hence any deviation of the potential from the steady-state value \( E_s \), which can be achieved by electrochemical polarisation of the metal from an external current source or by bringing the metal into contact with a dissimilar metal, will result in the acceleration of one reaction and in the deceleration of the other. It follows from this that if potential of the metal deviates significantly from the steady-state value, the external current will be practically equal to the rate of corresponding reaction (anodic at \( E >> E_s \) or cathodic at \( E << E_s \)). The kinetics of each of the reactions (1.3 and 1.4), which together make up the corrosion process, can be studied by recording the dependence of the current
on the electrode potential when the potential is shifted towards positive values with respect to $E_s$ (anodic polarisation curve) or towards negative values with respect to $E_s$ (cathodic polarisation curve).

The widely accepted interpretation of electrochemical corrosion is based on the concept of local-action cells [1–3, 6, 12], e.g., galvanic couples of microscopic (grain boundaries, impurities, metallic or nonmetallic inclusions, etc.) or of macroscopic (cut edges, scratches, couples of dissimilar metals, etc.) sizes. In accordance with the theory of local-action cells the existence of chemical or structural inhomogeneities on the surface of metal may cause a differentiation of the surface on sites with lower potential and sites with higher potential. This will lead to a partial localisation of both the anodic and the cathodic reactions on these sites. The anodic reaction $M \rightarrow M^{n+} + n e^-$ will be localised on the site with the lower potential (anodic site), while the cathodic reaction $Ox + n e^- \rightarrow \text{Red}$ will occur on the site with the higher potential (cathodic site). Thus, the surface of a corroded metal can be likened to a set of a large number of short-circuited galvanic couples. Within the metal, which acts as an external part of the circuit, the electrons flow from the anodic sites towards the cathodic sites. In the electrolyte solution, which acts as an internal part of the circuit, the transfer of ions occurs with the anions moving towards the anodic sites, while cations move towards the cathodic sites. A schematic diagram of how a corrosion local-action cell functions is shown in Figure 1.1.

Besides chemical and structural heterogeneities on the metal surface, there are other factors that may lead to the establishment of anodic and cathodic sites. These sites may be generated due to inhomogeneities in corrosive medium resulting from local differences in the concentration of metal and
Figure 1.1: Schematic illustration of corrosion local-action cell (cited from [12]).
other ions or pH; nonuniform access of oxygen or of other oxidisers towards the metal surface; or differences in physical conditions, i.e., temperature, pressure, radiation, external electric fields, etc.

Despite the significance of the corrosion local-action cells, self-dissolution of metals as an electrochemical process can proceed without the involvement of the galvanic couples. A good example of this is the dissolution of amalgams of electrochemically active metals (sodium and zinc) in electrolyte solutions studied by Frumkin [15], and Wagner and Traud [16]. Frumkin and Kolotyrkin [17, 18] have also established that not only amalgams, but solid metals (including those where deliberate surface preparation is employed to expose heterogeneities such as nickel covered partly with platinum), dissolve in a manner which obeys the laws of electrochemical kinetics. The experimental proof that the laws of electrochemical kinetics are applicable to corrosion processes on solid metals represents an important milestone in the advancement of corrosion science. It is now widely recognised that the corrosion rate of metals can be regulated by influencing the kinetics of the associated anodic and cathodic reactions. This, in turn, has stimulated a wide range of investigations of the kinetics and mechanism of these reactions, and search for ways of controlling their rates through the modification of the composition of the corrosive media, as well as by regulating the composition and structure of a metal.

1.2.1 Passivity of metals and anodic protection

Passivity can be defined generally as the state of a metal surface which is characterised by low corrosion rates in a potential region which is normally
strongly oxidising for the metal [19]. Generally, the low corrosion rates of a metal in a corrosive environment can be related to:

- the relatively high thermodynamic stability of the metal in a given corrosive medium;

- the absence of depolarisers in the medium or impediment of their access towards the metal surface; and/or

- the strong retardation of cathodic process.

However, it is customary to define passivity as a state characterised by high corrosion resistance of a metal, associated with retardation of the anodic process despite a marked thermodynamic tendency of the metal to react with the corrosive medium [1].

The accomplishment of passivity is often accompanied by:

(i) a sharp drop in corrosion rate of metal (anodic current density); and

(ii) a significant ennobling of metal potential.

The shift of the electrode potential towards positive values indicates that, as the passivity of the metal is approached, the anodic process of the electrochemical corrosion of the metal is retarded.

The following substances or processes can facilitate the passivation of a metal which has a tendency to become passivated (active-passive metal):
(i) oxidisers, such as oxygen (O₂), chromate (CrO₄²⁻), molybdate (MoO₄²⁻), tungstate (WO₄²⁻), etc., are well known for their ability to passivate active-passive metals; and

(ii) anodic polarisation of a metal from an external power supply (e.g., potentiostat), or the use of a metal as an anode in a galvanic couple with another metal acting as a cathode.

The study of electrochemical corrosion processes usually involves the construction and analysis of the polarisation curves, plotted as a rule in the semilogarithmic scale (potential (E) versus logarithm of current density (log i)). A typical anodic polarisation curve of an active-passive metal (such as titanium, stainless steels, nickel-based alloys, etc.) is shown in Figure 1.2.

The following parts of the curve can be highlighted:

- an active region, where the metal passes into solution as aquated ions Mⁿ⁺ · mH₂O (for iron, Fe²⁺ · mH₂O);

- a region of transition from active to passive state;

- a passive region, where the anodic current density is reduced by several orders of magnitude in comparison to the active state; and

- a transpassive region, where oxidation of a metal to a higher valence state or where oxygen evolution contributes to the measured anodic current.
Figure 1.2: Typical polarisation diagram for active-passive system (cited from [5]): $E_a^0$ and $E_c^0$ - the equilibrium potentials of the anodic and cathodic processes, respectively; $E_{pp}$ - passivation potential; $E_{br}$ - breakdown potential.
The passive state acquired by a metal surface after the initial passivation can be retained for some time, even if the external passivating conditions have been changed. For instance, a metallic chromium passivated in 0.5M H₂SO₄ at 50°C by means of anodic polarisation retains passivity in the same solution for ~ 3 hours after the anodic polarisation is interrupted [20].

The following substances or processes may cause the activation of passivated surface or may impede the accomplishment of passivity:

- reducing agents, such as sodium sulphite (Na₂SO₃), sodium thiosulphate (Na₂S₂O₃), etc., are known for their ability to activate passivated metal surfaces;

- cathodic polarisation from external power supply or by the use of a passivated metal as a cathode in a galvanic couple with another metal acting as an anode;

- some ions, such as the halogen ions (Cl⁻, Br⁻, I⁻);

- rise in temperature of solution; and

- mechanical disruption of the passivated surface, e.g., scratching of the surface leading to formation of a galvanic couple where the scratched site acts as an anode, while the undisturbed part of the passivated surface acts as a cathode.

Several theories have been proposed in an attempt to explain the phenomenon of passivity. At present, the two most fundamental and
generally accepted theories are: (i) film theory of passivity; and (ii) adsorption theory of passivity. The film theory of passivity was first proposed by Faraday [7, 12] in the middle of the last century. According to this theory the passive state is conditioned by the presence of a chemically bounded oxygen on the metal surface. This theory was further developed by Evans [21, 22], Bonhoeffer, Frank and Vetter [23–31], and other investigators [32–35]. The contemporary film theory of passivity explains the state of improved corrosion resistance through the formation of a thin (tens of angstroms), often invisible protective film on the metal surface, consisting of the products of reaction of the metal with some oxidising constituents of the corrosive media, usually with oxygen. The passive film is electrically conductive and acts as a cathode, while anodic reaction proceeds in pores of the film (Figure 1.3(a)). Owing to the formation of the protective oxide the pores close up and are again formed at other sites, where dissolution of the film or its cathodic reduction occurs. Thus, the phenomenon of passivity represents a dynamic equilibrium between the processes generating the passive film and the processes destroying it. Evidently, when the passive state is established, the behaviour of the metal, relative to the corrosive media, depend to a great extent on the properties of the passive film under the given conditions.

The adsorption theory of passivity was developed by Schwabe [36], Uhlig [37–39], Kabanov [40–43], and others [44, 45]. The theory assumes that adsorbed layers of oxygen or other substances are formed on metal surfaces. According to Kabanov, Ershler, and Frankenthal [40, 46, 47], even less than a monolayer of the adsorbed substance has been shown to have a passivating effect, hence it is suggested that the adsorbed film covers in the first place the most active sites of the metal surface. Ershler [46] has shown that the
covering of only 6% of platinum surface with adsorbed oxygen decreases the rate of anodic dissolution of the metal in 0.5M HCl by tenfold. The protective action of oxygen, when it is adsorbed, is associated with a significant suppression of the anodic reaction of the electrochemical corrosion of the metal. It is assumed that the adsorption of oxygen atoms, owing to the dipole character of the metal-oxygen bond, leads to a reorganisation of the electrode potential in the double layer. This, in turn, results in the inhibition of the metal dissolution.

The protective oxide film and adsorption theories of passivity do not contradict, but rather supplement each other. As the adsorbed film in the process of growing gradually passes into the three dimensional oxide film (Figure 1.3(b)), the retardation of the anodic process, promoted by change in the double layer structure, will also be supplemented by the greater difficulty encountered by the metal ions passing directly through the protective film.

On the basis of the analysis of the anodic polarisation curve of an active-passive metal, shown in Figure 1.2, it can be seen that passivity and, hence, improved corrosion resistance of the metal can be accomplished by effecting a shift of potential in the positive direction, towards the passive region by means of anodic polarisation from an external source. This method of corrosion protection achieved by maintaining an active-passive metal potential in the passive region by an externally applied anodic current is referred to as “anodic protection”. As a corrosion control technique, anodic protection is relatively new and less familiar to corrosion engineers than the other electrochemical techniques, such as cathodic protection. The main advantages of anodic protection are: (i) low current requirements; (ii) large reductions in corrosion rates (typically 10000-fold or more); and
Figure 1.3: Schematic diagram illustrating (a) film and (b) adsorption theories of passivity (cited from [12]).
(iii) applicability to some strong, hot acids where traditional cathodic protection is not applicable owing to high current requirements and to possible evolution of hydrogen, which often results in "hydrogen embrittlement" of metal to be protected. Essentially, anodic protection represents one of the most economical solution to many critical corrosion problems, in particular, in acid media.

The possibility of an application of anodic polarisation to the mitigation of corrosion rate with the use of a three electrode system consisting of (i) anode (metal to be protected); (ii) cathode (auxiliary electrode); and (iii) reference electrode was mentioned by Polin [48]. Following this, several approaches for the industrial application of anodic protection in corrosion control of steels, and in particular, stainless steels in acid sulphate solutions, have been demonstrated by other researchers [8, 9, 49-53].

In general, there are two different modes of anodic protection [4, 54]:

- the continuous polarisation mode, when potential of anodic protection is placed, usually, in the middle of the passive region; or

- the on-off control mode or synchronous anodic protection of several items by means of one potential controller. In the latter case protection potential is applied, usually, in the vicinity of the noble end of the passive region.

When the potential controller is turned off either by accident or deliberately (on-off control, synchronous protection) passivity is retained for some limited time. Evidently, an increase in the passivity retention time reduces
the frequency of connection and disconnection of the controller and, consequently, increases reliability of the protection. A special electrode, a galvanic cathode, can be introduced into the polarisation circuit to increase the passivity retention time [54]. It has been suggested that anodic protection cannot withstand the corrosive effect of some aggressive anions [7, 55]. Halogen anions, particularly chloride ions, are destructive to passivity and thus, can reduce the passivity retention time drastically. For this reason it is recommended that when applying anodic protection, the concentrations of halogen ions are kept as low as possible.

1.2.2 Local anodic depassivation and pitting corrosion of stainless steels

Passivated metals owe their high corrosion resistance to the presence of a thin protective oxide film. Anodic polarisation of a passivated metal, particularly of stainless steel, in solutions containing aggressive anions can lead to a local depassivation (breakdown) of the passive surface and, as a result, to an extremely localised corrosion process such as pitting corrosion. According to Shreir [3], pitting corrosion is "a highly localised attack at specific areas, resulting in small pits that penetrate into the metal and may lead to perforation".

In general, the process of pitting corrosion may be divided into two stages: (i) initiation of pits; and (ii) propagation of pits. By summarising the different viewpoints, discussed in the literature [56–76], it can be concluded that the initiation of steadily functioning pits on steel surface becomes possible if the following conditions are met simultaneously:
(i) the surface of steel is heterogeneous—the heterogeneity of the steel surface results in the inhomogeneity of the protective surface film and, consequently, in the presence of some relatively active sites;

(ii) the presence of some activating anions (such as halogen ions) in the corrosive medium;

(iii) the potential of steel is not less than a definite breakdown potential $E_{br}$;

and

(iv) the activating anions are accumulated at the active sites (nuclei of pits) at a concentration not less than a definite critical value.

The validity of the first statement (i) is supported by the available data on nonuniformity of the passivating film with respect to its thickness [56] or properties [57]. The nature of the active sites, acting as pits initiation centres is now well established. These include surface dislocations, cracks in protective oxide [58, 59], and boundaries between metal and nonmetallic inclusions, such as sulphides [60–68].

The second proposition (ii), relating to the need for the presence of activating anions in solution, can be demonstrated by recording anodic polarisation curves in solutions with and without the anions. In the absence of the activating anions the diagram PGDE (Figure 1.2) corresponds to the usual behaviour of a passive metal during anodic polarisation, where region DE is the transpassivity region. However, at sufficient concentration of the activating anions in solution the curve DGH will be recorded, where region GH represents pitting corrosion. According to Kolotyrkin [69] the
number of anions able to cause pitting corrosion in aqueous solutions decreases with the increase in the passivation properties of a metal, which depend on the affinity of the metal for oxygen. Thus, the number of anions which may cause pitting corrosion on stainless steels is significantly less than for zinc, aluminium, and iron. On the other hand, chromium does not undergo pitting corrosion in aqueous solutions. The halogen ions in the following order of aggressivity $\text{Cl}^- > \text{Br}^- > \Gamma$ are known to be the main reason for the pitting corrosion of stainless steels.

The third condition (iii) of pits formation requires the steel potential to exceed a breakdown potential $E_{br}$, and is associated with competition of activation-repassivation processes occurring on active sites of the passivated surface [69]. This theoretical proposition is the core of a dynamic model of pitting formation proposed with some variations by different investigators [70–76]. According to this model, the initiation of pits is possible even at potentials more negative than the potential of formation of steadily functioning pits (breakdown potential, $E_{br}$). However, these pits do not survive owing to the prevalent process of pits repassivation in this region of potentials. The competition between activation-repassivation processes make oscillations of current at potentials $E < E_{br}$ very typical for anodic polarisation curves of stainless steels in chloride-containing solutions, while with the potentiostatic polarisation of the steels in this region of potentials, the anodic current, despite the oscillations, drops in time acquiring values corresponding to the steady passive state. At potentials $E \geq E_{br}$, the activation of the metal surface at the pits initiation sites is not necessarily followed by repassivation and the nuclei of pits develop into the stable ones.
There are two commonly expressed viewpoints on the nature of the breakdown potential, $E_{br}$. The first viewpoint indicates that the breakdown potential is a value required to build up an electrostatic field within the passive oxide film, capable of inducing penetration of an activating anion to the metal surface (penetration theory) [77]. The ability of anions to penetrate the oxide depends on their size and charge, and here $\text{Cl}^-$, owing to its small radius, has an advantage. Alternatively, the second viewpoint explained the breakdown potential in terms of competitive adsorption of an activating anion ($\text{Cl}^-$) with oxygen in the passive film (adsorption theory) [69, 78, 79]. The stainless steels have typically greater affinity for oxygen than for $\text{Cl}^-$, but as the potential is made more noble, the concentration of $\text{Cl}^-$ ions at the metal surface increases, eventually reaching a definite value (critical concentration - the fourth condition (iv)) that allows $\text{Cl}^-$ to displace adsorbed oxygen. Adsorbed $\text{Cl}^-$, compared to adsorbed oxygen results in lower anodic overvoltage for metal dissolution, which accounts for a higher rate of corrosion at the site where the exchange has taken place.

The surface of a metal, subjected to pitting corrosion, usually contains a large number (up to $10^3 \text{cm}^{-2}$) of pits. These pits grow in size, while their number can change in time for various reasons. Repassivation of pits, associated for instance with competition for cathodic surface or coalescence of small pits, will tend to reduce the number. At the same time, the formation of new pits can occur owing to further activation of passivated surface caused, for instance, by highly corrosive solution flowing out from the functioning pits. Consequently, the experimental curves of the statistical distribution of pits sizes, which always include sizes of repassivated (dead) pits and do not include sizes of the smallest pits, are quite complex [80–85].
As a rule, investigators study kinetics of "average" pits propagation, performing the experiments under strictly controlled conditions. Some of these studies have been performed under potentiostatic conditions [86, 87], whereas according to Kolotyrkin [79, 88] the natural pitting corrosion conditions correspond better to the galvanostatic mode. In most cases results of electrochemical and chemical studies of the dependence of pits sizes (h - depth of pitting and r - radius of pitting mouth) on time (t) can be expressed by a simple power function

\[ r \ (or \ h) = at^K \]

Usually the registered values of K are equal to one-third [89, 90]; one-half [89, 91–94], two-thirds [93, 95, 96], and one [86, 87, 89, 95, 97–100].

1.3 **Principal characteristics of the atmospheric corrosion of metals**

Atmospheric corrosion is the most commonly experienced form of metal deterioration because of the vast number of metallic structures and artifacts that are exposed to the atmosphere. Owing to the several studies in this area, it is now certain that the corrosion rate of metals under atmospheric conditions is not negligible. Under certain circumstances atmospheric corrosion may proceed at a rate much higher than possible in the bulk of electrolyte. A typical example discussed by Rozenfeld [101] is that of the corrosion of ship plating and marine platform piles in water-line zone, where metal corrodes under cyclic conditions of wetting and evaporation of superficial layers of moisture.
Following the early investigations by Vernon [13], atmospheric corrosion is now recognised as a special form of electrochemical corrosion which differs from other forms of corrosion in that the corrosive media necessary to sustain the process are thin electrolyte layers. These thin electrolyte layers result from the direct deposition of atmospheric precipitations or from adsorption and condensation of moisture on the metal surface. The formation and properties of these layers, as well as their lifetime are influenced by a wide range of factors. Among these are the type, extent of pollution and physical properties of the atmosphere which are in turn related to seasonal or geographical factors, as well as to the industrial activity.

1.3.1 Moistening of metal surfaces with absorbed and phase layers of moisture

The moistening of metal surfaces is the most important precondition for the atmospheric corrosion of metals. The direct dependence of a metal corrosion rate on the relative humidity (RH) was first demonstrated by Vernon [13] who showed that at RH lower than a certain critical value, corrosion rate of iron was negligible even in the atmosphere with a high concentration of corrosive substances such as sulphur dioxide (SO₂) and fly ash. This threshold RH is referred to as critical relative humidity. Figure 1.4 illustrates the influence of RH on the atmospheric corrosion of iron. At \( \text{RH} \geq 70\% \), corrosion rate in polluted air (curves 2 and 3) increases sharply, indicating a change in the corrosion mechanism. The chemical process of dry oxidation, which is very slow at room temperature, has been
Figure 1.4: Effect of relative humidity and atmospheric pollution on the corrosion of iron: 1 - pure air; 2 - air polluted with 0.1% SO₂; 3 - air polluted with 0.01% SO₂ and particles of charcoal (cited from [13]).
replaced by the process of electrochemical corrosion which, in turn, proceeds at a considerably higher rate.

 Generally there are two moisture regimes [3, 6, 103]:

(i) moistening of metal surface by adsorbed moisture layers; and

(ii) moistening of metal surface by phase moisture layers.

Formation of the absorbed moisture layers occurs through binding of water molecules from vapour phase on a metal surface by means of adsorption forces at RH < 100%. Depending on the nature of the metal and RH, the thickness of the adsorbed layer may reach tens of molecular layers [6, 103–107]. The increase in the number of the molecular layers of adsorbed water on iron (a) and zinc (b) surfaces is shown in Figure 1.5. Assuming that the diameter of a water molecule is 0.31nm [108] the thickness of the adsorbed moisture layers at RH ≤ 100% would be ≤ 3.1 · 10^{-2}μm which is in a very good agreement with the data on the mass of adsorbed water per unit surface area on aluminium given in [109].

Formation of phase layers of moisture occurs through the direct contact of a metal surface with atmospheric precipitations (open atmosphere) or through the cooling of the metal to dew point (open atmosphere, non-heated premises) at RH > 100% (at least in the near surface layer of air).

The moistening of metal surfaces may also be affected by other factors. One phenomenon of importance in this regard is capillary condensation. The existence on a metal surface of the pores with wetting walls results in the
Figure 1.5: The relationship between the relative humidity and the number of layers of water adsorbed on (1) iron and (2) zinc surfaces (cited from [106, 107]).
condensation of vapour in the pores at RH < 100% [110]. Fyfe cited from [3, 106] has shown that the value of RH, at which capillary condensation begins to occur, decreases from 98% to 50% as pore radii decrease from 360Å to 15Å. Thus pores in corrosion products, crevices both between corroding surfaces and precipitated solid particles or parts of construction, as well as the presence on a metal surface of hygroscopic salts [111], can facilitate moistening of the metal surface and, hence, the development of corrosion at RH well below 100%.

Numerous data on the times of wetness (i.e., duration of atmospheric corrosion process) of metal (Zn, Fe, Cd, Cu, Al) surfaces with adsorbed ($t_a$) and phase ($t_p$) layers of moisture in different environments have been reported by some investigators [112–118]. A generalisation of the data shows that the duration of atmospheric corrosion processes, depending on the environment, varies from ~ 37% up to ~ 70% of exposure time, while $t_a$ and $t_p$ are approximately equal for all the test zones. Furthermore, it must be noted that the corrosion action of the atmosphere is not restricted to the region of the positive temperatures. The existence of the phase layers of moisture down to -10°C was identified by some workers [119–121]. The phenomenon was explained by relating the decreasing freezing point of water to the increasing concentration of the dissolved salts (e.g., sulphates in industrial atmospheres and chlorides in maritime atmospheres).
1.3.2 Corrosion rates of metals under the adsorbed and phase layers of moisture

The material effect (M), which is related to the exposure of metal to the atmosphere, is proportional to the duration of a particular corrosion process and can be expressed, as:

\[ M = \sum_{i=1}^{n} K_i(\delta, C) \cdot t_i \]  

(1.9)

where \( K_i \) - rate of a particular corrosion process and 
\( t_i \) - duration of a particular corrosion process.

The corrosion rate (K) under the given conditions is a function of moisture layer thickness (\( \delta \)) and of the nature and concentration of the corrosive substance (C) in the atmosphere.

Careful examination and analysis of the data given in the literature [104, 122–125] reveals that the corrosion rates of metals under phase layers of moisture (\( K_p \)) are always considerably higher than those in the adsorbed layers (\( K_a \)). The data on corrosion rates of different metals under the adsorbed and phase layers of moisture in the atmosphere polluted with SO\(_2\) are shown in Table 1.1.

González et al. [125] studied the corrosion of iron and aluminium under phase (400\( \mu \)m) and invisible adsorbed layers of electrolytes. The instantaneous corrosion rates for iron (10\(^{-4}\)NH\(_2\)SO\(_4\) and 10\(^{-3}\)NNaCl) and for aluminium (10\(^{-4}\)NH\(_2\)SO\(_4\)) derived from current-time recordings obtained by
Table 1.1: Comparison of corrosion rates of some metals under adsorbed and phase layers of moisture in an atmosphere polluted with SO₂ (2mg m⁻³). Data obtained from reference [124].

<table>
<thead>
<tr>
<th>Metal</th>
<th>$K_a$, g m⁻²h⁻¹</th>
<th>$K_p$, g m⁻²h⁻¹</th>
<th>$K_p/K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel</td>
<td>$1.98 \cdot 10^{-2}$</td>
<td>$6.6 \cdot 10^{-1}$</td>
<td>33.3</td>
</tr>
<tr>
<td>Stainless steel (13% Cr)</td>
<td>$2.7 \cdot 10^{-3}$</td>
<td>$7.3 \cdot 10^{-2}$</td>
<td>27.0</td>
</tr>
<tr>
<td>Copper</td>
<td>$6.9 \cdot 10^{-3}$</td>
<td>$4.19 \cdot 10^{-2}$</td>
<td>6.1</td>
</tr>
<tr>
<td>Brass</td>
<td>$1.12 \cdot 10^{-2}$</td>
<td>$7.84 \cdot 10^{-2}$</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Electrochemical atmospheric corrosion monitors (EACM) under phase layer exceeds those under adsorbed layer by approximately 1.5–2 orders of magnitude. Mansfeld and Tsai [126] measured the galvanic current generated with the EACM in the time period immediately before the surface of the monitor dried out. In general these current-time curves demonstrated a continuous increase of the current related to thinning of the moisture layers and followed then by sharp drop of this current to the extremely low values. This increase in current is, to all probability, associated with the increase in the limiting current of oxygen diffusion as the thickness of the moisture layer decreases. The pronounced increase in the galvanic current observed by Mansfeld and Tsai [126] when the visible electrolyte layer starts to disappear may be associated with the phenomenon of self-stirring in thin electrolyte layers. This process may be accelerated during the evaporation of electrolyte from the metal surface. The self-stirring results in convection transportation of oxygen to the electrode surface. According to Razentsev [101], this process is based on changes in surface tension of the superficial
moisture layer associated with small variations of temperature from point to point.

The significantly higher corrosion rates obtained under phase layers of moisture than those under the adsorbed layers and the approximate equality of the times of moistening of metal surfaces with the adsorbed and phase layers, lead to the conclusion that major degradation of metals in atmospheric conditions occurs due to corrosion under the phase rather than the adsorbed moisture layers.

1.3.3 Composition and thickness of superficial phase layers of moisture

The nature and concentration of corrosive substances in the atmosphere can affect the composition of the superficial layers of moisture significantly and, hence can have a marked influence on the mechanism and the rate of atmospheric corrosion of metals.

It is well known that the pollution of the atmosphere with SO₂ imparts an acid reaction to the atmospheric precipitations and dews [11, 22, 101, 117, 127, 128]. For example, Evans [22] has reported that a control sample of dew, taken in 1935 near Berlin (Germany) was essentially a dilute solution of sulphuric acid (CH₂SO₄ = 10⁻²M). Sanial et al. [129] have carried out pH measurements on moisture taken from samples of mild steel exposed to an atmosphere polluted with SO₂. The results revealed that the pH of the superficial moisture depends on the concentration of SO₂ and the RH, and can be as low as ≤ 3. Similar pH values in superficial moisture have been reported by other workers [101, 130–132]. Bubenick [11] reported that an
extremely low pH value such as 1.4 has been observed for fog and precipitation (with a 2.5:1 ratio of nitrogen oxides to sulphur dioxide in the samples) in California, United States of America, 1982. Field measurements of the pH of rainwater samples conducted at 32 sites between October 1984 and March 1986 in Hunter Region (New South Wales, Australia), where major industrial emissions of concern are sulphur dioxide and nitrogen oxides, are revealed in [133]. Values of the measured pH were described as mildly acidic and rainwater samples with pH below 4.5 were observed in rare cases. Porteous and Barratt [134] performed measurements of rainfall acidity at a large number of sites throughout the United Kingdom in 1986–1987. It has been shown that the mean pH of rainwater samples can drop to 4.4. However, a simple calculation based (i) on the assumption that the experimental data obey the normal distribution [135] and (ii) on the data on standard deviations revealed in the same paper, show that approximately in 15% of rainfall events pH of rainwater was 3.7, while in 3% of rainfall events the pH was 2.6. A further acidification of the superficial moisture can occur due to the accumulation of sulphates in the corrosion products. The resulting pH depends on the sulphates concentration as well as on the thickness of the moisture layer. Knotkova-Čermáková, et al. [130, 136, 137] reported that, depending on the surface roughness, the thickness of the phase superficial moisture layer on the horizontal and vertical surfaces changes within the ranges of 50–150µm and 10–50µm respectively. Berukshtis and Clark [121] have demonstrated that the thickness of the moisture layer retained after a rainfall on a metallic surface, oriented at the 45° angle to horizontal is equal to 40–50µm. The approximate concentrations of the sulphuric acid solutions formed, deduced from the evaluated volumes of superficial moisture and contents of sulphates in corrosion products on Fe, Zn and Cd after two months of exposure in
different environments, are given in the same study. Results of these calculations are shown in Table 1.2.

Table 1.2: Sulphate ion concentrations in the corrosion products and calculated concentrations of solutions on metallic surfaces (thickness of layer $\delta = 50\mu m$). Data obtained from reference [121].

<table>
<thead>
<tr>
<th>Environment</th>
<th>in corrosion products</th>
<th>in solution, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>1.5 - 2.0</td>
<td>0.20 - 0.25</td>
</tr>
<tr>
<td>Rural</td>
<td>0.4 - 1.2</td>
<td>0.05 - 0.15</td>
</tr>
<tr>
<td>Maritime (North*)</td>
<td>0.2 - 0.6</td>
<td>0.03 - 0.08</td>
</tr>
<tr>
<td>Maritime (South*)</td>
<td>0.2 - 0.7</td>
<td>0.03 - 0.09</td>
</tr>
</tbody>
</table>

* Northern hemisphere

Metals in the marine and maritime atmospheres are often subjected to corrosion, accelerated by sea-salt aerosols containing Cl$^-$ ions. The importance of chloride as a corrosive substance has been demonstrated by the strong influence of coastal proximity on corrosion rate of metals [101]. Ballance and Duncan [138] have carried out measurements on the ratio of elements collected at 18 sites in maritime atmosphere of New Zealand and have shown that sodium chloride is a major component (up to 90%) of the precipitated chlorides. Also the continuous rainfall monitoring (Leatherhead, United Kingdom, 50km inland) during the storm of a rare strength which hit southeast England on the night of 15 October, 1987 [139], showed peaks in NaCl concentration of up to 0.03M, with an average of 0.01M. Evaluation of the concentration of chloride-containing solutions, formed on metal surfaces in atmospheric conditions, based on chloride
content in corrosion products has been performed by Berukshtis and Clark in [121]. The results of the evaluation are shown in Table 1.3.

Table 1.3: Chloride ion in concentrations in corrosion products and calculated concentrations of solutions on metallic surfaces (thickness of layer $\delta = 50\mu m$). Data obtained from reference [121].

<table>
<thead>
<tr>
<th>Environment</th>
<th>in corrosion products g m$^{-3}$</th>
<th>in solution, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>0.04 - 0.07</td>
<td>0.03 - 0.05</td>
</tr>
<tr>
<td>Rural</td>
<td>0.03 - 0.09</td>
<td>0.02 - 0.06</td>
</tr>
<tr>
<td>Maritime (North*)</td>
<td>0.20 - 0.50</td>
<td>0.14 - 0.36</td>
</tr>
<tr>
<td>Maritime (South*)</td>
<td>0.04 - 0.06</td>
<td>0.03 - 0.04</td>
</tr>
</tbody>
</table>

* Northern hemisphere

The quantities of chlorides precipitated on metal surfaces in the marine and maritime atmospheres have been reported in the literature [138–142]. Calculations of the concentrations of the chloride-containing solutions based on these data and the assumption that: (i) chlorides precipitated during one day dissolved completely, and (ii) the thickness of the superficial moisture layer $\delta = 50\mu m$, shows that $C_{Cl^-}$ can be in the range 0.001–0.4M which is in good agreement with the data provided in Table 1.3. Furthermore the accumulation of the sea-salts and the subsequent increase in the concentration of the superficial solutions can occur in the conditions excluding direct contact of the corroding surfaces with the atmospheric precipitations. The accumulation of the sea-salts can also enhance hygroscopicity of the corrosion products and, hence, increase time-of-wetness of the corroding surfaces [111, 143, 144]. These circumstances may be
responsible for a greater corrosion damage of specimens corroding under a shelter rather than in open atmosphere, or of surfaces corroding in open atmosphere but directed downward rather than upward [145, 146].

1.4 Atmospheric corrosion of stainless steels

Generally, the data on atmospheric durability of stainless steels reported in the literature are, to some extent, contradictory. For example, Rozenfeld [101] reported that eight year tests of steels Cr18Ni9, Cr18Ni9Mo2 and Cr18Ni12Mo2 in industrial and marine atmospheres have shown that the steels were not subject to uniform or pitting corrosion. Ibidem reported that five year tests in very humid atmospheres of stainless steels in which nickel was either partially or completely replaced by manganese did not produce any signs of uniform or pitting corrosion. However it was demonstrated that steels 304 and 316 corrode in atmosphere polluted with sulphur dioxide and chlorides [147]. Johnson [148] has reported the results of 12 year full-scale atmospheric corrosion tests of 430, 304 and 316 stainless steels at Stratford (London, United Kingdom; industrial atmosphere) and Shoreham (United Kingdom, 30m from the sea in the grounds of an electricity generating plant; severe marine-industrial atmosphere). All steels (except of steel 316 in industrial atmosphere) were subjected to pitting corrosion. The synergistic effect of sodium chloride and sulphur dioxide was found to be the main cause of the pitting corrosion of stainless steels under the atmospheric conditions. In the absence of either of these two substances little pitting occurred. The tendency of steels 304 and 316 to undergo spot corrosion, pitting corrosion and crevice corrosion in marine atmosphere (18 months tests) was noted [149]. Steels 304, 316 and 444 practically did not
corrode in urban atmosphere of Stóckhólhm (over five years). However, investigations of the surface of the steels by the use of scanning electron microscopy have shown small sites of localised corrosion [150].

The corrosion resistance of stainless steels under atmospheric conditions is directly related to the alloy content. The improvement in the atmospheric corrosion resistance of stainless steels can be related to the increased content of the alloying elements such as chromium, nickel and molybdenum [101, 148, 151–153, etc.].

The corrosion behaviour of stainless steels in atmospheric conditions can be affected by the presence of small quantities of alloying elements and impurities. Nonmetallic inclusions, in particular manganese sulphide, have been found to produce defects in the surface protective film and, consequently, initiate atmospheric localised corrosion [153]. Initial stage of the corrosion of low-alloyed steel with high content of sulphur (0.002% C, 0.02% Si, 1.11% Mn and 0.123% S) in humid atmosphere of the climatic chamber has been studied [154]. Microscopic examination has shown that dissolution of sulfide inclusions ((Mn, Fe) S) followed with formation of a rust nest occurred at the early stage of corrosion under the condensed droplets of moisture. Dégerbeck et al. [150] reported that stainless steel 444 notwithstanding absence of nickel and somewhat lesser content of molybdenum shows better atmospheric corrosion resistance than steel 316. The authors have associated the improved corrosion resistance of steel 444 with the presence of titanium, which formed sulphides that are significantly less soluble than manganese sulphides.
The corrosion resistance of stainless steels in the atmosphere depends on surface finish [148, 150, 155]. Henrikson [cited from [148]] has shown that a high surface finish on 430 and 304 steels made these materials as corrosion resistant as 316 steel, while at the same surface finish these steels are in the following order of resistance to the atmospheric pitting: 430 < 304 < 316. Andre [155] indicated that the polishing of stainless steels surface hampers the trapping and confinement of different atmospheric pollutants with the surface. According to Sanial et al. [129] surface roughness predetermines the number of active centres adsorbing sulphur dioxide from the atmosphere. The authors have proposed that surface roughness reduces partial pressure of saturated vapour and, as a result, stimulates vapour condensation. Furthermore, the surface roughness affects the thickness of superficial phase electrolyte layers [130, 136] which, evidently, results in an increase in the corrosion rate.

Hence, stainless steels, including ones with higher content of chromium, nickel and molybdenum, corrode under atmospheric conditions and the corrosion processes are affected by a number of diverse factors. This highlights practical significance of the study of atmospheric corrosion of stainless steels, as well as the benefits of accelerated electrochemical estimations of their atmospheric durability.

1.5 Corrosion-electrochemical studies of metals in thin electrolyte layers

Owing to the electrochemical nature of corrosion processes the electrochemical methods comprise a substantial part of corrosion research
All electrochemical methods are based on Faraday's law relating the number of moles of material m undergoing reaction at the electrode to the charge Q passed. These methods are distinguished by the relatively short measuring time and the high accuracy. These qualities make electrochemical techniques irreplaceable both in the study of the mechanism of metal corrosion and in the accelerated estimations of corrosion resistance of metals based on laboratory measurements. However, there is a special problem in the use of these techniques in the case of atmospheric corrosion studies. The problem is associated with the limited amount of electrolyte involved in atmospheric corrosion of metals. These electrolyte solutions are present on metal surfaces in the form of very thin layers, the thickness of which can affect the mechanism of the electrochemical reactions on the metal surface, as well as the corrosion process.

The rates of cathodic and anodic reactions on metals under thin electrolyte layers may be quite different from the corresponding rates in bulk electrolytes. The rate of cathodic reaction is expected to increase in the first instance due to the weak opposition which the thin layers present to oxygen diffusion from air to the metal surface. On the other hand, the thin layers are more easily saturated with corrosion products and the limit of solubility of the products in the superficial electrolyte is reached more quickly as the layers become thinner.

The first electrochemical measurements on metals covered with thin layers of electrolyte, which are relevant to the problem of atmospheric corrosion, were carried out between 1950–1960 by Tomashov [162, 163]. In these experiments, it was shown that by moistening the upper flat surface of the assembly of plates of different metals (Cu/Fe) pressed tightly to each other, a
corrosion galvanic cell was formed. By moistening the working surface of the assembly a voltage developed between the cathodic (Cu) and the anodic (Fe) plates of the galvanic cell. The resulting current was associated with the process of dissolution of the anode. At present, the modelling of the atmospheric corrosion process by use of the corrosion galvanic couples, commonly referred to as electrochemical atmospheric corrosion monitors (EASM), has become widespread [125, 126, 164–168].

A variety of different electrochemical methods such as potentiodynamic, potentiostatic and galvanostatic polarisation, current versus voltage hysteresis, AC impedance and polarisation resistance are widely employed in corrosion studies. The majority of the studies are performed under the conditions of full immersion of the metal in bulk electrolyte solutions. However, the peculiarities of atmospheric corrosion, which occurs under thin adsorbed or phase electrolyte layers, make the conventional electrochemical cell unsuitable for the studies.

The use of the electrochemical techniques in atmospheric corrosion studies requires appropriate solution to some specific problems such as:

- formation of an electrolyte layer on metal surface;

- measurement of the layer thickness $\delta$ and maintenance of constant thickness during the experiment;

- accomplishment of electrolytic contact of the WE with AE and RE;
control of IR-drop, particularly important in these experiments due to potentially high electrical resistance of the thin layers; and

attainment of uniform polarisation of WE, etc.

Tomashov [162] has shown that cathodic (slightly) and anodic (significantly) polarisability of metals (Al, Zn, Fe and Cu) covered with the adsorbed layers of moisture increased with a decrease in the RH values. The anodic polarisation was associated in the first instance with the passivation of the metal surface. It was also assumed that with a decrease in the thickness of moisture layer (resulting from decrease in RH), the process of metal ion hydration can be impeded due to a shortage of water molecules. Clark et al. [169] have reported that the atmospheric corrosion of metals (Fe, Cu, Zn) under adsorbed moisture layers in unpolluted atmosphere proceeds by anodic control. Increase in corrosion rate with the increase in SO₂ concentration (up to 0.5v/v%) was associated with the acceleration of cathodic reaction due to the oxidising properties of sulphur dioxide. Fishman and Crow [170] have recorded polarisation curves on ARMCO iron electrodes, covered with the adsorbed moisture layers. To simulate the formation of the moisture layers, which are usually formed by natural condensation of moisture on a surface contaminated by atmospheric sediments in a coastal environment, a few drops of 3.5w/v% NaCl solution were dried on the electrode surface. The specimen was then placed in a chamber with a constant (67%, 78% or 93%) relative humidity to allow a moisture layer to condense on to the surface. Fishman and Crow reported that with the decrease in relative humidity from 93% to 67% corrosion current decreased by almost two orders of magnitude, while the cathodic
curves became less steep, indicating an increasing ease in the cathodic process. Stratmann and Streckel [171-173] have developed a method for the investigation of metal corrosion under adsorbed electrolyte layers using non electrochemical techniques of measuring electrochemical parameters. Corrosion potential was measured via a Kelvin probe (vibrating condenser method) and the corrosion rate was measured by a gas volumetric technique via the $O_2$-consumption in a closed volume. It was shown that during the drying-out of electrolyte on the surface of an iron electrode, the corrosion rate increased initially due to the acceleration of the transport of $O_2$ to the metal surface and then a sharp drop in the corrosion rate was observed. The drop in the corrosion rate was associated with a precipitation of corrosion products, resulting in the blockage of the anodic reaction of the metal dissolution.

Corrosion-electrochemical polarisation measurements on metals (Cu, Fe, Zn, and Mg) covered with thin phase layers of electrolytes (0.01M and 0.1M NaCl, 0.1M HCl, 0.05M Na$_2$SO$_4$) have been pioneered by Rozenfeld and his co-workers [101, 174, 175]. An electrolyte layer of desired thickness was applied to electrode surface and then the electrode was placed in the test chamber. To prevent evaporation of the superficial electrolyte, the RH in the chamber was maintained at 98% by means of a saturated solution of CaSO$_4 \cdot 5H_2O$. The chamber was placed into a constant temperature bath. The direct measurements of the electrolyte layer thickness were carried out by use of an electronic circuitry. The electrolytic contact of WE with AE and RE was provided by use of salt bridges placed on the top of the glass holder of the WE in order to avoid mixing of products of anodic and cathodic reactions. A second connecting method was used also, in which the electrolyte layer covered both WE and AE simultaneously (platinum wires
located on all four sides of the glass holder periphery in the same plane as the surface of the electrode under investigation).

The results of cathodic galvanostatic polarisation measurements on metals studied in bulk and thin (70–330μm) phase layers of electrolyte (0.1M NaCl) have shown that a decrease in the layer thickness accelerated cathodic reaction on all metals, except for Al. Rozenfeld ascribed the increase in the cathodic reaction rate to the easier access of oxygen to the metal surface. It was also shown that the transition from bulk to the thin (165μm) layer of 0.1M HCl (pH = 1) significantly enhanced the cathodic process on copper. Thus a decrease in the thickness of superficial acid solutions can result in the predominance of the oxygen depolarisation reaction over that of hydrogen due to the fast transport of oxygen from air to a metal surface. The anodic processes on the metals were retarded by the transition from bulk into the thin (165–330μm) layers of electrolyte (0.01M and 0.1M NaCl, 0.05M Na₂SO₄) and by further thinning of the layers. The retardation of the anodic processes was associated with the tendency of the metals to passivate due to formation of a compact layer of corrosion products.

Corrosion-electrochemical behaviour of zinc covered with thin phase layers of neutral chloride solutions has also been studied [176] by the use of a similar technique to that described above. It was shown that the corrosion rate of zinc depends on layer thickness only during the initial period (t ≤ 3h) and is maximum at δ = 150μm. Subsequently the metal corrodes from passive state with corrosion rate independent on the layer thickness. The authors suggested that the easy access of oxygen from air to the metal surface is responsible for the passivation.
Takehara et al. [177] studied corrosion of carbon steel in thin layers of electrolyte (0.005M H₂SO₄ + 0.1M Na₂SO₄) and reported that the diffusion of oxygen is the controlling step of the corrosion process even in acid solutions. In contrast to other known techniques of polarisation measurements in thin electrolyte layers the authors used an electrode, partly immersed in solution and rotating in the vertical plane. Data on the thickness of the thin layers which will depend on frequency of the rotation were not given. It is obvious that the conditions of diffusion and convection in these experiments are far from natural.

Anodic and cathodic polarisation curves on metals (steel, Zn, Cu, Al) under thin layers (δ = 100–1000μm) of electrolytes (0.1M NaCl and 0.05M H₂SO₄) were recorded by Mansfeld [178]. With a decrease in δ, a slight decrease in Tafel slope of anodic reaction and an increase in the limiting diffusion current of oxygen reduction were observed.

Cell used by Fiaud [179] in the study of the electrochemical behaviour of atmospheric pollutants in thin electrolyte layers and by Keddam [180] in the study of zinc corrosion in thin layers of chloride-containing solutions were similar to the one employed in thin layer electrochemistry, as well described in the literature [181]. The arrangement involves disk shaped working and auxiliary electrodes mounted on the jaws of a precision micrometer with a very small distance of separation. The electrolyte solution is then placed between the electrodes. The tip of a capillary tube leading to the RE is touched on the side of the assembly to make contact with the electrolyte. The low ohmic drop in such arrangement due to the very small distance between WE and AE is an advantage. However, in this cell gaseous species from the atmosphere have a limited access to the WE surface only through
the sides of the assembly. In the device used in another study [179] the upper plane of the assembly is made of a semi-permeable membrane allowing permeation of gases. The whole assembly was immersed in a thermostated cell containing the working solution.

Stratmann et al. [171–173, 182] have presented a new arrangement which enables polarisation measurements to be made on metal surfaces covered with electrolyte layers as thin as 2μm. A Kelvin probe instead of a conventional Luggin capillary was used for the measurement of electrode potential. The distance between the Kelvin probe and the electrolyte on top of the working electrode is about 100μm, which makes the IR-drop negligible. The WE and AE in the cell arrangement were positioned under the same electrolyte layer and, hence, can result in undesirable mixing of the products of the anodic and cathodic reactions. The circuitry used for the measurement of electrolyte layer thickness was very similar to the one used by Rozenfeld [101]. The electrochemical behaviour of Pt and Fe electrodes under thin (2–700μm) layers of different electrolytes was studied. The measurements performed on the Pt electrode showed that for the very thin electrolyte layers the transport of oxygen through the phase boundary electrolyte/gas is the rate determining step. On iron surfaces, besides an enhancement of the rate of the oxygen reduction, a strong inhibition of the rate of the metal dissolution was observed for the thin electrolyte layers. The authors ascribe this to the possible change of pH of the superficial electrolyte or due to the precipitation of dense corrosion products, blocking the corrosion process.

A generalisation of the results on corrosion-electrochemical behaviour of metals covered with thin electrolyte layers shows that the behaviour does
have some peculiarities mainly associated with the (i) weak opposition of
the thin layers to the transport of oxygen from air to the metal surface; and
(ii) easy saturation of the layers with the corrosion products. However, no
investigations have been made on how the peculiarities of the anodic and
cathodic reactions under thin electrolyte layers can affect processes of
passivation, depassivation, local anodic depassivation and pitting corrosion
of metals, and particularly of stainless steels. This additional information
may lead to a better understanding of the mechanism of atmospheric
corrosion of metals. Also, it may enable the development of accelerated
electrochemical corrosion tests for rapid evaluation of the durability of
metals under atmospheric conditions.
Chapter 2

Experimental procedure
2.1 Metals; specimens and surface preparation

A number of stainless steels were used in this work. The chemical compositions of the steels are given in Table 2.1.

Table 2.1: Chemical compositions of the stainless steels studied, wt. %.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Other elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>conventional SS430 (Cr17)</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>17.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr14Mn15</td>
<td>0.1</td>
<td>0.8</td>
<td>14.7</td>
<td>14.5</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Cr25Mn15</td>
<td>0.1</td>
<td>1.0</td>
<td>14.7</td>
<td>24.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr18Ni10Ti</td>
<td>0.12</td>
<td>0.8</td>
<td>1.2</td>
<td>18.4</td>
<td>9.8</td>
<td>0.65 Ti</td>
</tr>
<tr>
<td>Cr22Ni10Ti</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>21.7</td>
<td>9.8</td>
<td>0.7 Ti</td>
</tr>
<tr>
<td>Cr18Ni11 (heat 3)</td>
<td>0.025</td>
<td>0.5</td>
<td>0.41</td>
<td>18.3</td>
<td>12.3</td>
<td>0.002 S</td>
</tr>
<tr>
<td>Cr18Ni11 (heat 32)</td>
<td>0.025</td>
<td>0.5</td>
<td>0.5</td>
<td>18.1</td>
<td>12.5</td>
<td>0.013 S</td>
</tr>
<tr>
<td>conventional SS316 (Cr18Ni10Mo2)</td>
<td>≤ 0.08</td>
<td>-</td>
<td>-</td>
<td>18.0</td>
<td>10.0</td>
<td>2.25 Mo</td>
</tr>
<tr>
<td>Cr18Ni20Si3Mo3 Cu3Nb</td>
<td>0.03</td>
<td>2.5</td>
<td>0.7</td>
<td>17.5</td>
<td>19.5</td>
<td>2.8 Mo; 2.5 Cu; 0.41 Nb</td>
</tr>
<tr>
<td>Cr18Ni20</td>
<td>0.041</td>
<td>0.29</td>
<td>-</td>
<td>17.37</td>
<td>19.19</td>
<td>-</td>
</tr>
<tr>
<td>Cr18Ni20Si3</td>
<td>0.053</td>
<td>2.61</td>
<td>-</td>
<td>17.60</td>
<td>19.35</td>
<td>-</td>
</tr>
<tr>
<td>Cr18Ni20Cu3</td>
<td>0.035</td>
<td>0.14</td>
<td>-</td>
<td>17.73</td>
<td>19.75</td>
<td>2.5 Cu</td>
</tr>
<tr>
<td>Cr18Ni20Nb</td>
<td>0.053</td>
<td>0.38</td>
<td>-</td>
<td>17.75</td>
<td>19.75</td>
<td>0.39 Nb</td>
</tr>
<tr>
<td>Cr18Ni20Mo3</td>
<td>0.045</td>
<td>0.14</td>
<td>-</td>
<td>18.00</td>
<td>19.75</td>
<td>2.8 Mo</td>
</tr>
</tbody>
</table>
Experiments were carried out with specimens made from sheet metal only. In most of the electrochemical measurements in bulk and under thin phase electrolyte layers, specimens of a cylindrical shape were used. The specimens were mounted into cold-curing acrylic resin and the upper flat surface of the assembly was thoroughly ground. The working surface area of the electrode (end of the cylinder) was 0.1cm\(^2\) in all cases. In experiments under thin layers of electrolyte the ratio of the electrode surface area to the surface area of the electrolyte solution (upper flat surface of the assembly) was 1:100. The two main reasons for using small (0.1cm\(^2\)) electrode surface area are:

(i) the attainment of a higher uniformity in electrolyte layer thickness throughout the working electrode surface; and

(ii) lowering of the required polarisation current resulting in smaller IR-errors.

For a number of the electrochemical experiments the flag-type specimens with working surface area 1–2cm\(^2\) were used. The working electrodes employed in this study are shown in Figure 2.1. Each of the two types of electrode have some advantages and disadvantages. For instance, the flag-type specimen is easier to make, but it is more difficult to polish. However, the most important peculiarities are:

(i) In the case of flag-type specimen, the edges of the electrode are the sites where corrosion preferentially starts and a situation is possible when the edges corrode while the flat surface of the specimen is still passive. In addition to this, the presence of a water-line, resulting in a

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Figure 2.1: Types of working electrodes employed and the mode of immersion in test solutions: a - flag type electrode; b - mounted electrode; 1 - metal; 2 - insulation.
formation of a converging meniscus, where conditions of corrosion in the thin electrolyte layers apply, complicates the analysis of the experimental data; and

(ii) In the case of the electrode mounted into resin, the only flat working surface is to be in a contact with corrosive medium, but there is always a problem of interface between metal and insulation. Crevices between metal and insulation can significantly affect experimental results. In the study of cathodic processes or of active dissolution of metals the crevices are not of a great importance, but in the study of anodic behaviour of a metal in the passive region these can become significant.

According to equation 2.1, the potential of the crevice bottom \( (E_{\text{bot}}) \) due to ohmic voltage drop \( (IR) \) can be significantly (by hundreds of millivolts [183, 184]) more negative than the potential of the flat metal surface \( (E_{\text{sur}}) \).

\[
E_{\text{bot}} + IR = E_{\text{sur}} \tag{2.1}
\]

In some cases \( E_{\text{bot}} \) can correspond to the region of active dissolution of the metal, while \( E_{\text{sur}} \) corresponds to the passive region. Furthermore, an accumulation of corrosion products (halides in particular) in the crevices, insufficient access of passivating constituents of the solution into the crevices and poor quality of the metal surface finishing inside the crevices can impede passivation. In this work every electrode (after mounting into resin and abrading of the working surface) was checked with the use of a metallographical microscope with a 100x magnification and the electrodes
with poor metal/insulation interface were re-abraded. If the treatment does not remove crevice(s), the electrode was not used.

The initial condition of the electrode surface can affect the corrosion-electrochemical behaviour of an electrode to an extent which is comparable with the influence of the metal and solution compositions, temperature, etc. For this reason, the appropriate preparation of the working electrode was of great importance in this study. The main task was to select surface preparation method which gives highly reproducible experimental data. The methods used (separately or in combination) for the preparation of the specimens employed for the electrochemical measurements are listed below:

(i) mechanical abrading and polishing (up to P-1000);

(ii) degreasing with ethanol or acetone followed by rinsing in distilled or Milli-Q water and (experiments in neutral electrolytes) in test solutions;

(iii) cathodic reduction in test solution (experiments in acid solutions); and

(iv) potentiostatic standardisation.

Laboratory immersion tests and full-scale atmospheric tests were conducted by use of rectangular coupons measuring 50mm by 30mm by 1.5mm or 3mm as corrosion specimens. All coupons were stamped with an appropriate identifying mark and abraded by hand. Final surface treatment of the corrosion specimens included finishing with P-360 abrasive paper. The specimens were finally degreased, rinsed in distilled (or Milli-Q water),
weighed on an analytical balance to an accuracy of ± 0.05mg and kept in a desiccator prior to the commencement of the experiments. During the corrosion immersion tests, a minimum ratio of test solution volume to specimen area was 20mL/cm², which is in agreement with the ASTM standard G31-72 [19]. Corrosion products were removed by use of mechanical cleaning methods such as brushing and ultrasonic procedures. After completion of the corrosion experiments, the surface of the corroded specimens was studied by the use of a magnifying glass and in some cases with an optical microscope.

Investigations of metal surface by use of physical methods, such as electron diffraction pattern, Aüger electron spectroscopy and quantitative metallography were carried out with square coupons measuring 10mm by 10mm by 3mm. Final surface treatment of the coupons included finishing by polishing paste with sizes of diamond abrasive particles (1-2μm), followed by a careful degrease of the surface with analytical grade ethanol.

2.2 Reagents and test solutions

The corrosion-electrochemical behaviour of steels was studied mostly in acid sulphate and neutral chloride solutions. For the preparation of test solutions, the following analytical grade reagents were used:

(1) salts - NaCl, FeCl₃, Na₂S, and Na₂SO₄; and

(2) acids - H₂SO₄ and HCl.
The reagents were dissolved in distilled or Milli-Q water. The Milli-Q water (with a resistivity > 18 MΩcm) was prepared from distilled water by passage through Millipore system consisting of a Super-C carbon cartridge, two ion exchange cartridges, and an Organex Q cartridge, successively. Electrochemical experiments were performed mostly in naturally aerated solutions. A small number of the experiments were conducted in deaerated solutions. Test solutions were deaerated by bubbling pure nitrogen for 1h prior to immersion of the specimens, and during the experiments an excess pressure of nitrogen was maintained over the solutions. pH measurement were made on a pH-meter which was calibrated by use of standard pH buffer solutions. Stirring of solutions was carried out with a magnetic stirrer.

2.3 Cells for electrochemical measurements in bulk and under thin phase electrolyte layers

The construction of electrochemical cells, and the working electrodes used in corrosion studies are strictly defined by the peculiarities of the specific experimental problem. In this work several different cells were used. Electrochemical measurements in bulk electrolytes were performed mostly in the ordinary three and five neck cells. Experiments at high temperatures were conducted in the cells with a water jacket. Water circulating through the jacket was supplied by a thermostat, with a temperature accuracy of ±0.2°C.

Corrosion-electrochemical measurements under thin phase electrolyte layers were conducted in humid atmosphere (RH = 100%) of 25°C or 30°C. The experimental arrangement was placed in a working chamber of Perspex
measuring 250mm by 200mm by 150mm. In order to prevent the evaporation of the test solution and, therefore, to keep thickness of electrolyte layer constant the relative humidity of air in the chamber was maintained at 100% by means of an automatic system consisting of a water evaporator, two resistance thermometers (acting in psychrometric mode), and relays. The dry thermometer was also connected to an automatic temperature control system, which is more convenient to use than an external thermostat [101, 179]. A block-diagram of the automatic systems of relative humidity and temperature regulation is shown in Figure 2.2.

The device for the automatic control of relative humidity and temperature in the working chamber was designed around two differential amplifiers DA1 and DA2. When the temperature in the chamber is below (above) the imposed value, then the voltage at the positive terminal (pin 3) of DA1 will be higher (lower) than the voltage at the negative terminal (pin 2), subsequently the relay R1 is on (off) and the heater is switched on (off). The heater, which is a spiral made from Ni-Cr alloy wire, had a low thermal lag and the hysteresis provided with DA1 did not exceed 0.4°C. Similarly, when the relative humidity in the chamber is below the required 100%, then the voltage at the positive terminal (pin 3) of DA2 will be higher than the voltage at the negative terminal (pin 2), the relay R2 is on and the evaporator is switched on. The water evaporator used in this work is an ordinary fish tank aerator.

The arrangement of the electrode and electrolytic bridges employed for electrochemical polarisation measurements in thin phase layers of electrolyte is shown in Figure 2.3. The electrolytic bridges were filled with working solution or with the agar gel. In the latter case, in order to avoid
Figure 2.2: Circuit diagram for the automatic controller of relative humidity and temperature in the working chamber.
Figure 2.3: Arrangement of the working electrode and electrolytic bridges employed for electrochemical polarisation measurements in thin phase electrolyte layers: $B_1$ - electrolytic bridge connecting working electrode with a reference electrode; $B_2$ - electrolytic bridge connecting working electrode with an auxiliary electrode.
presence of bubbles in the bridges, the hot gel was kept for some time in ultrasonic bath before filling. The tips of the bridges, were placed on the acrylic holder in the same plane as the surface of the electrode under investigation. Four tips of the electrolytic bridge, connecting working electrode with auxiliary electrode, were positioned on all sides of the WE at a distance of 7mm from its centre. Such a disposition of the bridge tips secured uniform polarisation of working electrode.

The auxiliary electrode was a platinum wire and the reference electrode was either a silver-silver chloride (Ag/AgCl) or saturated calomel electrode (S.C.E.). All potentials in the thesis are quoted with respect to the standard hydrogen electrode (S.H.E.).

The thickness of the electrolyte layer was measured by means of a circuitry similar to the one previously described by Rozenfeld [101] and later used by Stratmann et al. in [182]. The measurement of the layer thickness was carried out by use of a sharp Pt (or steel coated with Au) needle in the arrangement shown in Figure 2.4. The needle is attached to a micrometer screw and is slowly moved towards the electrolyte surface and on contact of the needle with the electrolyte a small deflection of the galvanometer pointer is observed. When the needle is brought in contact with the working electrode a significant deflection of the galvanometer pointer is observed. The thickness of the electrolyte layer is determined as a difference in the readings of the micrometer which correspond to these two observed pointer deflections.
Figure 2.4: The set-up for measurement of the thickness of the electrolyte layers: 1 - working electrode; 2 - electrolyte layer; 3 - micrometer screw; 4 - platinum needle; 5 - power supply; 6 - galvanometer.
In contrast to the circuitry described by Rozenfeld [101], the one used in the present work did not include a battery as a current source. An audio-frequency generator with the output signal voltage $0.3 \text{V}$ at the frequency $2 \cdot 10^4 \text{Hz}$ was used instead. The use of the alternate current of high frequency results in the reduction of the specimen polarisation during the measurement of the electrolyte layer thickness ($\delta$) to $\Delta E \approx 10-15 \text{mV}$.

In experiments where test solutions of high conductivity were used the measurements were conducted without the use of an external power supply. In this case, on contact of the needle with the electrolyte surface a current will appear due to the build up of an electromotive force between the needle and the electrolyte. Consequently, on contact of the needle with the working electrode surface the electromotive force drops and the current disappears or is reduced considerably. The current was measured by a digital microammeter with a $0.01 \mu\text{A}$ resolution and to minimise the current a variable resistance ($500 \Omega$) was connected in series. This circuitry enabled the reduction of the specimen polarisation during the measurement of $\delta$ to a minimum ($\Delta E = 5 \text{mV}$).

2.4 Modes of electrochemical polarisation and measured electrochemical characteristics

Electrochemical measurements were carried out with use of the electronic potentiostats P-5848, P-5827M (USSR) and computer controlled potentiostats UTAH (Model 0160) and THBC9202. The latter was designed within the Faculty of Science and Technology Electronics Workshop (UWS, Nepean). Potentiodynamic (1.44 and 3.6 V h$^{-1}$), potentiostatic, galvanodynamic
(72μAcm−2 · h−1) and galvanostatic modes of polarisation were used. Measurements of polarisation resistance and corrosion current density were conducted by the UTAH Potentiostat Non-Linear Curve Fitting program.

The electrodes were polarised from established corrosion potential (steady-state potential $E_{cor}$). Irrespective of the pH of the test solution, the value of the electrode potential, providing that its change for the last ten minutes does not exceed 20mV, was assumed as $E_{cor}$.

In acid sulphate solutions anodic potentiodynamic polarisation curves were recorded by potential sweep from active to transpassive region. In particular experiments, polarisation curves were recorded at a reverse potential sweep from passive region to the transitional region. Such characteristics were determined experimentally as follows:

(i) the critical current density of passivation ($i_{cc}$) - the maximum current density of an electrode exhibiting active-passive behaviour; and

(ii) the potential of passivation ($E_{pp}$) - the potential corresponding to the ($i_{cc}$).

During the potentiostatic experiments at potentials within the passive and cathodic loop regions of the anodic polarisation curve the current decay curves were recorded and stationary values of anodic and cathodic current density were determined. After the potentiostatic polarisation of the stainless steels at potentials within the two regions of the anodic polarisation curves, potential decay curves were recorded. The effect of
diverse factors on the retention of passivity by stainless steels in acid solutions was studied in these experiments. In galvanostatic experiments, the critical current density of passivation was measured.

In neutral chloride solutions a comparative electrochemical evaluation of the resistance of some stainless steels to pitting corrosion was carried out. Starting in the 1930's [185] the evaluation was based on the appearance of certain boundary potentials separating the areas of pitting corrosion and passivity. Despite the wide agreement on the validity and usefulness of such an approach, the classification of these potentials and, therefore, the methods for their measurement remain a subject of dispute [186–189]. The basic reason for the difficulties encountered in attempting to establish some common boundary potential of pitting corrosion is that to the processes of pit (i) formation, (ii) stable growth and (iii) repassivation may correspond their own characteristic potentials, which coincide only in particular cases [187, 190].

On the basis of the results presented in [69, 88, 191] it was acknowledged as desirable to use in the general case three boundary potentials of pitting corrosion: the basic and two supplementary. As the basic boundary potential between the areas of stable passivity and pitting corrosion was taken the minimum galvanostatic potential of pitting corrosion $E_{\text{pit}}^{\text{min}}$. The $E_{\text{pit}}^{\text{min}}$ is the limit of the reduction in the electrode potential of steel with time of anodic galvanostatic polarisation at that lowest density of anodic current which provides stable functioning of the originated pits.

The two supplementary characteristics were measured by the method of reversible anodic potentiodynamic polarisation under controlled conditions.
of measurement. The first of these two boundary potentials - breakdown potential $E_{br}$ corresponds to the sharp increase in current density on anodic polarisation curve of a passive metal (Figure 1.2, curve PGH) in a solution containing activating ions. The second-repassivation potential $E_{rp}$ corresponds to the sharp drop in the current density at the reverse sweep of potential. Breakdown potential, $E_{br}$, is the potential of pits origin. Above (more positive than) the $E_{br}$ new pits can initiate while the existing pits can continue to propagate. Repassivation potential, $E_{rp}$, is the potential of pits death. Below (more negative than) the $E_{rp}$ the pits can neither initiate nor propagate. Between the breakdown and repassivation potentials the existing pits can continue to propagate but no new pits can be initiated.

2.5 Investigation of metal surface

Physical methods were employed for the investigation of the metal surface. The chemical composition of passive films and depth profile of elements in the films were studied by Auger Electron Spectroscopy. The measurements were carried out on spectrometer LAS-200 (Riber, France) using incident electron beam with energy 3-5keV focused to a small spot $2 \cdot 10^{-5}$cm$^2$. Sputtering of the studied surface was conducted by argon ion beam.

The structure of passive films on Cr-Mn stainless steel Cr25Mn15 formed during the passivation in acid sulphate solution was studied by the analysis of electron diffraction patterns. The patterns were obtained by the diffraction of the electrons reflected from the studied surface. The electron diffractometer UEMV-100K (USSR) with an accelerating voltage 75kV and $\lambda L = 22.6$ was used.
For the study of the kinetics of pits formation \((0.15\mu m < r < 8\mu m)\) the specimen surface was photographed under a scanning electron microscope Nanolab-7 (Opton, Germany) with a 1000× magnification. Each frame corresponds to a specimen surface area of \(2.225 \cdot 10^{-4}cm^2\) and at least ten frames were obtained on each specimen. The negatives obtained were processed on a textural structure analyser TAS (Leitz, Germany) according to the program Tassep. Lab u Diare 2 Aut. In accordance with the program, the pits in the mentioned range of radii were divided into fractions in steps of 0.6μm, and the number of pits in each fraction was counted separately. The background number of surface inhomogeneities, which were not pits, was found by processing the negatives of a "clean" specimen (with no pits) on the TAS.

The growth and number of comparatively large pits \((r > 10\mu m)\) were studied with the use of a metallogographical microscope MMU-3 (USSR) with a 270× magnification. The pits situated on the boundary with the insulation were disregarded in the calculation. The formed pits, as a rule, had "caps" with small holes. Therefore, prior to the study of the surface, the pits mouths were revealed, by carefully grinding away a very fine surface layer of the metal.

The radius of pits mouth was measured with the aid of an eye-piece micrometer. The depth of pits was determined as a difference between the two readings of the picture sharpness fine adjustment screw: the first reading corresponds to the specimen surface, while the second one to the bottom of the pit.
2.6 Full-scale atmospheric corrosion tests

Full-scale corrosion tests of some stainless steels studied were carried out under the conditions of: (i) a seaside clean atmosphere (city of Batumi, atmospheric corrosion station of Institute of Metallurgy, Academy of Sciences, Republic of Georgia, USSR) and (ii) an industrial atmosphere highly polluted with sulphur dioxide (chemical plant, production of bisulphite, city of Rustavi, Republic of Georgia, USSR).

The seaside atmospheric corrosion station is located within 250 meters from the seashore line and is significantly removed from all factories and housing estates. The following weather data were recorded continuously: temperature, relative humidity, and with aid of the galvanic couple Ti/Zn time-of-wetness of metallic surfaces. The average temperature during the tests was $t_{av} = 14.5^\circ C$, with the maximum $t_{max} = 40^\circ C$ and minimum $t_{min} = -6^\circ C$. The average relative humidity was RH = 78%. Overall, the time of moistening of metal surface determined with the Ti/Zn time-of-wetness sensor was in a good agreement with the total time when the relative humidity was higher than 70%. Pollution of the atmosphere with chlorides and sulphur dioxide was monitored periodically. The experimental values were $C_{Cl} = 8-17 \text{mgm}^{-2}\text{day}^{-1}$ and $C_{SO_2} = 0.01-0.02 \text{mgm}^{-3}$.

During the tests in the chemical plant atmosphere, the temperature, relative humidity and the extent of pollution with sulphur dioxide were recorded. The average temperature was $t_{av} = 13^\circ C$, with the maximum $t_{max} = 43^\circ C$ and minimum $t_{min} = -10^\circ C$. The average relative humidity was RH = 66%. Pollution of the atmosphere with sulphur dioxide was in the interval $C_{SO_2} = 1.5-6.0 \text{mgm}^{-3}$. 

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Chapter 3

Determination of ohmic voltage drop in electrochemical polarisation measurements in thin phase electrolyte layers
3.1 Introduction

Generally, in electrochemical polarisation measurements, the voltage $E_m$ measured between the working electrode and reference electrode (or Luggin capillary if in use) always contains, as a summand, the ohmic voltage drop $\Delta E = IR$, and

$$E_m = E_t + IR \quad (3.1)$$

where $E_t$ is the true voltage, $I$ is a polarisation current, while $R$ is the electrical resistance of the test solution between the WE and RE. The IR-error is positive during anodic polarisation and negative during cathodic polarisation. A schematic diagram of the IR-error associated with the ohmic voltage drop in solution is shown in Figure 3.1, where the equivalent circuit of the WE is presented for simplicity as a capacity $C$ of the double layer [157]. As it can be seen from the diagram the error can be significantly reduced if the Luggin capillary is placed in close proximity to the WE (point b). However such a position of the capillary causes a shielding of the WE, and the current distribution on the WE surface can be seriously disturbed by the capillary tip [157, 181, 192].

Errors caused by the ohmic voltage drop result in the distortion of the polarisation curves and in erroneous values of some of the measured critical potentials. In electrochemical polarisation measurements in thin layers of electrolytes, in view of a possible high resistance in the system, the IR-error can substantially affect the accurate measurement of the WE potential, and, hence, IR control is of vital importance in this system. For systems with low resistance, various methods of determination and
Figure 3.1: Schematic diagram of the IR-error associated with the ohmic voltage drop in solution: L - tip of Luggin capillary; r - resistance of the solution between working electrode and auxiliary electrode; R - resistance of the solution between working electrode and reference electrode (cited from [157]).
automatic compensation of the ohmic drop, based on the measurement of the potential decay during an interruption of the polarisation current, have been successfully employed [170, 181, 193–195]. These methods involve interruption of the polarisation current with the aid of a fast switch that is in series with the auxiliary electrode. A mercury-wetted or a solid-state relay which electronically interrupts the circuit are usually employed as the interrupter. The decay of the potential of the WE with respect to RE is recorded as a function of time with the aid of a fast storage oscilloscope (a typical potential decay is shown in Figure 3.2). The instantaneous potential drop in the potential versus time profile, followed by the smooth reduction of the potential due to the decrease in the polarisation, is the IR-error in the system.

Due to the possibly high resistance in the system the application of the interruption method for the evaluation of ohmic voltage drop during electrochemical polarisation measurements in thin electrolyte layers may be inadequate. When the polarisation current is interrupted, the capacitor C starts to discharge through the resistor R (Figure 3.1). The solution of the differential equation of the discharge [196]

\[ R \frac{dq}{dt} + \frac{q}{C} = 0 \]  

(3.2)

is

\[ q = q_0 e^{-t/RC} \]  

(3.3)

where \( q_0 \) is the initial charge on the capacitor. The capacitive time constant \( RC \) governs the discharging process. At \( t = RC \) the capacitor charge is
Figure 3.2: Typical decay of the potential of the working electrode as a function of time after the interruption of polarisation current (cited from [194]).
reduced to the value which is about 37% of its initial charge. Hence, the larger the value of RC the longer it takes for the capacitor to discharge. Thus, at a high value of R, which could be expected because of the thinness of electrolyte layer, the ohmic decay in the potential and the decrease in the polarisation can overlap. Consequently, this could make the determination of IR-error rather unreliable.

The application of some of the existing methods of reducing or eliminating the IR drop in the electrochemical polarisation measurements under thin layers of electrolytes is also problematic. For example, the introduction of a Luggin capillary or metallic RE (e.g., Ag/AgCl) into the thin electrolyte layer from the gas side leads to the formation of a converging meniscus. If it is inserted from the inside of the WE, or if a Kelvin probe is used [171–173], the technique is considerably complicated. Thus the development of a method based on the theoretical evaluation of ohmic voltage drop in thin layers of electrolyte was investigated.

3.2 Theoretical and experimental evaluation of ohmic voltage drop in thin layers of electrolyte

One theoretical and three experimental methods of IR determination during electrochemical polarisation measurements in the thin layers of electrolyte have been compared. In all cases, the values of the resistance R were determined (with the knowledge of R, the calculation of IR offers no difficulty).
The theoretical method was based on the assumed applicability of a formula for the electrolyte resistance between two coaxial cylindrical electrodes [197] to the determination of $R$ in thin layers of electrolyte

$$R = \frac{1}{2\pi\lambda\delta} \ln \frac{r_2}{r_1}$$  \hspace{1cm} (3.4)

where $\lambda$ is the conductivity of the solution, $\delta$ the height of the cylinder (in the present case thickness of electrolyte layer); $r_1$ the radius of the internal cylinder (in the present case the radius of the flat end of the cylindrical WE with surface area 0.1cm); $r_2$ the radius of the external cylinder (in the present case distance 0.71cm from the centre of the flat end of the WE to a capillary of the electrolytic bridge $B_1$, introduced in the electrolyte layer at some distance from WE) - Figure 3.3.

The first experimental method (A) is a modification of a well known two-probe method of IR determination. In this case (Figure 3.3), the potential difference was measured between electrolytic bridge $B_2$ and the specially designed electrolytic bridge $B_3$ (with the end of its capillary next to the cylindrical surface of WE in the same plane as the working surface of the latter). The internal and external diameters of the electrolytic bridge $B_3$ capillary were 400 and 600$\mu$m respectively. In accordance with the data in [181], based on the utilisation of such a capillary, the IR drop between $B_3$ and the WE at a current density $i = 10^4\mu\text{A cm}^{-2}$ (current $I = 10^3\mu\text{A}$) and $\lambda = 10\Omega^{-1}\text{cm}^{-1}$ will not exceed a few millivolts and, thus, it can be assumed to be negligible. The value of $R$ was determined from the ratio of the potential difference between bridges $B_2$ and $B_3$ and the current of polarisation.
Figure 3.3: Cell arrangement employed for the determination of IR-error during electrochemical polarisation measurements in thin layers of electrolyte. The working electrode (WE) is connected via electrolytic bridges (B₁, B₂ and B₃) with the auxiliary electrode (B₁) and two reference electrodes (B₂ and B₃).
The second method (B) involves the determination of $R$ from the slope of the polarisation curve, plotted in $E$-$I$ coordinates (not in $E$-log$i$ coordinates as usual) when the electrode process proceeds under ohmic control. Under these experimental conditions that regime is often realised in the potential interval between the Tafel region and the region of limiting current.

The third experimental method (C) is based on the utilisation of an IR correction program on the Utah Potentiostat. In this case, the data for IR correction were generated with the interruption of a polarisation current by fast electronic switching.

Table 3.1 provides the data for $R$ determined by the theoretical and two experimental methods (A and B) for two thicknesses of electrolyte layer (aqueous 0.1M NaCl). All measurements were performed at room temperature during the cathodic polarisation of stainless steel 321 electrodes at current densities $i \leq 10^{4}\mu$Acm$^{-2}$.

**Table 3.1:** Values of $R$ determined by theoretical method and by experimental methods A and B.

<table>
<thead>
<tr>
<th>Thickness of electrolyte layer $\delta$, $\mu$m</th>
<th>Calculation from equation 3.4</th>
<th>$R$, $\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$4.8 \cdot 10^{3}$</td>
<td>(5.3-6.5) $\cdot 10^{3}$</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>(4.0-5.1) $\cdot 10^{3}$</td>
</tr>
<tr>
<td>100</td>
<td>$2.4 \cdot 10^{3}$</td>
<td>(1.8-2.3) $\cdot 10^{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.8-2.0) $\cdot 10^{3}$</td>
</tr>
</tbody>
</table>

As can be seen from Table 3.1, the theoretical method gave results that are close to those obtained from the two experimental methods (A and B). This provides a basis for using the theoretical method in the evaluation of the IR
Figure 3.4: Calculated (curve 1) and experimental (curve 2) values of $R$ versus the reciprocal thickness of electrolyte layer; 0.1M NaCl, 30°C.
drop during electrochemical polarisation measurements in the thin layers of electrolyte.

The data obtained for $R$ by means of the IR correction program of the Utah Potentiostat, together with values calculated from equation 3.4, are plotted in Figure 3.4. The good agreement between the calculated and measured values of $R$ for electrolyte thicknesses $\delta \geq 400\mu m$ ($\delta^{-1} = 0.0025\mu m^{-1}$) is evident, but further thinning of the layer causes a large discrepancy between them.

### 3.3 Conclusions

The results presented in this chapter confirm the suggestion that the determination of IR-error based on the interruption of polarisation current can be unsuitable in some cases for the electrochemical polarisation measurements in thin electrolyte layers. In such cases, the use of the theoretical approach of evaluating the ohmic voltage drop is evidently preferable. Calculations from the equation 3.4 can also be used for the solution of reciprocal problems. For example, at a given tolerated IR-error, it is necessary to evaluate the maximal densities of the polarisation current which can be applied in thin layers of the electrolyte for a given thickness, without measurements of the error.
Chapter 4

Passivation of stainless steels in bulk and under thin electrolyte layers
4.1 Introduction

The remarkable corrosion resistance of stainless steels in many corrosive environments is rendered by the formation of a passive film which develops on the metal surface and protects the steels from corrosion attack. Therefore, the corrosion behaviour of stainless steels in corrosive media is largely dependent on the protective properties of the passive film.

Despite the vast amount of work reported on passivation of stainless steels in bulk electrolytes, no data are available on the effects of thickness of electrolyte layer on the passivation process, and on the factors controlling the establishment and maintenance of the passive state on steels covered with thin layers of electrolyte. Yet, this information is important for:

(i) gaining a better understanding of the corrosion behaviour of stainless steels under atmospheric conditions; and

(ii) obtaining useful information for the accelerated evaluation of the atmospheric durability of stainless steels, based on the comparison of results obtained from laboratory electrochemical tests in bulk and under thin electrolyte layers.

Furthermore, the considerable ease of oxygen access from air to the metal surface through the thin electrolyte layer provides an opportunity for studying the effect of oxygen reduction on the passivation of stainless steels and the retention of the passivity. The ability of oxidisers to induce passivity on active-passive metals has long been known [198]. It has been established that the nature of an oxidiser action depends on its concentration. At a
concentration (C) of an oxidiser lower than a critical value \( (C_{cr}) \), increase in C results in acceleration of corrosion process, while at a concentration higher than \( C_{cr} \) the corrosion rate abruptly drops [33, 199, 200]. Thus, the thinning of electrolyte layer beyond some critical value, \( \delta_{cr} \), can result in conditions similar to those at which the concentration of an oxidising constituent in bulk corrosive solution exceeds \( C_{cr} \) and, therefore, self-passivation of stainless steels in thin electrolyte layers may be expected.

The direct participation of some oxidisers in the formation or improvement of passive films on active-passive metals has been described in the literature [33, 201–204]. However, many problems of corrosion processes on active-passive metals in the presence of oxidisers can be explained without regard for any special passivating features of the oxidisers [88, 198, 205]. Accordingly, oxidisers may be considered ordinarily as depolarisers which are completely consumed during the cathodic reduction, resulting in a shift of the electrode potential towards more positive values. Such an approach allows for the interpretation of the corrosion behaviour of metals in solutions containing oxidising constituents on the basis of the governing role of potential, independent of how the potential is maintained; e.g., by anodic polarisation from external power supply or by cathodic reaction of reduction of oxidising constituents of the solution. This, in turn, could be useful in regulating the corrosion resistance of metals with the aid of oxidisers. For example, as investigated in this work, some stainless steels can be protected by means of anodic protection in the potential region within the cathodic loop—a section of anodic polarisation curve between active and passive regions of the curve at which the rate of cathodic reaction exceeds the rate of anodic reaction [54, 156, 206, 207].
In this study, the passivation of stainless steels in bulk and under thin layers of acid sulphate solutions has been investigated. The associated effects of the cathodic reduction of oxygen in the region of anodic dissolution of the steels and the possible use of the cathodic loop region as a preferred region for the implementation of anodic protection were carefully examined. The composition and structure of passive films formed on Cr-Mn stainless steel (Cr25Mn15) in acid sulphate solutions at potentials from the middle of the passive region and within the cathodic loop region were also studied.

4.2 Comparative study of corrosion-electrochemical behaviour of stainless steels in bulk and under thin layers of acid sulphate solutions

Passivation of stainless steels Cr25Mn15 and Cr17 in bulk and under thin phase layers of acid sulphate solutions was studied. Electrochemical measurements were conducted on the steel specimens in sodium sulphate solutions for which the pH was adjusted by the addition of sulphuric acid, and the overall concentration of SO\text{4}^{2-} ions was kept constant (0.5M). The electrolyte layer thickness was varied between 25 and 350\mu m. The data for the bulk electrolyte were obtained with a layer of 2–3\,mm thickness and in a conventional three electrode electrochemical cell (~ 500\,mL). The corrosion-electrochemical characteristics of the electrodes studied under these two conditions were identical. Prior to the commencement of the experiments, the electrode surfaces were cathodically reduced in galvanostatic mode (i = 10^4\mu Acm^-2, 3min) and after this operation in thin electrolyte layer the test solution was replaced. Immersion corrosion tests were conducted with
specimens of the stainless steels (coupons measuring 50mm by 30mm by 1.5mm) in bulk 0.5M sulphuric acid at room temperature.

The stainless steels Cr25Mn15 and Cr17 in bulk solutions (pH < 4) corrode in the active state, but at a higher pH (≥ 4) the steels undergo self-passivation, i.e. spontaneous transition into passive state without anodic polarisation. The anodic potentiodynamic polarisation curves and critical current densities of passivation (i_{cc}) for the Cr25Mn15 steel obtained in bulk solutions with different pH are shown in Figures 4.1 and 4.2, respectively. Increasing solution pH results in a decrease of i_{cc} (Figure 4.1, curves 1–3; Figure 4.2) and at pH = 4 the steel self-passivates. However, the behaviour of the steels Cr25Mn15 and Cr17 in thin layers of the electrolyte can differ significantly from that in the bulk of the same electrolyte. The anodic polarisation curves of the steels in thin layers of the solutions show that while δ is higher than some critical value (δ_{cr}), the steels corrode in the active state (Figure 4.3, curves 1–3; Figure 4.4, curves 1–3). However, the reduction of δ beyond δ_{cr} results in abrupt ennobling of corrosion potential (E_{cor}) and in subsequent self-passivation of the steels (Figure 4.3, curve 4; Figure 4.4, curve 4).

Figures 4.3 and 4.4 show that the thinning of the solution layer leads to a decrease in the critical current densities of passivation (i_{cc}) of the steels. The phenomenon was observed for the steel Cr25Mn15 also in experiments carried out in acid sulphate solutions containing chloride (Figure 4.5), where the decrease in δ also enables the ennobling of pits' formation potential (E_{br}).
Figure 4.1: Anodic potentiodynamic (3.6Vh⁻¹) polarisation curves of Cr25Mn15 steel in bulk acid sulphate solutions: (1) - pH1; (2) - pH2; (3) - pH3; and (4) - pH4.
Figure 4.2: Critical current density for the passivation of Cr25Mn15 steel versus pH of acid sulphate solution (bulk).
Figure 4.3: Anodic potentiodynamic (3.6Vh⁻¹) polarisation curves of Cr25Mn15 steel in bulk and thin layers of acid (pH1) sulphate solution: (1) - bulk; (2) - 250µm; (3) - 125µm; and (4) - 50µm.
Figure 4.4: Anodic potentiodynamic (3.6Vh⁻¹) polarisation curves of Cr17 steel in bulk and thin layers of acid (pH2) sulphate solution: (1) - bulk; (2) - 150µm; (3) - 100µm; and (4) - 50µm.
Figure 4.5: Anodic potentiodynamic (3.6Vh⁻¹) polarisation curves of Cr25Mn15 steel in: (1) - 0.5M H₂SO₄ (bulk); (2) - 0.5M H₂SO₄ + 0.5M HCl (bulk); (3) - 0.5M H₂SO₄ + 0.5M HCl (δ = 250μm); and (4) - 0.5M H₂SO₄ + 0.5M HCl (δ = 50μm).
The reduction of $\delta$ results in an increase in the cathodic current for oxygen reduction due to the ease of oxygen access from air to the metal surface. This is accompanied by a drop in $i_{cc}$ and thus promotes the passivation of the steels. The drop in $i_{cc}$ can be partly attributed to the retarded removal of corrosion products from the electrode surface with subsequent screening of the surface by the accumulated products. An additional contribution to the drop in the $i_{cc}$ can be associated with the possible increase in pH of the test solution during the experiments due to the reduction of molecular oxygen, which also increases with the decrease in $\delta$ value. This latter view is supported by the results shown in Figure 4.6. However, in accordance with the data in Figures 4.4 and 4.6, and the well known equation

$$E_{pp} = E_{pp}^0 - 0.059pH$$

(4.1)

(in which $E_{pp}$ is the potential corresponding to the critical current of passivation $i_{cc}$), the expected shift of $E_{pp}$ due to the noted possible alkaalisation of the test solution cannot exceed the values $\Delta E_{pp} = -20mV$ (at $\delta = 150\mu m$) and $\Delta E_{pp} = -35mV$ (at $\delta = 100\mu m$). Taking into consideration that the values of IR-error in the determination of $E_{pp}$ based on theoretical calculations, described in section 3.2, are $\Delta E_{pp} = 25mV$ (at $\delta = 150\mu m$) and $\Delta E_{pp} = 22mV$ (at $\delta = 100\mu m$), the constancy of $E_{pp}$ (Figures 4.3–4.5), within the spread of the experimental data, with change of $\delta$ can be explained.

Evidently, the stainless steels Cr25Mn15 and Cr17 in acid sulphate solutions may corrode in either the active state or the passive state, depending on thickness of the electrolyte's layer. The thickness of electrolyte at which self-passivation occurs (critical self-passivation thickness $\delta_{cr}$) depends on the acidity of the test solution (Figure 4.7). At higher pH, the value of $\delta_{cr}$ is
Figure 4.6: Critical current density for the passivation of Cr17 steel versus pH of bulk acid sulphate solutions.
Figure 4.7: Critical thickness of self-passivation ($\delta_{cr}$) versus pH of acid sulphate solutions for: (1) - Cr25Mn15 and (2) - Cr17.
higher and, hence, serves as an evidence of the easier conditions of self-passivation. The critical self-passivation thickness may therefore be adopted as one of the criteria for the evaluation of corrosion resistance of stainless steels in atmospheres polluted with sulphur dioxide. In this regard, it is expected that steel Cr17 and steel Cr25Mn15 will corrode in such the environment at similar corrosion rates.

The dependence of the corrosion current density \( (i_{\text{cor}}) \) of steel Cr17 on \( \delta \) was investigated as a basis for confirming that the ennobling of \( E_{\text{cor}} \) by reducing \( \delta \) towards \( \delta_{\text{cr}} \) (Figure 4.3, curve 4; Figure 4.4, curve 4) results in passivation and, subsequently, in an increase in the corrosion resistance of the steels. Figure 4.8 shows that, while \( \delta \) stays in the region \( \delta > \delta_{\text{cr}} \), a decrease of \( \delta \) does not change \( E_{\text{cor}} \) and \( i_{\text{cor}} \) significantly. At \( \delta \leq \delta_{\text{cr}} \), \( E_{\text{cor}} \) ennobles abruptly, while \( i_{\text{cor}} \) drops by nearly two orders of magnitude. The drop in \( i_{\text{cor}} \) coupled with the shift of \( E_{\text{cor}} \) into the passive region of the anodic polarisation curve re-affirms the observed phenomenon of self-passivation of the stainless steels in thin phase layers of acid sulphate solutions.

The self-passivation of steels Cr25Mn15 and Cr17 in thin layers of acid sulphate solutions is irreversible, as the passive state achieved can be retained for a long time, even in the bulk electrolyte in which the steel usually corrodes actively prior to the self-passivation or in a more corrosive solution (50% H\(_2\)SO\(_4\)). The resulting passivity can only be disturbed by mechanical means (scratching of the metal surface) or by a sufficiently energetic cathodic reduction. The time dependence of \( E_{\text{cor}} \) and \( i_{\text{cor}} \) of the steels in bulk solution, after self-passivation under a thin layer, is given in Figure 4.9. The data show that during exposure in the bulk solution, after the self-passivation under a thin layer, the protective passivating film
Figure 4.8: Influence of the thickness of acid sulphate layer on corrosion current density ($i_{\text{cor}}$) and corrosion potential ($E_{\text{cor}}$) for Cr17 steel: Δ - pH = 1 and o - pH = 2.
Figure 4.9: Corrosion current density ($i_{cor}$) and corrosion potential ($E_{cor}$) for Cr25Mn15 steel and Cr17 steel versus time of immersion in bulk sulphate solutions after self-passivation in thin layer: △ - Cr25Mn15 steel, bulk (pH1); self-passivation at $\delta = 35\mu m$; ○, ◇ - Cr17 steel, bulk (pH2), self-passivation at $\delta = 50\mu m$. 
continues to grow and, hence, results in a further shift in $E_{\text{cor}}$ towards the passive potential region, resulting also in a corresponding decrease of $i_{\text{cor}}$.

The above results suggest that simple but effective method of protecting the steels in bulk acid sulphate media may be possible. In effect, such an approach, which is usually carried out by anodic protection based on the use of an external power supply, can be carried out easily by a surface modification procedure resulting in a preliminary short term activation with subsequent drying up of the metal surface. The treatment can ensure high corrosion resistance of the metal in the corrosive environment. Typical examples of corroded steel coupons (Cr17) and test solutions (0.5M $\text{H}_2\text{SO}_4$, room temperature) are shown in Figure 4.10. The difference in corrosion behaviour of the specimens with and without the surface modification treatment is obvious and is supported by the data on corrosion rates determined by a weight loss method: $k = 15\text{mmyear}^{-1}$ (specimen A) and $k = 1.35 \cdot 10^3\text{mmyear}^{-1}$ (specimen B). The high corrosion resistance of specimen B is attributed to the self-passivation of the steel Cr17 in thin electrolyte layers during the drying of the specimen after preliminary activation. The data in Figures 4.9 and 4.10 also suggest that a high corrosion resistance of steels Cr25Mn15 and Cr17 in atmospheres polluted with sulphur dioxide is possible as the corrosion occurs in conditions of intermittent wetting and subsequent drying.
Figure 4.10: Exposure of Cr17 steel coupons to 0.5M $\text{H}_2\text{SO}_4$: A - 6 days' exposure; before immersion the specimen was stored at room temperature for 24h; B - 3 months' exposure; before immersion the specimen was activated in the same solution for several minutes and then left to dry at room temperature for 24h.
4.3 Cathodic reduction of oxygen in the region of anodic dissolution of stainless steels

The anodic potentiodynamic polarisation curves of stainless steels in acid solutions often contain the so-called cathodic loop which is a region of cathodic currents between the active and passive sections of the polarisation curve [54, 156, 206, 207]. The existence of these loops is associated with the fact that the rate of the cathodic reaction within the corresponding range of potentials exceeds the rate of the anodic reaction. For stainless steel Cr18Ni10Ti in a naturally aerated solution of 5% H₂SO₄ + 0.1gL⁻¹ KSCN only the anodic curves of electrodes with a water-line possess the cathodic loops [208]. In the absence of the water-line, only a small anodic current minimum is observed within the potential range in question. This is attributed to the marked improvement in the access of oxygen to the metal surface through the thin layer of electrolyte in the meniscus zone. However, the results of the present study show that the form of anodic polarisation curve in the region of the active-passive transition depends on the condition of the electrode surface as much as, if not more than, it does on the water-line.

A number of stainless steels were investigated: Cr25Mn15; Cr17; Cr18Ni20Si3Mo3Cu3Nb, and two heats of steel Cr18Ni11, one of which (heat 32) contained manganese bearing sulphide inclusions, while the other (heat 3) did not. The experiments were conducted in naturally aerated (bulk and thin layers) and in deaerated (bulk) 0.5M H₂SO₄ solutions at room temperature. Individual series of tests were carried out at room temperature in solutions of H₂SO₄ + Na₂SO₄ (pH 0.4–4), with the constant concentration of SO₄²⁻ ions equal to 0.5M, and in 30% H₂SO₄ at 80°C. The working surface
area of the electrodes used were 0.1cm² and from 1 to 10cm² without and with a water-line respectively.

A distinct cathodic loop is present on the typical anodic potentiodynamic polarisation curves (Figures 4.1 and 4.3, curves 1–3; Figure 4.4, curves 2 and 3; Figure 4.5; Figure 4.11, curve 1) of electrodes (with no water-line) of steels Cr25Mn15 and Cr17 recorded at a direct potential sweep from corrosion potential in the naturally aerated acid sulphate solutions. An anodic potentiodynamic polarisation curve of steel Cr17 recorded in bulk 0.5M H₂SO₄ at a potential sweep 3.6Vh⁻¹ (Figure 4.4, curve 1) displays all the principal characteristics of a curve recorded at a sweep rate 0.72Vh⁻¹ with the exception of the cathodic loop potential region where little or no cathodic current was evident.

The presence of the cathodic loop is associated with the reduction of dissolved oxygen in the limiting diffusion current regime. This finding is supported by:

(i) the disappearance of the loop when the solution is deaerated with nitrogen (Figure 4.11, curve 2; Figure 4.12, curve 3); and

(ii) the substantial (by more than one order of magnitude) increase in cathodic current in the loop when the solution is stirred (Figure 4.12, curve 2), or at a transition from bulk into thin electrolyte layers (Figures 4.3, 4.4, 4.5 and 4.13).
Figure 4.11: Anodic potentiodynamic (0.72Vh⁻¹) polarisation curves of Cr17 steel in 0.5M H₂SO₄: (1) - naturally aerated solution, potential sweep in anodic direction from open circuit potential; (2) - deaerated solution, potential sweep in anodic direction from open circuit potential; and (3) - naturally aerated solution, reverse potential sweep from $E_{HPP} = 0.65V$ following sweep in anodic direction from open circuit potential.
Figure 4.12: Anodic potentiodynamic (3.6Vh\(^{-1}\)) polarisation curves of Cr25Mn15 steel in the bulk of acid (pH = 1) sulphate solution: (1) - quiescent solution; (2) - stirred solution; and (3) - deaerated solution.
Figure 4.13: Maximum cathodic current density (in the region of cathodic loop on the anodic potentiodynamic polarisation curve (direct sweep) of Cr25Mn15 steel) versus thickness of acid (pH1) sulphate solution layer.
It is evident that in the region of the cathodic loop

\[ i_{mc} = i_C - i_a \]

(4.2)

where \( i_{mc} \) is the measured cathodic current density; \( i_C \) the true current density of cathodic reaction (reduction of oxygen); \( i_a \) the true current density of anodic reaction (ionisation of metal atoms). Under the test conditions, the value of \( i_{mc} \) largely depends on the extent of passivity of the electrode surface. However, the effect of the latter is directly opposite to what might be expected, considering only the obvious character of the \( i_a \) changes during the passivation. In fact, with a constant \( i_C \), the value of \( i_{mc} \) should increase with an increase in the extent of passivity (and vice versa) due to a decrease in \( i_a \). Yet, an exposure of the stainless steel electrodes to a potential within the passive region (\( E_{pas} \)), resulting in a significant decrease in \( i_a \) (by more than one order of magnitude), provided a marked decrease in \( i_{mc} \). The values of \( i_{ma} \) after passivation at \( E_{pas} \) were determined from polarisation curves recorded at a reverse potential sweep from \( E_{pas} \) (Figure 4.11, curve 3; Figure 4.14).

Considering the reduction in \( i_a \) in the region of the active-passive transition as a consequence of an increase in the extent of passivity and conversely, the same conclusion can be reached in regard to the dependence of \( i_{mc} \) on other factors. Thus, an increase in the acidity of the solution results in an increase in the anodic currents (\( i_a \)) within the potential region in question and also markedly increases the value of \( i_{mc} \) (Figure 4.1).

It is also known that \( H_2S \) molecules (or \( HS^- \) ions) added to the solution or entering near the electrode solution layer during the dissolution of sulphide
Figure 4.14: Maximum cathodic current density (in the region of cathodic loop on anodic potentiodynamic polarisation curve (reverse) sweep) versus passivation time at potential corresponding to the middle of passive region: (1) - Cr25Mn15 steel, 0.5M H₂SO₄; (2) - Cr18Ni11 (heat 32), 0.5M H₂SO₄; and (3) - Cr18Ni20Si3Mo3Cu3Nb, 30% H₂SO₄, 80°C.
inclusions in stainless steels may increase the anodic currents \( i_a \) and expand the active dissolution peak, shifting the active-passive transition to a region of more positive potentials [209]. The anodic polarisation curve of steel Cr18Ni11 (heat 3) which is free of manganese sulphides contains neither an active peak nor a cathodic loop. In contrast, regardless of the presence or absence of a waterline, both the active peak and cathodic loop are present in the anodic polarisation curve of steel Cr18Ni11 (heat 32) which contains the sulphide inclusions (Figure 4.15), or when Na\(_2\)S is added to the solution (Figure 4.16).

The values of \( i_{mc} \) depend also on the presence of corrosion products on the electrode surface, which appears to facilitate the reduction of oxygen. Stationary values of \( i_{mc} \) were obtained for steel Cr25Mn15 from potentiostatic experiments in quiescent acid (pH = 1) sulphate solution at a potential \( E_c \) within the cathodic loop region. Prior to the potentiostatic experiments the specimens were held at the corrosion potential \( (E_{cor}) \), after which the potential \( E_c \) was imposed. The experimental data show that by holding the specimens at \( E_{cor} \) a significant increase of \( i_{mc} \) can be obtained (Figure 4.17, curve 1), while the removal of the corrosion products by stirring of the test solution during the exposure at \( E_{cor} \) (Figure 4.17, curve 2) or due to the orientation of the specimen surface (Table 4.1) results in drop of \( i_{mc} \).

\[
\begin{array}{c|c|c}
\text{Orientation of specimen surface} & \text{Upward} & \text{Vertical} & \text{Downward} \\
\hline
33.3 \mu \text{Acm}^{-2} & 23.3 \mu \text{Acm}^{-2} & 16.7 \mu \text{Acm}^{-2} \\
\end{array}
\]

\textit{Table 4.1:} Stationary values of current density \( i_{mc} \) at a potential \( E_c \) within cathodic loop after 30min exposure at \( E_{cor} \); steel Cr25Mn15, acid sulphate solution (pH = 1).
Figure 4.15: Anodic potentiodynamic (3.6Vh\(^{-1}\)) polarisation curves of Cr18Ni11 steel in the bulk acid (pH1) sulphate solution: (1) - heat 3; and (2) - heat 32.
Figure 4.16: Anodic potentiodynamic (3.6 V h⁻¹) polarisation curves of Cr18Ni11 (heat 3) steel in bulk solutions: (1) - 0.5M H₂SO₄; (2) - 0.5M H₂SO₄ + 10⁻⁴M Na₂S; (3) - 0.5M H₂SO₄ + 10⁻³M Na₂S; and (4) - 0.5M H₂SO₄ + 10⁻²M Na₂S.
Figure 4.17: Stationary values of cathodic current density (determined during potentiostatic polarisation in quiescent solution at potential within cathodic loop) versus exposure time at open circuit potential in (1) quiescent and (2) stirred solutions; Cr25Mn15 steel, acid (pH1) sulphate solution.
The observed dependence of $i_{mc}$ on the extent of passivation of the stainless steels cannot be associated with the change in the true surface area during the anodic dissolution because, as it follows from equation (4.2), with the constant values of the true current densities of cathodic ($i_{c}$) and anodic ($i_{a}$) reactions, the value of $i_{mc}$ must also remain constant. The drop in $i_{mc}$ with the increase in the extent of passivity is, as proposed, of theoretical interest, particularly since these effects are observed in the region of the limiting diffusion current of oxygen reduction. In accordance with the data previously reported [210], the increased limiting current density for oxygen reduction on stainless steel in sodium chloride solution is associated with the activation of the steel surface by specific adsorption of chloride ions. On the other hand, blockage of active centres on the surface by the adsorption of organic inhibitors may lead to a reduction in the limiting diffusion current for the oxygen reduction [211].

However, a change in the extent of passivity of the stainless steels obviously changes the fraction of the active surface which provides the major contribution to the cathodic current of oxygen reduction. For this reason, a change in the extent of passivity of the surface of the stainless steels may lead to changes in $i_{c}$. In some instance these changes may be great enough to eliminate the effect of a decrease in the rate of the anodic reaction ($i_{a}$) on the cathodic current $i_{mc}$ measured at potentials corresponding to the cathodic loop.
4.4  Effect of oxygen reduction on the retention of passivity by stainless steels in acid sulphate solutions

The use of stainless steels in various corrosive environments, particularly in dilute sulphuric acid, is rendered by the formation of the thin protective surface oxide films. These passive oxide films are formed either spontaneously or as a result of externally applied anodic polarisation depending on the specific features of the corrosion-electrochemical system under consideration. The passivity in the latter is retained for some time $t_r$ required for the passivated electrode potential to decay back to the active potential region. Generally, the value of $t_r$ is determined by the chemical stability of the passive film in a given solution, which in turn depends on the composition and thickness of the film, the acidity and temperature of the solution, and other characteristics of the system studied. However, as has been demonstrated [3, 20, 212, 213], $t_r$ can also depend on the presence or absence of oxidising agents in solution.

It has previously been demonstrated in sections 4.2 and 4.3 that the anodic polarisation curves of stainless steels studied in naturally aerated acid sulphate solutions include cathodic loops. These loops are regions of cathodic currents resulting from the rate of the cathodic reaction of oxygen reduction being in excess of that of the anodic reaction of ionisation of metal atoms within the potential region considered. According to Tomashov [156], cathodic loops serve as evidence of the presence of a sufficiently effective cathodic process in the system. Thus, with the presence of a cathodic loop on anodic polarisation curves of stainless steel in sulphuric acid solution, it can be assumed that the rate of the oxygen reduction is comparable with the rate of the anodic dissolution of steel even at potentials outside the cathodic
loop region. Consequently, it would be expected that oxygen reduction will have some effect on the retention of passivity.

In this part of the thesis, the passivation of stainless steel Cr17 in dilute sulphuric acid at potentials within the passive and cathodic loop regions was investigated. The decay of the passivity in naturally aerated and deaerated sulphuric acid solutions was also investigated in an attempt to elucidate the role of oxygen reduction on the retention of passivity by stainless steel in dilute sulphuric acid. Electrochemical measurements were conducted on specimens of steel Cr17 in 0.5M H₂SO₄ (pH = 1.3) at room temperature. A cylindrical specimen, mounted in cold curing acrylic resin with a working surface of area 0.1cm² and a flag type specimen with a working surface of area 1.4cm² were used. Retention of passivity by steel Cr17 after passivation at E\textsubscript{HPP} (high potential passivation at a potential corresponding to the middle of passive region) and E\textsubscript{LPP} (low potential passivation at a potential corresponding to the highest cathodic current within cathodic loop region) was studied.

The typical anodic potentiodynamic polarisation curves of steel Cr17 in 0.5M H₂SO₄, with free access to air are shown in Figure 4.11. In contrast to curve 1, the curve 2 obtained in deaerated solution and the curve 3 recorded at a reverse potential sweep from potential E\textsubscript{HPP} = 0.65V (immediately after sweeping from corrosion potential E\textsubscript{Cor} in the anodic direction) do not possess the cathodic loop. The absence of the cathodic loop on curve 3 is attributed to the reduced ability of oxygen to undergo reduction on a passive surface. Hence, exposure of the electrode to potentials within the passive region results in surface passivation, leading to a drop in the oxygen reduction current which is large enough to eliminate the effect of the drop
in the anodic current on values of the cathodic current measured in the cathodic loop.

Taking the above observations into consideration and based on previously reported data [214–217] which demonstrate that an increase in the passivation potential (in our case from $E_{LPP} = 0.2V$ to $E_{HPP} = 0.65V$) increases the extent of passivity, the role of oxygen reduction in the processes during and after HPP will be expected to be lower in comparison with similar processes during and after LPP. The passivity retention time $t_r$ for stainless steel Cr25Mn15, the anodic polarisation curves of which in naturally aerated dilute sulphuric acid solutions include cathodic loops, greatly depends on the position of the passivation potential. Passivity of the steel could be retained for a long time after LPP (months in comparison with minutes after HPP) and could only be disturbed by scratching of the metal surface or by polarising the electrode cathodically, provided that the imposed cathodic current density exceeded a certain critical value.

A similar behaviour is also observed for steel Cr17 in naturally aerated 0.5M $H_2SO_4$. The corresponding potential decay curves of the steel after HPP ($E_{HPP} = 0.65V$) and LPP ($E_{LPP} = 0.2V$) are given in Figure 4.18. It would be expected that soon after the passivation treatment is interrupted and samples are released to open circuit, the electrode potential shifts back towards negative values, until a value corresponding to an active metal surface is attained. The behaviour of the electrode potential after HPP (Figure 4.18, curves 1–4) follows this pattern both in naturally aerated and in deaerated solutions, and also shows a natural rise of $t_r$ with increase of HPP time. Potential decay curves recorded in open to air and in deaerated solutions after 3h of HPP are close (Figure 4.18, curves 2 and 4), and thus
Figure 4.18: Potential decay curves of Cr17 steel in 0.5M H₂SO₄ after HPP ($E_{\text{HPP}} = 0.65\text{V}$) and LPP ($E_{\text{LPP}} = 0.2\text{V}$): (1) - HPP, passivation time 1h, naturally aerated solution; (2) - HPP, passivation time 3h, naturally aerated solution; (3) - HPP, passivation time 1 week, naturally aerated solution; (4) - HPP, passivation time 3h, deaerated solution; (5) - LPP, passivation time 5min, naturally aerated solution; and (6) - LPP, passivation time 5min, deaerated solution, before immersion in deaerated solution specimen was exposed to naturally aerated solution for 1 week.
indicate that $t_r$ after HPP (at least for passivation time $t = 3$ h), depends mainly on chemical stability of oxide film and there is no significant influence of oxygen reduction.

The behaviour of the electrode in naturally aerated solution after LPP shows an opposite effect. Soon after LPP is interrupted the potential moves towards positive values until it is stabilised and attained a value between $E_{LPP}$ and $E_{HPP}$. Even a brief (5 min) passivation at $E_{LPP} = 0.2$ V produces unusually high values of passivity retention time ($t_r > 7$ months, after which the experiment was discontinued while the electrodes still retained passivity (Figure 4.18, curve 5)). At the same time $t_r$ in deaerated solutions after LPP is comparatively low ($t_r \sim 4$ h) which clearly indicates the dominating role of oxygen reduction in maintaining passivity after LPP in the naturally aerated solution. These results provide a basis for concluding that no activation of the electrodes after LPP will occur if the concentration of oxygen in solution is sufficient for the rate of its reduction to exceed that of the dissolution of metal. The deaeration of the solution leads to a decrease in oxygen concentration in the solution which reverses the situation, and with the excess of rate of dissolution of metal over that of oxygen reduction the electrode potential will tend to move towards the active region.

Generally the passivity retention time in solutions containing oxidising constituents can be determined from the equation:

$$t_r = \frac{Q_d}{i_A - i_c}$$

(4.3)
where $Q_d$ is the value of electric charge passing through the electrode during the passivity decay process. At $i_a < i_c$ the electrode potential will move towards positive values until the rates of the anodic and cathodic reactions are about equal. Provided that $i_a = i_c$, the electrode potential stabilises and never decays back into the region of active potentials (Figure 4.18, curve 5). At $i_a > i_c$ the electrode potential will move towards negative values and the active potential region will be achieved sooner, when the difference between the rates of the anodic and cathodic reactions is larger.

The value of $Q_d$, corresponding to the passage from passive to active state, can be evaluated by integrating the electrode capacitance versus potential curve, given the latter is known. Kolotyrkin [20] estimated $Q_d$ for a chromium electrode (which has similar electrochemical behaviour during anodic passivation to that of stainless steel) passivated in 0.5M $\text{H}_2\text{SO}_4$ to be product of the capacitance $C$ of the condenser, in which the surface oxide acts as a dielectric, and the potential shift $\Delta V$, such as accompanies the passage from the passive to the active state. Adopting the same approach and taking values $C = 20\mu\text{Fcm}^{-2}$ [20, 156, 210] and potential shift after HPP $\Delta V = 0.9V$ (Figure 4.18, curves 1, 2 and 4), the value $Q_d = 18\mu\text{Ccm}^{-2}$ is obtained. However, this approach does not take into account the probable decrease of the oxide thickness as the potential moves towards negative values [214–217] which can result in an increase in the capacitance $C$. For this reason, the calculated values of $Q_d$ and subsequent evaluation of $t_r$ could be significantly undervalued.

In the present work, an attempt of a theoretical evaluation of passivity retention time along with some other parameters, relating to the formation and dissolution of passive oxide films on steel Cr17 in sulphuric acid
solution, and their comparison with the parameters found experimentally is undertaken. In Figure 4.19 the measured anodic current density $i_{ma} = i_a - i_c$ is plotted against time of HPP. The similar dependencies of anodic current density were received also by other investigators [214, 218–221]. From Figure 4.19, it is clear that an equation of the form

$$i_{ma} = i_0 t^{-n} \quad (4.4)$$

where $n = 1.1$ can be used as an approximation. The value of $i_0$ is numerically equal to the value of $i_{ma}$ at $t = 1s$ and extrapolation of the graph in Figure 4.19 gives $i_0 = 8.32mAm^{-2}$ which is close enough to the values of starting current densities (6–11.5mAcm$^{-2}$). This value was determined independently by a digital ammeter connected in series with the electrochemical cell, while the electrode potential was shifted from $E_{cor}$ to $E_{HPP}$.

The total electric charge passed through a unit electrode area during HPP was measured experimentally ($Q_e$) and was compared with that evaluated theoretically ($Q_t$) by integrating the current density-time curve shown in Figure 4.19. The average values of $Q_e$ and values of $Q_t$ given in Table 4.2 are in good agreement. However, only part of the total charge passing through the electrode during HPP is used for the passive film formation, the rest is consumed during the anodic dissolution of the metal [217, 218, 222–225]. The efficiency of the film formation $k$, i.e., the fraction of total charge which is consumed in the process of protective oxide formation, varies for different systems [217, 222–225]. Castle and Qui [217] have demonstrated that $k$ for Cr17 steel in 0.1M H$_2$SO$_4$ at 750mV (S.H.E.), which is very much similar to that considered in the present work, is equal to 0.383. Thus, multiplying
Figure 4.19: Decay of the anodic current density of Cr17 steel in 0.5M $\text{H}_2\text{SO}_4$ under HPP ($E_{\text{HPP}} = 0.65\text{V}$).
values of $Q_t$ by the $k$ value, charge consumed during the oxide formation ($Q_d$) were obtained

$$Q_f = kQ_t$$  \hspace{1cm} (4.5)

Assuming that the number of moles of electrons required to produce 1mol of the protective oxide ((Fe, Cr)$_2$O$_3$) [217] is $n = 6$ [157, 217, 219], while the number of moles of electrons required to reduce 1mol of the same oxide $n = 2$ [157, 218, 219, 226], the charge consumed by the electrode during passivity decay can be calculated in accordance with

$$Q_d = \frac{Q_f}{3}$$  \hspace{1cm} (4.6)

The corresponding values of $Q_d$ over different times of HPP are given in Table 4.2 and can be used for the calculation of the expected passivity retention time. The calculated passivity retention times $t_f^c$ presented in Table 4.2, are obtained by division of the corresponding values of $Q_d$ by $i_{ma}$ measured at $E_{HPP}$

$$t_f^c = \frac{Q_d}{i_{ma}}$$  \hspace{1cm} (4.7)

and can differ from the experimentally measured values of $t_f^c$ as a result of a possible increase of the cathodic component of $i_{ma}$, while the electrode potential moves from $E_{HPP}$ towards negative values.
Table 4.2: Parameters concerning formation and dissolution of passive oxide films on stainless steel Cr17 in 0.5M H₂SO₄ at E_{HPP}65V.

<table>
<thead>
<tr>
<th>Time of HPP, s</th>
<th>( i_{ma} ) ( \mu \text{Acm}^{-2} )</th>
<th>( Q_{av}^{+} ) ( \mu \text{Ccm}^{-2} )</th>
<th>( Q_\lambda ) ( \mu \text{Ccm}^{-2} )</th>
<th>( Q_d ) ( \mu \text{Ccm}^{-2} )</th>
<th>( t_\xi ) ( \text{s} )</th>
<th>( t_\zeta ) ( \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 10</td>
<td>4.81\times10^2</td>
<td>18.71\times10^3</td>
<td>17.11\times10^3</td>
<td>6.55\times10^3</td>
<td>2.18\times10^3</td>
<td>4.53\times10^0</td>
</tr>
<tr>
<td>2.0\times10^2</td>
<td>2.14\times10^1</td>
<td>32.28\times10^3</td>
<td>34.21\times10^3</td>
<td>13.10\times10^3</td>
<td>4.37\times10^3</td>
<td>2.04\times10^2</td>
</tr>
<tr>
<td>3.4\times10^3</td>
<td>9.00\times10^1</td>
<td>47.27\times10^3</td>
<td>46.29\times10^3</td>
<td>17.73\times10^3</td>
<td>5.91\times10^3</td>
<td>6.57\times10^3</td>
</tr>
<tr>
<td>1.1\times10^4</td>
<td>3.00\times10^1</td>
<td>53.88\times10^3</td>
<td>50.32\times10^3</td>
<td>19.27\times10^3</td>
<td>6.42\times10^3</td>
<td>2.14\times10^4</td>
</tr>
<tr>
<td>*6.0\times10^5</td>
<td>3.60\times10^3</td>
<td>-</td>
<td>61.21\times10^3</td>
<td>23.44\times10^3</td>
<td>7.18\times10^3</td>
<td>1.99\times10^5</td>
</tr>
</tbody>
</table>

*Flag type specimen

where \( i_{ma} \) is the measured anodic current density; \( Q_{av}^{+} \) the average value of total experimentally measured electric charge passing through a unit electrode area; \( Q_\lambda \) the equivalent theoretically evaluated value; \( Q_d \) the charge consumed by oxide formation; \( Q_d \) the charge passing through electrode during passivity decay process; \( t_\xi \) the calculated passivity retention time; and \( t_\zeta \) the experimentally obtained passivity retention time.

Comparison of the values \( t_\xi \) and \( t_\zeta \) shows that with an increase in the HPP time convergence between these two values increases. The result again proves that the increase in the extent of passivity of the steel electrodes reduces the cathodic current of oxygen reduction and \( t_\xi \) after HPP (in contrast to \( t_\zeta \) after LPP) depends not on the cathodic process of oxygen reduction, but mainly on the chemical stability of the oxide film.

The observed phenomenon of extremely high \( t_\xi \) after LPP passivation can be of some practical significance. The presence of a passive potential region on
the anodic polarisation curve of steel Cr17 in 0.5M H₂SO₄ makes it possible to control corrosion by means of anodic protection. The potential of anodic protection is usually chosen in the middle of the passive region (continuous polarisation mode) or fluctuates between noble and negative ends of the passive region (on-off control mode or synchronous anodic protection of several items by means of one potential controller [4, 54]). When the potential controller is turned off either by accident or deliberately (on-off control; synchronous anodic protection) passivity is retained for a time \( t_r \) so that an increase of \( t_r \) reduces the frequency of connections and disconnections of the controller and always maintains reliability of the protection. An increase in \( t_r \) can be brought about by introducing an additional electrode, a galvanic cathode, into the polarisation circuit [54]. However, this method does not always produce a radical increase of \( t_r \) and its use complicates the protection system. From the results of the present work it follows that the presence of the cathodic loop on the anodic polarisation curve suggests an easier way of increasing \( t_r \) without the use of a galvanic cathode. In such cases a radical increase of \( t_r \) and, as a consequence, anodic protection reliability, can be achieved by placing the protection potential in the cathodic loop region. Passivation in this potential region provides high passivity retention time at the expense of the cathodic process of oxygen reduction, which will maintain the passivity until the rate of the oxygen reduction exceeds that of the anodic dissolution of metal.
4.5 **Low potential passivation and anodic protection of stainless steels**

The technique of anodic protection is less known to most corrosion engineers than the other widely used methods of corrosion control, such as cathodic protection, inhibitors, protective coatings, etc., and for this reason does not have large-scale industrial applications. Anodic protection may be considered to be more dangerous than cathodic protection because possible over or under protection can result in unacceptably high rates of corrosion. However, this method of corrosion control, which is applicable to metals with active-passive behaviour in given corrosive media, appears to offer some advantages such as: (i) low current requirements (at the level of corrosion rate in the passive potential region); (ii) large reductions in corrosion rate (10000-fold or more); and (iii) applicability in acidic media, where the acid purity is of primary importance and the use of cathodic protection technique is impeded due to high current requirements and possible intensive hydrogen evolution.

The major prerequisite for the application of anodic protection to a given corrosion-electrochemical system is the presence on anodic polarisation curve of a passive potential region in which the anodic current density does not exceed $1-2 \mu \text{Acm}^{-2}$ [54]. The length of the passive region depends on the metal properties and on the corrosivity of the solution. Shock et al. [227] using electromechanical potentiostat have shown that anodic protection can be implemented even at a passive region length of 50mV. With the use of contemporary electronic potentiostatic devices the minimal length of the passive potentials region may be even lower.
Anodic protection can be carried out in a continuous polarisation mode, where the protection potential corresponds to a minimal current density within the passive region (usually in the middle of the passive region) or in on-off control mode. In the latter case, the potential controller switches the polarisation current on when the potential of the surface under protection reaches the chosen lower limit ($E_l$) and switches it off when the upper limit ($E_u$) of the chosen potential regulation region is achieved. The similar fluctuations of potential between noble and negative ends of the passive region are typical for synchronous anodic protection when several items are protected by means of one potential controller.

The implementation of the on-off control mode and synchronous anodic protection is possible only because the drift of potential to the lower end of passive region does not occur instantly, but during some time (passivity retention time $t_r$) which depends on the stability of the passive film in the given medium. An increase in $t_r$ reduces the frequency of connections and disconnections of potential controller and, hence, increases the reliability of anodic protection in all modes.

With the on-off mode of anodic protection the passivity retention time can be increased [54] by the introduction of an additional electrode—galvanic cathode (anodic protector) into the polarisation circuit. The stationary potential of the galvanic cathode has to be within the potential regulation region, but at the commencement of polarisation the potentials of the metal under protection and that of the galvanic cathode will shift towards $E_u$. When the potential of the metal under protection achieves the value $E_u$, the polarisation current is switched off and a redistribution of accumulated by the galvanic cathode electric charge slows down the potential drift of the
protected metal towards $E_i$. Yet, this method may not always produce a radical increase in $t_r$ and its use complicates the protection system. Also, its use is impeded in some types of equipment and there are some difficulties in the selection of material for the galvanic cathode and its fabrication.

Equipment made of steels Cr25Mn15 can be operated under anodic protection in acid (pH 0.6–0.7) sulphate solutions [8, 9]. The values of passivity retention time $t_r$ for this system after HPP are low enough, and, hence, make the use of the galvanic cathode an attractive option. However, it was shown previously that the passivation of stainless steels Cr25Mn15 and Cr17 in the cathodic loop region (LPP) produces extremely large values of $t_r$. In this work, the possibility of implementing anodic protection for these and other stainless steels at potentials within the cathodic loop region was investigated.

Passivity of steels Cr25Mn15 and Cr17 in sulphuric acid solutions after LPP can be retained for months (at least), whereas the steels return into active state in minutes or hours after HPP (Figures 4.20 and 4.21). From the viewpoint of the $t_r$ values for these two steels, the LPP is obviously preferred over HPP. However the corrosion rates of Cr25Mn15 and Cr17 steels determined by a weight loss method were approximately the same both under LPP and HPP; $k = 1.1 \cdot 10^{-2} \text{mm year}^{-1}$ (Cr25Mn15, 10% H$_2$SO$_4$, room temperature, averaged over 8h) and $k = 4.3 \cdot 10^{-3} \text{mm year}^{-1}$ (Cr17, 0.5M H$_2$SO$_4$, room temperature, averaged over 7 days).

The LPP of steel Cr25Mn15 is effective within a fairly broad range of sulphuric acid concentrations (Figure 4.22). For example, the corrosion rate of the steel in 50% H$_2$SO$_4$ at room temperature after LPP was
Figure 4.20: a - Anodic potentiodynamic (3.6Vh⁻¹) polarisation curve and b - potential decay curves after 1h HPP (curve 1) and 5min LPP (curve 2); Cr25Mn15 steel, bulk of the naturally aerated acid (pH = 0.4) sulphate solution.
Figure 4.21: a - Anodic potentiodynamic (3.6Vh$^{-1}$) polarisation curve, and b - potential decay curves after 1h HPP (curve 1) and 5min LPP (curve 2); Cr17 steel, bulk of the naturally aerated acid (pH = 1.3) sulphate solution.
Figure 4.22: Variation of the effective temperature range with concentration of sulphuric acid (below the curve) for the LPP of Cr25Mn15 steel; duration of tests performed: at room temperature - 6 months, at high temperature - 8h.
\[ k = 8.7 \cdot 10^{-3} \text{mm/year}^{-1} \] which only slightly exceeded the corrosion rate of acid-resistant steel Cr20Ni28 under the same conditions \[ k = 5.54 \cdot 10^{-3} \text{mm/year}^{-1} \] (averaged over 6 months).

Passivation in the cathodic loop region also ensures high \( t_r \) values for the other three steels investigated in the experiments (Figures 4.23–4.25; Table 4.3).

**Table 4.3:** Comparison of results obtained at LPP and HPP of some stainless steels.

<table>
<thead>
<tr>
<th>Steel, medium, temperature</th>
<th>( i_{cr} ) ( \mu \text{Acm}^{-2} )</th>
<th>( i_{cl} ) ( \mu \text{Acm}^{-2} )</th>
<th>( E_{LPP} ) ( \text{V} )</th>
<th>( E_{HPP} ) ( \text{V} )</th>
<th>( t_r )</th>
<th>( i_{\text{av, start}} ) ( \mu \text{Acm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr25Mn15, 10% H(_2)SO(_4), 25°C</td>
<td>( 1.5 \times 10^5 )</td>
<td>( 6.8 \times 10^0 )</td>
<td>0.1</td>
<td>0.60</td>
<td>&gt;6 months</td>
<td>20min</td>
</tr>
<tr>
<td>Cr17, 0.5M H(_2)SO(_4), 20°C</td>
<td>( 6.3 \times 10^3 )</td>
<td>( 2.6 \times 10^1 )</td>
<td>0.2</td>
<td>0.65</td>
<td>&gt;7 months</td>
<td>4h</td>
</tr>
<tr>
<td>Cr18Ni10Ti, 30% H(_2)SO(_4), 80°C</td>
<td>( 4.8 \times 10^5 )</td>
<td>( 1.5 \times 10^3 )</td>
<td>0.1</td>
<td>0.60</td>
<td></td>
<td>7.0 \times 10^5</td>
</tr>
<tr>
<td>Cr20Ni20Si3Mo3 Cu3Nb, 30% H(_2)SO(_4), 80°C</td>
<td>( 1.6 \times 10^2 )</td>
<td>( 5.8 \times 10^1 )</td>
<td>0.2</td>
<td>0.60</td>
<td></td>
<td>1.0 \times 10^3</td>
</tr>
<tr>
<td>Mild steel, 25% NH(_4)OH, 25°C</td>
<td>( 3.2 \times 10^2 )</td>
<td>( 1.4 \times 10^1 )</td>
<td>-0.3</td>
<td>0.60</td>
<td></td>
<td>2.3 \times 10^2</td>
</tr>
</tbody>
</table>
Figure 4.23: (1) - Anodic potentiodynamic (3.6Vh⁻¹) polarisation curve, (2) - potential decay curve after 1h HPP and (3) - potential decay curve after 5min LPP; Cr18Ni10Ti steel, 30% H₂SO₄, 80°C.
Figure 4.24: (1) - Anodic potentiodynamic ($3.6 \text{Vh}^{-1}$) polarisation curve, (2) - potential decay curve after 1h HPP and (3) - potential decay curve after 5min LPP (3); Cr18Ni20Si3Mo3Cu3Nb steel, 30% $\text{H}_2\text{SO}_4$, 80°C.
Figure 4.25: (1) - Anodic potentiodynamic (3.6Vh⁻¹) polarisation curve; (2) - potential decay curve after 1h HPP and (3) potential decay curve after 5min LPP; mild steel, 25% NH₄OH.
It has been well established that halide ions, in particular Cl\(^-\) ion, can cause a local breakdown of passive oxide films on metal surfaces [7, 55, 228–231]. Hence the presence of Cl\(^-\) ions can reduce the reliability of anodic protection by reducing the passivity retention time.

Measurements were conducted on Cr18Ni10Mo2 stainless steel specimens in acid sulphate solutions of constant pH (~ 1.3) in the presence and absence of Cl\(^-\) ions. In 0.5M H\(_2\)SO\(_4\) solution, the steel corrodes from passive state (Figure 4.26, curve 1) with a corrosion potential \(E_{\text{cor}} = 0.35\text{V}\). This steel undergoes self-passivation (Figure 4.27, curves 1 and 2) in the 0.5M H\(_2\)SO\(_4\) and in 0.5M H\(_2\)SO\(_4\) + 0.025M Cl solutions even after cathodic reduction \((i_c = 10^4\mu\text{Acm}^{-2}, 3\text{min})\). An increase in the Cl\(^-\) ions concentration to 0.05M results in the breakdown of the passivity and subsequent corrosion from active state (Figure 4.26, curve 2; Figure 4.27, curve 3) with a corrosion potential \(E_{\text{cor}} \equiv 0.1\text{V}\).

There is an obvious similarity between the behaviour of Cr18Ni10Mo2 steel in chloride free and chloride-containing solutions (Figure 4.26) and behaviour of Cr18Ni11 steel in solutions free from sodium sulphide and containing sodium sulphide (Figure 4.16, curves 1 and 4). The anodic polarisation curves of the steels in acid sulphate solutions in the absence of the activating anions contain neither an active peak nor a cathodic loop. However, both are present when the solutions contain the activating anions in a sufficient concentration.

Potential decay curves of Cr18Ni10Mo2 stainless steel in 0.5M H\(_2\)SO\(_4\) + 0.2M Cl solution after HPP (\(E_{\text{HPP}} = 0.55\text{V}\)) and LPP (\(E_{\text{LPP}} = 0.2\text{V}\)) are illustrated in Figure 4.28. The results indicate that LPP
Figure 4.26: Anodic potentiodynamic (3.6Vh$^{-1}$) polarisation curves of Cr18Ni10Mo2 steel in: (1) 0.5M H$_2$SO$_4$ + 0.025M Cl$^-$ and (2) 0.5M H$_2$SO$_4$ + 0.2M Cl$^-$. 

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Figure 4.27: Open circuit potential of Cr18Ni10Mo2 steel versus time after cathodic reduction ($i_c = 10^3 \mu A cm^{-2} \text{min}^{-1}$) in: (1) 0.5M H$_2$SO$_4$; (2) 0.5M H$_2$SO$_4$ + 0.025M Cl$^-$ and (3) 0.5M H$_2$SO$_4$ + 0.05M Cl$^-$. 
Figure 4.28: Potential decay curves for Cr18Ni10Mo2 steel after (1) 1h HPP and (2) 5min LPP in 0.5M H$_2$SO$_4$ + 0.2M Cl$^-$. 
provides significantly larger values of $t_r$, even in the presence of Cl$^-$ ions in the acid sulphate solutions.

Thus, the data obtained indicate that in the presence of a cathodic loop on the anodic polarisation curve, anodic protection may be implemented in potential region within the loop (LPP). The LPP is particularly effective for steels Cr25Mn15 and Cr17 where usual HPP does not produce satisfactory values of passivity retention time $t_r$, and increase of $t_r$ is possible only with use of an additional electrode (galvanic cathode). From the viewpoint of the $t_r$ values, there is no difference between LPP and HPP for the other three stainless steels (Table 4.3). However the LPP may be considered as a preferred option in regards to the lower starting currents, which is of importance during implementation of anodic protection under practical conditions [3].

4.6 Composition and structure of passive films formed on Cr25Mn15 stainless steel in acid sulphate solutions

The composition and structure of passive films formed on stainless steel Cr25Mn15 in acid sulphate solutions at potentials of LPP (cathodic loop region) and HPP (middle of passive region) were studied by Aüger electron spectroscopy (AES) and by the analysis of electron diffraction patterns, respectively.

The data obtained by AES showed that the chemical composition of the passive films formed under conditions of LPP and HPP are identical. The typical Aüger spectra of passive films studied is given in Figure 4.29. The
Figure 4.29: Typical Aüger electron spectra of passive film on Cr25Mn15 steel formed in 10% H$_2$SO$_4$. a - sputtering time 1h; b - sputtering time 2h.
films, apart from iron, contain basic alloying elements and oxygen. AES depth profiling was used to obtain information on the depth distribution of elements. The depth profiles of elements (Figure 4.30, (a) and (b)) attained with the change of intensity of the corresponding spectral lines demonstrate a difference between the passive films formed under conditions of LPP and HPP. In contrast to the film formed at HPP, the distribution of elements with respect to depth of the passive film formed at LPP, is non-monotonic which indicates the presence in the passive film of two layers with different quantitative composition of the elements; the upper layer is enriched with oxygen in comparison with the inner one. Furthermore, the duration of complete sputtering of the passive films formed at LPP and HPP were 8h and 5h, respectively. These values indicate a larger thickness of the passive film formed under LPP conditions.

The structure of the passive films formed at LPP and HPP was studied by the analysis of electron diffraction patterns obtained by the reflection of electrons from the surface of the passivated specimen. The typical diffraction patterns of the passive films formed under these conditions are shown in Figure 4.31, (a), (b) and (c). Comparison of these experimental patterns shows that both the passive films consist of fine-dispersed polycrystalline material. Yet, the passive film formed under HPP conditions contains a definite crystalline phase producing a spot pattern. The same crystalline phase, supposedly identified as the manganese sulphide (MnS), is present on the surface of the active steel Cr25Mn15 after exposure in the test solution at the corrosion potential, but it is absent in passive film formed at LPP. The appearance of the spot pattern, ascribed to MnS inclusions, in the experimental electron diffraction patterns obtained after HPP may be explained by the presence in the passive film of pores located above the inclusions. The heterogeneity of
**Figure 4.30**: Sputter depth profiles obtained by Auger electron spectroscopy for: a - sample passivated at $E = 0.1\,\text{V}$ (LPP), and b - sample passivated at $E = 0.6\,\text{V}$ (HPP); Cr25Mn15 steel, 10% $\text{H}_2\text{SO}_4$. 
Figure 4.31: Electron diffraction patterns of passive film formed on Cr25Mn15 in 10% H₂SO₄ at $E_{LPP} = 0.1\text{V}$ (a) and at $E_{IPP} = 0.6\text{V}$ (a, b and c).
the passive film on the surface of Cr25Mn15 steel formed at HPP can be one of the reasons for its low protective properties in the test solutions. This is supported by the observation that the increasing exposure time at $E_{\text{cor}}$, which has no influence on quasi-stationary values of $i_{\text{ma}}$ (Figure 4.32), results in a decrease in the passivity retention time $t_r$ after HPP (Figure 4.33). At the same time the increased thickness of the passive film formed at LPP on the steel Cr25Mn15 may be one of the reasons for the absence of the spot reflexes on the corresponding electron diffraction pattern.

The values of interplanar distances $(d)$ obtained from ring electron diffraction patterns together with the reference values of $d$ and corresponding Miller indices $(hkl)$ are given in Table 4.4.

Comparison of the experimental and reference values of interplanar distances together with the estimation of structure factor [233, 234], according to which a fulfilment of the relationship

$$d_1^{-1} : d_2^{-1} : d_3^{-1} \ldots : d_n^{-1} =$$

$$\sqrt{h_1^2 + k_1^2 + l_1^2} : \sqrt{h_2^2 + k_2^2 + l_2^2} : \sqrt{h_3^2 + k_3^2 + l_3^2} \ldots : \sqrt{h_n^2 + k_n^2 + l_n^2}$$

indicates the cubic structure of the phase studied, leads to the following conclusion: (i) the passive films formed on the Cr25Mn15 steel have a lattice of face-centred cube, and (ii) the polycrystalline material of the passive films consists of the oxides $\text{Fe}_3\text{O}_4$ and $\gamma - \text{Fe}_2\text{O}_3$. In this respect the structure passive films on the Cr-Mn stainless steel is similar to that on the Cr-Ni and chromium stainless steels [235–239].
Figure 4.32: Stationary values of anodic current density at $E_{HPP} = 0.6V$ versus exposure time at open circuit potential; Cr25Mn15 steel, acid (pH0.4) sulphate solution.
Figure 4.33: Potential decay curves of Cr25Mn15 steel after 1h HPP in acid (pH = 4) sulphate solution: exposure time at open circuit potential - 1min (curve 1); 2min (curve 2); 5min (curve 3); 15min (curve 4) and 60min (curve 5).
<table>
<thead>
<tr>
<th>Experimental values</th>
<th>Reference values</th>
<th>Reference values</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, Å</td>
<td>d, Å</td>
<td>d, Å</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄ [232]</td>
<td>γ - Fe₂O₃ (ASTM)</td>
</tr>
<tr>
<td>2.655</td>
<td>-</td>
<td>2.642</td>
</tr>
<tr>
<td>2.480</td>
<td>-</td>
<td>2.451</td>
</tr>
<tr>
<td>2.182</td>
<td>-</td>
<td>2.208</td>
</tr>
<tr>
<td>1.682</td>
<td>1.710</td>
<td>-</td>
</tr>
<tr>
<td>1.586</td>
<td>1.610</td>
<td>-</td>
</tr>
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<td>1.433</td>
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<td>1.340</td>
<td>1.326</td>
<td>-</td>
</tr>
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<td>1.281</td>
<td>1.279</td>
<td>-</td>
</tr>
<tr>
<td>1.190</td>
<td>1.210</td>
<td>-</td>
</tr>
<tr>
<td>1.071</td>
<td>1.092</td>
<td>-</td>
</tr>
<tr>
<td>1.019</td>
<td>1.049</td>
<td>-</td>
</tr>
<tr>
<td>0.948</td>
<td>0.940</td>
<td>-</td>
</tr>
<tr>
<td>0.903</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.877</td>
<td>0.880</td>
<td>-</td>
</tr>
<tr>
<td>0.850</td>
<td>0.859</td>
<td>-</td>
</tr>
<tr>
<td>0.782</td>
<td>0.814</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4: Experimental and reference values of d and corresponding Miller indices.
4.7 Conclusions

The passivation of stainless steels in bulk and under thin phase layers of acid sulphate solutions and the associated effects of cathodic reduction of oxygen in the anodic potential regions of the steels have been studied. The composition and structure of the passive films formed on stainless steel Cr25Mn15 were identified by Aüger electron spectroscopy and electron diffraction technique. The data obtained from the study revealed that:

i) the passivation of the stainless steels thin phase of acid sulphate solution is facilitated through the deceleration of the anodic process of ionisation of the metal and acceleration of the cathodic process of oxygen reduction;

ii) the critical self-passivation thickness, $\delta_{cr}$, may be adopted as one of the criteria for the evaluation of corrosion resistance of stainless steels in atmospheres polluted with sulphur dioxide;

iii) self-passivation of stainless steels in thin phase acid sulphate electrolyte layers produces high corrosion resistance in sulphur dioxide contaminated industrial atmospheres as well as in bulk electrolytes in which the steels corroded actively prior to self-passivation;

iv) corrosion-electrochemical tests of stainless steels in thin phase acid electrolyte layers can give valuable information on the durability of the steels in sulphur dioxide contaminated industrial atmospheres,
which cannot be obtained by conventional measurements in the bulk of the same electrolytes;

v) cathodic reaction of oxygen reduction increases passivity retention time of the stainless steels and this effect is especially significant if passivation potential is within the region of the cathodic loop on the anodic polarisation curve;

vi) considerable decrease in the influence of oxygen on the behaviour of the steels after passivation at a potential corresponding to the middle of the passive region is associated with a decline in the ability to reduce oxygen on the surface of steel as the extent of passivity increases;

vii) the presence of a cathodic loop region on the anodic polarisation curve of stainless steels may enable the implementation of anodic protection at potentials within the loop region. This provides a much longer after-effect of the protection of Cr25Mn15 and Cr17 steels compared with anodic protection at potentials corresponding to the middle of passive region; and

viii) the structure of the passive film on Cr-Mn stainless steel (Cr25Mn15) has a lattice of the face-centred cube and consists of oxides Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$, which is similar to those found on Cr-Ni and chromium stainless steels.
Chapter 5

Local anodic depassivation of stainless steels in bulk and under thin layers of neutral chloride solutions
5.1 Introduction

Pitting corrosion is one of the widespread and most destructive forms of metal corrosion. According to Kumada (cited from [240]), of the 315 cases of corrosion deterioration registered in one of the big Japanese companies for 11 years, 47.5% were caused by pitting corrosion, 31.6% by corrosion cracking, 12.7% by fatigue corrosion, 6.3% by intercrystalline corrosion, and 1.9% by general corrosion.

Pitting corrosion is an integral part of a number of the contemporary corrosion problems which include:

- use of chloride-containing heat-transfer agents, for instance sea or geothermal water;
- design of equipment for water desalination;
- construction of offshore platforms;
- production of economically alloyed corrosion-resistant materials;
- selection of conditions of electrochemical (anodic) protection;
- accelerated evaluation of metal resistance to pitting corrosion; and
- corrosion control in working conditions, etc.
Over the last decades the number of metal/solution systems known to be susceptible to pitting corrosion has increased significantly. It has become clear that this form of corrosion is not only typical for the intensively studied metals such as iron, zinc, aluminium and some stainless steels, but also for magnesium, nickel, cobalt, zirconium, niobium, copper and numerous stainless steels. Even the amorphous alloys which previously seemed to be completely resistant to pitting corrosion [241–243], according to data reported in [244], can be subjected to this form of corrosion attack.

In general, it has been established that:

(a) some anions, given that their concentrations in the solution exceed a critical value, are responsible for the local anodic depassivation (break of passivity); and

(b) pitting corrosion occurs when the potential of Q metal (due to the action of some oxidisers or due to anodic polarisation) exceeds a critical value (so called breakdown potential).

In practice, various chemical and electrochemical methods of accelerated determination of pitting corrosion resistance of stainless steels are used. These methods of testing for pitting corrosion can indicate the resistance of a steel in a given corrosive medium, or the relative corrosiveness of different media to the same steel.

The chemical methods are based on the use of solutions containing both an activator (usually Cl⁻ ions) and an oxidising agent (Fe³⁺ ions, etc.). For this reason these methods cannot predict the pitting corrosion resistance of steels
in process or natural corrosive media which differ in composition to the test solutions. Nevertheless, it is possible to determine the relative corrosion resistance characteristics by the chemical methods, e.g.:

- by comparing different brands of stainless steels or different batches of the same brand;

- by preliminary screening to obtain the best experimental compositions in developing new steels; and

- by investigating the effect of smelting technology, heat and mechanical treatments, methods of welding and surface finishing, etc. on pitting corrosion resistance.

The electrochemical methods usually involve the determination of the corrosion-electrochemical characteristics of a given stainless steel in a given corrosive medium. These characteristics known as the boundary potentials for pitting corrosion have been briefly described in section 2.4. In this chapter, the electrochemical accelerated testing of stainless steels for resistance to pitting corrosion and the results of the measurements of the boundary potentials for pitting corrosion of different stainless steels in bulk and under thin layers of neutral chloride solutions are discussed.
5.2 Electrochemical accelerated tests for the evaluation of stainless steels resistance to pitting corrosion

As it was reported previously [69, 88] the accelerated electrochemical evaluation of stainless steels resistance to pitting corrosion can be based on the measurement of three boundary potentials: the basic and two supplementary potentials. The basic boundary potential between the regions of stable passivity and pitting corrosion is the minimal galvanostatic potential of pitting corrosion ($E_{\text{pit}}^{\text{min}}$). The value of $E_{\text{pit}}^{\text{min}}$ is equal to the limit of change in electrode potential (Figure 5.1) at the lowest anodic current density ($i_{\text{min}}$) which provides stable functioning of the pits initiated on the very early stage of the polarisation.

This potential may be considered as a stationary characteristic of the corrosion system which is dependent on the physical and chemical parameters of the metal and the test solution. The experimental values of the $E_{\text{pit}}^{\text{min}}$ do not depend on the original condition of the metal surface and on the extent of the pit development. Due to the possible dependence of $E_{\text{pit}}^{\text{min}}$ on the current density of the anodic galvanostatic polarisation, a preliminary determination of $i_{\text{min}}$ is necessary.

The two supplementary characteristics are the potential of pit formation (breakdown of the passive film), $E_{\text{br}}$, and the pit repassivation potential, ($E_{\text{rp}}$). These correspond to the lowest potentials at which pits may originate with an increase in potential ($E_{\text{br}}$) and may still develop with a decrease in it ($E_{\text{rp}}$). These two potentials were determined by the method of reversible anodic potentiodynamic polarisation under controlled measurement conditions (Figure 5.2). The simple method of maintaining a constant
Figure 5.1: Typical potential-time response for Cr18Ni10Ti steel under galvanostatic polarisation. Anodic current density $i_a = 150 \mu \text{Acm}^{-2}$; 0.1M NaCl solution.
maximal anodic current density \( i_{\text{max}} \), reached during the anodic polarisation when measuring \( E_{\text{rp}} \) from the reverse anodic curve, provides the best reproducibility of the measured values. In this study the value of \( i_{\text{max}} = 10^3 \mu \text{Acm}^{-2} \) was maintained.

The quasi-stationary values of the breakdown potential \( E_{\text{br}} \) and repassivation potential \( E_{\text{rp}} \) which are independent or less dependent on the potential scanning rate \( R \) may be obtained at certain \( R \) range such as 0.3–5.0Vh\(^{-1}\) [192, 245, 246]. An unnecessary reduction in \( R \) increases the time required for the experiment but may not increase the reproducibility of the data.

The boundary potentials which characterise the anodic processes occurring in pitting corrosion are useful theoretical criteria. However from practical viewpoint, probability \( W_{\text{pit}} \) of appearance of stable functioning pits, which depends on kinetics of both anodic and cathodic reactions, is more important. In this respect the difference between the corrosion potential \( E_{\text{cor}} \) and the boundary potentials of pitting corrosion becomes significant [191, 247–249]. At first approximation \( W_{\text{pit}} \) is determined not by the value of \( E_{\text{pit}}^{\min} \) but by the difference \( \Delta E_{\text{pit}}^{\min} = E_{\text{pit}}^{\min} - E_{\text{cor}} \). This relationship may be referred to as the basis for pitting resistance and, hence, it follows that the greater the \( \Delta E_{\text{pit}}^{\min} \), the lower the \( W_{\text{pit}} \). Accordingly, the relationships \( \Delta E_{\text{br}} = E_{\text{br}} - E_{\text{cor}} \) and \( \Delta E_{\text{rp}} = E_{\text{rp}} - E_{\text{cor}} \) may serve as supplementary characteristics for establishing the resistance to pitting corrosion. The validity of this approach can be supported by the fact that most methods of protection from pitting corrosion are based on the increase in \( \Delta E \). This is accomplished either as a result of an increase in the boundary potentials or as a result of a reduction
Figure 5.2: Anodic potentiodynamic (1.44Vh⁻¹) polarisation (direct and reverse) curves of Cr18Ni10Ti steel in (1) bulk and (2) thin (δ = 50μm) layer of 0.1M NaCl solution.
in the corrosion potential of the metal (decreasing the rate of the cathodic reaction by different ways, or electrochemical protection).

The corrosion potentials \( E_{\text{cor}} \) of some stainless steels are less reproducible in neutral chloride solutions, and this can affect the evaluation of the resistance to pitting corrosion. Chemical pre-treatment of the electrode surface prior to commencement of the measurements can be useful in improving the reproducibility of \( E_{\text{cor}} \) without affecting the boundary potentials. The following simple chemical treatment method has been used on the specimen surface in this work: etching in 50% \( \text{H}_2\text{SO}_4 \) solution at room temperature for 7–10 minutes, followed by thorough washing of the specimen. The corrosion potentials obtained for two stainless steels in 0.5M \( \text{NaCl} \) with and without the chemical pre-treatment are given in Table 5.1. The results show that the pre-treatment reduces the values of variance \( S^2 \), which is a measure of the spread of the experimental results about their mean and, therefore, improves the reproducibility of the corrosion potential measurements. The pre-treatment did not affect the boundary potentials of the two steels used in this experiment.
Table 5.1: Corrosion potentials of stainless steels in 0.5M NaCl obtained without (A) and with (B) preliminary etching in 50% H₂SO₄.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Specimen number</th>
<th>A</th>
<th>B</th>
<th>S²</th>
<th>S²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr18Ni9Ti</td>
<td>1</td>
<td>0.181</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.139</td>
<td>0.142</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.150</td>
<td>0.121</td>
<td>0.00170</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.160</td>
<td>0.166</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.070</td>
<td>0.165</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr17Ni12Mo2Ti</td>
<td>1</td>
<td>0.108</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.108</td>
<td>0.185</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.112</td>
<td>0.184</td>
<td>0.00094</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.132</td>
<td>0.159</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.180</td>
<td>0.165</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3 Electrochemical screening of the resistance of Cr18Ni20 type stainless steels to pitting corrosion

The use of ΔE criteria as a basis for assessing the resistance of Cr18Ni20 type stainless steels to pitting corrosion in accelerated tests was investigated in this study. The tests were carried out in the following solutions:

1. 0.5M NaCl, 25°C;
2. 0.3gL⁻¹ Na₂SO₄ + 0.4gL⁻¹ NaCl, 25°C; and
3. 0.5M NaCl, 50°C.
The first solution was used as a simulated sea water and is very similar to the 3% (wt) NaCl widely used in different corrosion tests. The second solution is used as a simulated circulating water polluted with chloride. The third solution is recommended for the tests of stainless steels with an enhanced resistance to pitting corrosion, as is the case for Cr18Ni20 type steels.

The minimal galvanostatic potentials for the pitting corrosion $E_{\text{pmin}}^{\text{pit}}$ of the steels were determined by the application of an anodic polarisation current density $i = 150 \mu \text{Acm}^{-2}$. The breakdown potential $E_{\text{br}}$ and repassivation potential $E_{\text{rp}}$ were determined from the reversible anodic potentiodynamic polarisation curves recorded at $R = 1.44 \text{Vh}^{-1}$. Prior to the commencement of the experiments all specimens were treated chemically as described in section 5.2. The values of the boundary potentials and the $\Delta E$ criteria for resistance to pitting corrosion, obtained by averaging of five or more parallel experimental results, are given in the Tables 5.2–5.4.

**Table 5.2:** Boundary potentials and $\Delta E$ criteria for resistance to pitting corrosion; Cr18Ni20 type stainless steels, 0.5M NaCl, 25°C.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$E_{\text{cor}}, V$</th>
<th>$E_{\text{pmin}}^{\text{pit}}, V$</th>
<th>$E_{\text{br}}, V$</th>
<th>$E_{\text{rp}}, V$</th>
<th>$\Delta E_{\text{pmin}}^{\text{pit}} = E_{\text{pmin}}^{\text{pit}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{br}} = E_{\text{br}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{rp}} = E_{\text{rp}} - E_{\text{cor}}, V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr18Ni20</td>
<td>0.030</td>
<td>0.177</td>
<td>0.417</td>
<td>0.045</td>
<td>0.147</td>
<td>0.387</td>
<td>0.015</td>
</tr>
<tr>
<td>Cr18Ni20Si3</td>
<td>0.046</td>
<td>0.082</td>
<td>0.475</td>
<td>0.040</td>
<td>0.036</td>
<td>0.429</td>
<td>-0.006</td>
</tr>
<tr>
<td>Cr18Ni20Cu3</td>
<td>0.080</td>
<td>0.204</td>
<td>0.492</td>
<td>0.225</td>
<td>0.124</td>
<td>0.412</td>
<td>0.145</td>
</tr>
<tr>
<td>Cr18Ni20Nb</td>
<td>-0.180</td>
<td>-</td>
<td>0.342</td>
<td>-0.062</td>
<td>-</td>
<td>0.522</td>
<td>0.242</td>
</tr>
<tr>
<td>Cr18Ni20Mo3</td>
<td>-0.220</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.3: Boundary potentials and $\Delta E$ criteria for resistance to pitting corrosion; Cr18Ni20 type stainless steels, 0.3gL$^{-1}$ Na$_2$SO$_4$ + 0.4gL$^{-1}$ NaCl, 25°C.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$E_{\text{cor}}, V$</th>
<th>$E_{\text{min, pit}}, V$</th>
<th>$E_{\text{br}}, V$</th>
<th>$E_{\text{rp}}, V$</th>
<th>$\Delta E_{\text{min, pit}} = E_{\text{min, pit}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{br}} = E_{\text{br}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{rp}} = E_{\text{rp}} - E_{\text{cor}}, V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr18Ni20</td>
<td>0.068</td>
<td>0.295</td>
<td>1.033</td>
<td>0.183</td>
<td>0.227</td>
<td>0.965</td>
<td>0.115</td>
</tr>
<tr>
<td>Cr18Ni20Si3</td>
<td>0.150</td>
<td>0.193</td>
<td>0.577</td>
<td>0.018</td>
<td>0.043</td>
<td>0.427</td>
<td>-0.132</td>
</tr>
<tr>
<td>Cr18Ni20Cu3</td>
<td>0.140</td>
<td>0.332</td>
<td>0.492</td>
<td>0.256</td>
<td>0.192</td>
<td>0.352</td>
<td>0.116</td>
</tr>
<tr>
<td>Cr18Ni20Nb</td>
<td>0.140</td>
<td>0.272</td>
<td>0.650</td>
<td>0.018</td>
<td>0.137</td>
<td>0.510</td>
<td>-0.122</td>
</tr>
<tr>
<td>Cr18Ni20Mo3</td>
<td>-0.100</td>
<td>0.313</td>
<td>1.000</td>
<td>0.100</td>
<td>0.413</td>
<td>1.100</td>
<td>0.200</td>
</tr>
</tbody>
</table>

Table 5.4: Boundary potentials and $\Delta E$ criteria for resistance to pitting corrosion; Cr18Ni20 type stainless steels, 0.5M NaCl, 50°C.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$E_{\text{cor}}, V$</th>
<th>$E_{\text{min, pit}}, V$</th>
<th>$E_{\text{br}}, V$</th>
<th>$E_{\text{rp}}, V$</th>
<th>$\Delta E_{\text{min, pit}} = E_{\text{min, pit}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{br}} = E_{\text{br}} - E_{\text{cor}}, V$</th>
<th>$\Delta E_{\text{rp}} = E_{\text{rp}} - E_{\text{cor}}, V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr18Ni20</td>
<td>-0.062</td>
<td>0.075</td>
<td>0.311</td>
<td>0.134</td>
<td>0.137</td>
<td>0.373</td>
<td>0.199</td>
</tr>
<tr>
<td>Cr18Ni20Si3</td>
<td>-0.150</td>
<td>0.035</td>
<td>0.292</td>
<td>0.055</td>
<td>0.185</td>
<td>0.442</td>
<td>0.205</td>
</tr>
<tr>
<td>Cr18Ni20Cu3</td>
<td>0.146</td>
<td>0.157</td>
<td>0.393</td>
<td>0.168</td>
<td>0.011</td>
<td>0.247</td>
<td>0.022</td>
</tr>
<tr>
<td>Cr18Ni20Nb</td>
<td>-0.190</td>
<td>0.143</td>
<td>0.291</td>
<td>0.050</td>
<td>0.333</td>
<td>0.481</td>
<td>0.240</td>
</tr>
<tr>
<td>Cr18Ni20Mo3</td>
<td>-0.225</td>
<td>0.176</td>
<td>0.625</td>
<td>0.375</td>
<td>0.401</td>
<td>0.850</td>
<td>0.600</td>
</tr>
</tbody>
</table>

A comparison of the data given in Tables 5.2–5.3 indicates that the steels can be ranked with respect to their resistance to pitting corrosion in the test solutions as follows:
Solution Number 1; 0.5M NaCl, 25°C according to

\[ \Delta E_{\text{pit}}^{\text{min}} \quad \text{Cr18Ni20Si3} < \text{Cr18Ni20Cu3} \leq \text{Cr18Ni20} \]

\[ \Delta E_{\text{br}} \quad \text{Cr18Ni20Si3} < \text{Cr18Ni20} \leq \text{Cr18Ni20Cu3} < \text{Cr18Ni20Nb} \]

\[ \Delta E_{\text{rp}} \quad \text{Cr18Ni20Si3} < \text{Cr18Ni20} < \text{Cr18Ni20Cu3} < \text{Cr18Ni20Nb} \]

Solution Number 2; 0.3gL\(^{-1}\)Na\(_2\)SO\(_4\) + 0.4gL\(^{-1}\)NaCl, 25°C according to

\[ \Delta E_{\text{pit}}^{\text{min}} \quad \text{Cr18Ni20Si3} < \text{Cr18Ni20Nb} < \text{Cr18Ni20Cu3} \leq \text{Cr18Ni20} < \text{Cr18Ni20Mo3} \]

\[ \Delta E_{\text{br}} \quad \text{Cr18Ni20Cu3} < \text{Cr18Ni20Si3} < \text{Cr18Ni20Nb} < \text{Cr18Ni20} < \text{Cr18Ni20Mo3} \]

\[ \Delta E_{\text{rp}} \quad \text{Cr18Ni20Si3} \leq \text{Cr18Ni20Nb} < \text{Cr18Ni20} \leq \text{Cr18Ni20Cu3} < \text{Cr18Ni20Mo3} \]

Solution Number 3; 0.5M NaCl, 50°C according to

\[ \Delta E_{\text{pit}}^{\text{min}} \quad \text{Cr18Ni20Cu3} < \text{Cr18Ni20} < \text{Cr18Ni20Si3} < \text{Cr18Ni20Nb} < \text{Cr18Ni20Mo3} \]

\[ \Delta E_{\text{br}} \quad \text{Cr18Ni20Cu3} < \text{Cr18Ni20} < \text{Cr18Ni20Si3} < \text{Cr18Ni20Nb} < \text{Cr18Ni20Mo3} \]

\[ \Delta E_{\text{rp}} \quad \text{Cr18Ni20Cu3} < \text{Cr18Ni20} \leq \text{Cr18Ni20Si3} < \text{Cr18Ni20Nb} < \text{Cr18Ni20Mo3} \]
Analysis of the data shows that the first solution (0.5M NaCl, 25°C) cannot be used for the accelerated electrochemical evaluation of the resistance of Cr18Ni20 type stainless steels because some of the steels do not activate in the solution. All the stainless steels undergo activation in the second and third solutions, but preference was given to the third solution (0.5M NaCl, 50°C) because of the better consistency of the experimental results.

5.4 Boundary potentials for pitting corrosion of stainless steels in bulk and under thin layers of neutral chloride solutions

The measurement of the boundary potentials for pitting corrosion in bulk and under thin layers of chloride solutions were carried out for the Cr-Ni and Cr-Mn stainless steels.

The corrosion potential $E_{cor}$, breakdown potential $E_{br}$, repassivation potential $E_{rp}$ and critical current density for the pits formation $i_{pit}^{cr}$ determined in the galvanodynamic mode (72μAcm$^{-2}$h$^{-1}$) for stainless steel Cr22Ni10Ti in bulk and under thin layers (25–300μm) of neutral chloride solutions (0.001–4.0M NaCl) are given in Table 5.5.

The data given in Table 5.5 indicate that the steel was initially passive over a wide range of sodium chloride concentrations both in bulk and under thin layers of the electrolyte. However the characteristic pitting corrosion potentials were the same for the different thicknesses of the electrolyte layer.
Table 5.5: Electrochemical characteristics of pitting corrosion of steel Cr22Ni10Ti in bulk and under thin (25-300μm) electrolyte layers.

<table>
<thead>
<tr>
<th>Solution NaCl, M</th>
<th>$E_{\text{cor}}, \text{V}$</th>
<th>$E_{\text{br}}, \text{V}$</th>
<th>$E_{\text{RP}}, \text{V}$</th>
<th>$\Delta E_{\text{br}} = \frac{E_{\text{br}} - E_{\text{cor}}}{V}$</th>
<th>$\Delta E_{\text{RP}} = \frac{E_{\text{RP}} - E_{\text{cor}}}{V}$</th>
<th>$i_{\text{cr}} \mu\text{Acm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>+0.23</td>
<td>+1.20</td>
<td>+0.75</td>
<td>+0.97</td>
<td>+0.52</td>
<td>-</td>
</tr>
<tr>
<td>0.010</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
</tr>
<tr>
<td>0.100</td>
<td>+0.05</td>
<td>+0.53</td>
<td>+0.37</td>
<td>+0.48</td>
<td>+0.32</td>
<td>6.0</td>
</tr>
<tr>
<td>4.000</td>
<td>-0.10</td>
<td>+0.33</td>
<td>+0.12</td>
<td>+0.43</td>
<td>+0.22</td>
<td>-</td>
</tr>
</tbody>
</table>

The independence of the steel corrosion potential on the thickness of the electrolyte layer indicates that an increase in the access of oxygen towards the metal surface under the thin layer conditions does not affect the potential over the range of concentrations used in the experiments. It is obvious that the corrosion potential of the steel is located in the kinetic region of oxygen reduction more positive than the diffusion region. At the same time the decrease of the electrolyte layer thickness results in an increase of the limiting diffusion current of oxygen reduction (Figures 5.3 and 5.4), and this observation is consistent with the data revealed by Rozenfeld [101].

The approximately Tafel behaviour of the cathodic polarisation curves of the steel obtained in bulk and under 50μm layer of 0.1M NaCl solution observed at $i \leq 30\mu\text{Acm}^{-2}$ and their similarity indicates an absence of a significant IR-error in this range of polarising currents. This observation supports the use of the theoretical approach for the ohmic voltage drop evaluation described in section 3.2, since at $i = 30\mu\text{Acm}^{-2}$, $A = 0.1\text{cm}^2$ and $\delta = 50\mu\text{m}$ the calculation of IR in 0.1M NaCl solution provides the value of only 15mV. The similar estimations of the IR-errors accompanied with the measurements of the
Figure 5.3: Cathodic potentiodynamic (3.6Vh⁻¹) polarisation curves of Cr18Ni10Ti steel in: (1) bulk and (2) thin (δ ≥ 50µm) layer of 0.1M NaCl solution.
Figure 5.4: Limiting diffusion current density of oxygen reduction versus thickness of electrolyte layer; Cr18Ni10Ti, 0.1M NaCl solution.
breakdown \( E_{br} \) and repassivation \( E_{rp} \) potentials even in the case of the lowest thickness (25\( \mu \)m) of the most diluted solution (0.001M NaCl) provide the negligible error values (~ 2mV). This extremely low IR-error is evidently associated with small magnitudes of polarising currents (~ 0.3\( \mu \)A) which correspond to these potentials.

The independence of the characteristic potentials of pitting corrosion of stainless steel Cr22Ni10Ti in neutral sodium chloride solutions on the thickness of the electrolyte layer indicates that the basic peculiarities of the corrosion in thin layers, such as easy access of oxygen to the metal surface and possible easy saturation of the limited amount of electrolyte involved with the corrosion products, by no means affect the processes of the formation and repassivation of the atmospheric pits on the surface of the steel.

The boundary potentials for pitting corrosion in bulk, and under thin layer \( (\delta = 50\mu m) \) of 0.1M NaCl solution have been determined for a number of stainless steels with different corrosion resistance. The experimental results after ohmic voltage drop correction (which can be of significance only during the measurements of \( E_{pit}^{min} \)) are given in Table 5.6.

The data given in Table 5.6 demonstrate that the independence of the boundary potentials of pitting corrosion on the thickness of neutral chloride solution layer is typical for all the stainless steels. However, as can be seen from Table 5.5 and Table 5.6, over the ranges of concentrations and thicknesses of the sodium chloride electrolytes the corrosion potentials of the steels are more negative than all the boundary potentials. Only for Cr-Mn steels \( E_{rp} < E_{cor} \Delta E_{pit}^{min} \) and \( E_{br} > 0 \). With such relationship between
the corrosion and the boundary potentials, pitting corrosion of the stainless steel cannot occur without anodic polarisation in bulk and under thin layers of the unpolluted neutral chloride solutions. Thus, the pitting corrosion of the steels in atmospheric conditions can occur only as a result of some additional factors such as the presence in the atmosphere of sulphur dioxide and other corrosive agents or a deposition of dust, containing electropositive metals, etc. According to Johnson [148], the simultaneous action of sulphur dioxide and chlorides is responsible for pitting corrosion of stainless steels in the atmosphere.

**Table 5.6:** Boundary potentials for pitting corrosion of stainless steels studied in bulk and under thin layer ($\delta = 50\mu$m) of 0.1M NaCl solutions.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$C_{NaCl}$ M</th>
<th>$E_{cor}$ V</th>
<th>$E_{pp}$ V</th>
<th>$E_{\text{pit}}$ V</th>
<th>$\Delta E_{\text{pp}}$ =</th>
<th>$\Delta E_{\text{pit}}$ =</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr14Mn15</td>
<td>0.10</td>
<td>0.05</td>
<td>0.25</td>
<td>&lt;0.05</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr25Mn15</td>
<td>0.10</td>
<td>0.05</td>
<td>0.30</td>
<td>&lt;0.05</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>Cr18Ni10Ti</td>
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<tr>
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<td>0.55</td>
<td>0.37</td>
<td>0.37</td>
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</tbody>
</table>

As demonstrated in the data given in Table 5.6, the electrochemical criteria proposed for the evaluation of the resistance of stainless steels to pitting corrosion in bulk electrolytes can also be successfully used in the study of corrosion under thin electrolyte layers. Moreover, with respect to the electrochemical criteria of resistance to pitting corrosion, the steels studied
can be ranked equally both in bulk and under thin layers of the neutral chloride solution as follows:

\[ \text{Cr14Mn15} < \text{Cr25Mn15} < (\text{Cr18Ni10Ti}, \text{Cr22Ni10Ti}) \]

Therefore, the ease of oxygen access through thin electrolyte layers does not affect the relative resistance of the stainless steels to pitting corrosion in neutral chloride solutions and the processes of formation of and repassivation of pits on the steels under thin layers proceed with no visible difference. Thus, for the accelerated electrochemical evaluation of the relative resistance of stainless steels to pitting corrosion under atmospheric conditions there is no need to use the technique of electrochemical measurements in thin layers of electrolytes because the conventional method of the measurements in bulk electrolytes provides the same information.

In section 1.4, it was indicated that the corrosion conditions in thin electrolyte layers differ from those in the bulk electrolytes due to the difficulties in removing corrosion products from the reaction zone. Resulting accumulation and subsequent hydrolysis of the corrosion products can decrease pH of the test solution. The less the thickness of electrolyte layer the more significant the corresponding decrease in pH may be expected. Thus, the conditions of corrosion under thin layers may be considered analogous to conditions of crevice corrosion. However, the observed independence of all the measured electrochemical characteristics of pitting corrosion of stainless steels on the thickness of the layers is inconsistent with this proposition. Meanwhile during the formation of crevice in the employed experimental conditions the measured characteristics undergo a
significant change. The crevice was formed with a glass bead pressed to the surface of the electrode (Cr18Ni10Ti) covered with the layer of 0.1M NaCl solution (thickness 100μm). Anodic reversible potentiodynamic polarisation curves obtained with the electrode in presence of this artificially created crevice (Figure 5.5) show a substantial shift of the $E_{\text{cor}}$, $E_{\text{rp}}$ and $E_{\text{br}}$ into the negative direction. The magnitude of the shift depends on the diameter of the bead used, and increases with an increase in the bead size, which is in agreement with the principles of crevice corrosion.

5.5 Conclusions

The electrochemical criteria for the assessment of the resistance of stainless steels to pitting corrosion in neutral chloride solutions, as well as the methods for their determination and a number of approaches for increasing the reproducibility of the measured values are discussed in this chapter.

(i) The application of $\Delta E$ criteria as the basis for evaluating the relative resistance of stainless steels to pitting corrosion in bulk and under thin layers of the chloride solutions has been demonstrated.

(ii) The boundary potentials for pitting corrosion do not depend on thickness of the electrolyte layer, and it was concluded that the peculiarities of the corrosion in thin layers do not affect processes of local anodic depassivation and repassivation of the stainless steels. Thus, with respect to the electrochemical criteria of resistance, the steels can be ranked equally both in bulk and under thin layers of the neutral chloride solutions.
Figure 5.5: Anodic potentiodynamic (1.44Vh$^{-1}$) polarisation (direct and reverse) curves of Cr18Ni10Ti under thin ($\delta = 100\mu m$) layer of 0.1M NaCl solution: 1 - no crevice; 2 - bead's diameter 4.0mm; 3 - bead's diameter - 7.9mm.
(iii) Accelerated evaluation of the relative resistance of the stainless steels to pitting corrosion under atmospheric conditions, where the formation of neutral chloride superficial electrolytes is expected, may be based on the conventional measurements in bulk electrolytes.

(iv) The correlation of the corrosion potential and the boundary potentials of the stainless steels leads to the conclusion that the steels cannot undergo pitting corrosion in clean seaside or marine atmospheres, unless they are polarised anodically. Subsequently a proposition is made that the atmospheric pits on the stainless steels result from the presence of some industrial pollutants, such as sulphur dioxide, and/or from presence of some electropositive metals in the depositions on metal surface.
Chapter 6

Kinetics of the pitting corrosion of stainless steels
6.1 Introduction

Pitting corrosion, being a localised attack at specific areas of metal surface, results in the formation of pits. The size of the resulting pits depend on physical and chemical characteristics of the metal and test solution, as well as on the conditions of their initiation and development. The rates of dissolution of a metal at the specific areas can exceed rates of dissolution of the surrounding metal surface by up to $10^3$--$10^6$ times [240].

From a formal viewpoint, pits develop because some layer either protects surrounding metal surface against corrosion (Figure 6.1 (a)) or prevents highly corrosive solution inside a pit from mixing with less corrosive solution of bulk composition (Figure 6.1 (b)). The third "mixed" case is also possible (Figure 6.1 (c)). Pitting corrosion may occur if there are pores or discontinuities in the precipitations of metal dissolution products which are more cathodic than the substrate [250--256] as shown in Figure 6.1 (b). For the stainless steels considered in this study, the pits where a passive film acts as a protective layer are typical (Figure 6.1; (a) and (c)).

If the protective layer surrounding a pit does not possess electronic conductivity (e.g. salt precipitation), the cathodic reaction occurs inside the pit. Such an "autonomous" pit usually grows relatively slowly. However, the growth rate can increase significantly in the presence of anodic stray currents or due to appearance of an extensive galvanic macrocell with the anodic site localised in the pit. In the case of stainless steels a pit is surrounded with a passive film which possesses fairly high electronic conductivity and the most typical and dangerous type of the "conjugate" pit
Figure 6.1: Typical forms of pits (cited from [240])

a - open, with a protective layer on surrounding surface;
b - closed, with no protective layer on surrounding surface;
c - closed, with a protective layer on surrounding surface;
1 - metal; 2 - protective layer; 3 - porous precipitations of corrosion product;
4 - cap over pit; 5 - holes in the cap.
takes place, when the anodic process is localised inside the pit while the
cathodic process proceeds on the surrounding passive film.

The principle of equivalency between anodic polarisation and reduction of
oxidisers (88, 204, 205] may be applied to pitting corrosion. Exceptions to the
rule are associated with specific character of some oxidisers, especially if they,
like chromates [204], increase the protective properties of passive film.
However, the peculiarities of pitting corrosion provide a different
nonequivalence of potentials imposed by (i) anodic polarisation and, (ii) by
reduction of oxidisers. In the latter case, the surface area of the specimen is
of significance. For example the chemical tests of a stainless steel in
1.2M NaCl + 3M H₂O₂ [257] did not produce notable pits when a small
(~ 1.2cm²) sample was used. However, application of the same conditions to
a big (~ 11cm²) sample resulted in the formation of stable functioning pits.
The experimental data may be explained in terms of the fact that the every
"conjugate" pit functioning in conditions of self-dissolution (with no anodic
polarisation) needs a definite cathodic area able to provide the necessary
cathodic current [258] to support anodic process inside the pit. Also, the rate
of the anodic process inside a stable pit should not be less than some critical
value.

It is known [259] that out of a large number of pits formed on stainless steels
upon anodic polarisation in chloride solutions, only a small part grows,
while the others become repassivated. In connection with this and other
problems of pitting corrosion, various theories [240, 260–262] ascribe great
importance to the so-called critical dimension (the critical radius r_{cr}) of the
pits, i.e., the minimal dimension which has to be attained for the nucleus to
turn into an active (stable functioning) pit. In some cases it is also necessary
to know \( r_{cr} \) so that the average radius (\( r_{av} \)) of the pits and kinetics of their development in time can be correctly determined. Such calculations should contain solely the active pits with \( r > r_{cr} \) while repassivated, "dead" pits should be disregarded.

In this chapter, the results of the determination of the critical dimension of pits on stainless steels, as well as the kinetic data of pits' development on Cr-Ni and Cr-Mn stainless steels in potentiostatic and galvanostatic conditions, are presented.

6.2 Determination of critical dimension of pit on stainless steel

Experimental measurements of \( r_{cr} \) are rather difficult owing to the fact that both the incidence and the size of the pits are statistical quantities. For instance, Hisamatsu [260] carried out measurements in the zone of potentials that were higher than the repassivation potential \( E_{rp} \) and the smallest radius of such a pit which did not become repassivated when the potential was slightly reduced was assumed to be \( r_{cr} \). However, this method has no statistical basis because of the small number of pits studied.

In the present work we determined \( r_{cr} \) with the aid of the method of an automatic quantitative metallography which was used by Štefec et al. [82–84] in a study of the size distribution of the pits' mouths. Cylindrical specimens of Cr18Ni10Ti steel mounted into acrylic resin with working surface area (flat end of the cylinder) of 0.1cm\(^2\) were used. The electrodes were anodically polarised in the 1.4M and 0.1M NaCl solutions using the galvanostatic mode with a polarisation current density, \( i_a = 3 \times 10^3 \mu A cm^{-2} \).
The technique of statistical sampling of small repassivating pits with radii from 0.15 to 8μm is described in section 2.5. The image analysing computer divided all repassivating pits in the mentioned range of radii into fractions in steps of 0.6μm, with the subsequent counting of the number of pits in each fraction, separately. The kinetics of development of active pits with \( r > r_{cr} \) was studied with the aid of the ordinary metallographic microscope at \( \times 270 \) magnification.

According to the data obtained the number of the repassivating pits \( n \) increases linearly with time \( (t \geq 60\text{s}) \), while the rate of nucleation \( \frac{\partial n_{rp}}{\partial t} = K_r \) is the lower as the mean radius of pits in the given fraction becomes larger (Figure 6.2, curves 1–4). Conversely, the number of active pits \( n_{ap} \) under the same conditions is constant (Figure 6.2, curve 5). The value of \( K \) decreases exponentially with increasing pit radius \( r \) (Figure 6.3):

\[
K_r = K_0e^{-\gamma r}
\]  \hspace{1cm} (6.1)

where for the 1.4M and 0.1M NaCl solutions values of \( K_0 \) are equal to \( 3.5 \cdot 10^6 \) and \( 0.7 \cdot 10^6\text{m}^{-2}\text{s}^{-1} \), and values of \( \gamma \) are equal to 1.59 and 1.24μm\(^{-1}\), respectively. The number of repassivated pits with the given radius \( r \), generated within time \( t \), is equal to

\[
n_{rp} = K_r t = K_0e^{-\gamma rt}
\]  \hspace{1cm} (6.2)

Equation (6.2) makes it possible to plot a theoretical curve of the distribution of repassivated pits versus the radii at any instant \( t \) (\( t \geq 60\text{s} \) with the selected value of anodic current density). The theoretical curves have similar shapes as illustrated in Figure 6.4. It can be seen that the largest number of
Figure 6.2: Number of pits formed on Cr18Ni10Ti steel versus time of anodic galvanostatic polarisation \((i_a = 3 \cdot 10^3 \mu \text{Acm}^{-2})\) in 1.4M NaCl solution; mean radii of repassivated pits in \(\mu\text{m}\): 1 - 0.15; 2 - 0.61; 3 - 1.22; 4 - 1.84; active pits with \(r \geq 10\mu\text{m}\) - curve 5.
Figure 6.3: Rate of formation of repassivated pits versus radius; Cr18Ni10Ti, 1.4M NaCl, galvanostatic polarisation $i_a = 3 \cdot 10^3 \mu A cm^{-2}$. 
repassivating pits lies in the range 0.15–0.5μm: with increase in r, the value of \( n_{rp} \) drops abruptly as the \( K_r \) decreases (see equation (6.1)).

The number of active pits \( n_{ap} \) depends neither on their radii nor on time of the galvanostatic polarisation (for \( t \geq 60s \)), as expressed in Figure 6.4 by the straight lines parallel to the abscissa axis. The point of intersection of the lines of distribution of \( n_{rp} \) and \( n_{cp} \) corresponds to the critical radius of the pits \( r_{cr} \) which, as illustrated in Figure 6.4 for 1.4M and 0.1M NaCl within the experimental error is equal to 7–8μm. This value is in satisfactory agreement with the value \( r_{cr} = 10μm \) obtained by another method in [260] for stainless steel 304 in a solution of 0.5M \( \text{H}_2\text{SO}_4 \) + 0.5M NaCl. As illustrated in Figure 6.4, only a limited number of the repassivated pits, which is negligibly small in comparison with \( n_{rp} \) and small in comparison with \( n_{ap} \), can have a radius slightly exceeding the critical value.

Since the values of \( n_{ap} \) and \( i_a \) are known, the current per active pit \( I_{ap} \) can be calculated and from this the current density \( i_{cr} \) in a pit with radius \( r = r_{cr} \) (assuming for simplicity that the pit has a hemispherical shape) may be obtained. The corresponding computation provides the value \( i_{cr} = 4.5 \cdot 10^6 \mu \text{Acm}^{-2} \) which is in good agreement with the literature data [240] for the initial period of the pit's formation on stainless steels. It should be emphasised that as an active pit grows (while \( n_{ap} = \text{const} \)), the current density in it decreases approximately in inverse proportion to the square of its radius; for example with \( r = 30μm \) current density according to calculation amounts to \( 1.0 \cdot 10^5 \mu \text{Acm}^{-2} \). This value agrees with previous data [259] and confirms the conclusion that the mean current density at the period of growth of an active pit is relatively low [240].
Figure 6.4: Distribution of pits radii: curves 1 and 2 for repassivated pits are calculated by the equation (6.2) for 1.4M and 0.1M NaCl solutions respectively; • and ▲ are the respective experimental data; curves 1' (○) and 2' (△) represent number of active pits in the same solutions; current density of anodic galvanostatic polarisation $i_A = 3 \cdot 10^3 \mu\text{A cm}^{-2}$. 
In section 2.5, it was mentioned that the pits formed under experimental conditions in this study were often caped, and before the surface study, the caps were revealed by carefully grinding away a very fine surface layer of metal. The presence of caps on the pits makes it difficult to calculate the total critical concentration $C_{cr}$ of aggressive anions at the pit surface. According to other workers [260–262] the attainment of $C_{cr}$ particularly predetermines the transformation of a pit's nucleus into an active pit. However, assuming that the numerous holes in the pit cap enables, at a rough estimate, consideration of the pit as open, then the formula proposed by Hisamatsu [260] can be used:

$$C_{cr} = \frac{i_{cr}r_{cr}}{2FD} \quad (6.3)$$

Assuming that the mean valency of dissolving metal ion $z = 2$ and the mean diffusion coefficient of the metal in the electrolyte $D \approx 10^{-9} \text{m}^2\text{s}^{-1}$ the value $C_{cr} = 1.64\text{M}$ is obtained, which is in a good agreement with the value reported previously [260], viz., $C_{cr} = 1.8\text{M}$.

One of the confirmations that the pits described by distributions (1) and (2) in Figure 6.4 belong to the repassivating ones is the fact that their mean dimension $\bar{r}_{cr}$ is constant. Indeed from the equations (6.1) and (6.2) it follows that

$$\bar{r}_{rp} = \frac{\int_{0}^{r_{cr}} K_0 e^{-\gamma r} r dr}{\int_{0}^{r_{cr}} K_0 e^{-\gamma r} dr} \quad (6.4)$$

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After integration we obtain

\[ \bar{r}_{rp} = \frac{1 - e^{-\gamma r_{cr}}}{\gamma + e^{-\gamma r_{cr}} (r_{cr} + \gamma^{-1})} \approx \gamma \]  

(6.5)

i.e., the mean radius of the repassivating pits is equal to the characteristic parameter \( \gamma \) in equation (6.1) which determines the actual rate of decrease of the number of repassivating pits with increase in their radius. It is understandable that since the smallest pits are a dominating part of the repassivating pits, an increase in \( \gamma \) which leads to reduced rate of pit formation increases the mean dimension \( \bar{r}_{rp} \approx \gamma \) of the pits. The approximate constancy of the mean dimension of the repassivating pits with time was discovered empirically by Tomashov [263] in the study of the pitting corrosion of Cr18Ni14V2.5 in 0.5M FeCl₃ solutions.

6.3 **Formation and development of pits on stainless steels**

In section 5.4, it was shown that the electrochemical characteristics of pitting corrosion of stainless steels determined by potentiodynamic (\( E_{br} \) and \( E_{rp} \)), galvanostatic (\( E_{\text{pit}}^{\text{min}} \)) and galvanodynamic (\( t_{\text{pit}}^{\sigma} \)) polarisation do not depend on thickness of neutral chloride electrolyte layers. Meanwhile, the kinetics of both pit's formation and development do acquire some special features with the thinning of the electrolyte layers.

The processes of formation and development of pits under conditions of potentiostatic and galvanostatic polarisation were studied mainly on steel Cr18Ni10Ti. Some experiments were carried out with specimens made from
steel Cr25Mn15. Samples mounted in acrylic resin were used. The surfaces of the samples were studied with the use of the metallographic microscope. Pits located at the border with insulation and repassivated pits with the \( r < 10 \mu m \) were disregarded. During some of the potentiostatic experiments the imposed potential \( E_{\text{imp}} > E_{\text{br}} \) was applied abruptly after a preliminary passivation of the sample for 10 min at a potential between corrosion potential \( E_{\text{cor}} \) and repassivation potential \( E_{\text{rp}} \). Preliminary stabilisation of the passive film was also carried out prior to commencement of all the galvanostatic experiments.

When the electrode potential is shifted from \( E_{\text{cor}} \) to a constant under conditions of these experiments value \( E_{\text{imp}} \), which exceeds the breakdown potential \( E_{\text{br}} \) by \( \sim 30 \text{mV} \), the number of active pits generated under the potentiostatic polarisation gradually decrease with the reduction in thickness of the solution layer (Figure 6.5). The number in bulk and under the relatively thick (300 \( \mu m \)) layer of 0.1M NaCl solution is much larger than under the 150 \( \mu m \) and 50 \( \mu m \) layers, which is conditioned by the significant growth of the number of pits in time (at \( t \leq 600 \text{s} \)) for bulk solution and 300 \( \mu m \) layer while for 150 \( \mu m \) layer the number increases only slightly and for 50 \( \mu m \) layer it is constant (Figure 6.5, curves 1–4). If, however, prior to the shift of electrode potential from \( E_{\text{cor}} \) to \( E_{\text{imp}} \) the electrodes were passivated at a potential \( E_{\text{cor}} < E_{\text{pas}} < E_{\text{rp}} \), only the small number of pits independent of both thickness of electrolyte layer and time of polarisation was generated at \( E_{\text{imp}} \) (Figure 6.5, curves 1 and 4). Apparently, the protective properties of passive film on the surface of Cr18Ni10Ti stainless steel at \( E_{\text{cor}} \) are relatively low and, correspondingly, the film (in absence of the preliminary passivation) has a larger number of potential centres of pits nucleation, which determines the number of active pits generated on the steel under
Figure 6.5: Number of active pits formed on Cr18Ni10Ti steel versus time of potentiostatic polarisation in bulk and thin layers of 0.1M NaCl solution: — after initial passivation at $E_{\text{cor}} < E_{\text{pas}} < E_{\text{rp}}$; --- no preliminary passivation; 1 and 1' - bulk; 2 - 300μm; 3 - 150μm; 4 and 4' - 50μm.
conditions of potentiostatic polarisation at potentials exceeding the breakdown potential.

A small difference in the numbers of pits formed in the 50\(\mu\)m layer at \(E_{\text{imp}}\) with and without preliminary passivation (Figure 6.5, curves 1 and 4) is obvious. It can be assumed that in view of the migration and subsequent characteristic accumulation of Cl\(^-\) ions in pits [264–267] the number of stable functioning pits (\(r > 10\mu\)m) generated in the thin electrolyte layers, contrary to bulk solution, is limited by an exhaustion of the electrolyte with respect to Cl\(^-\) ions. The preliminary passivation reduces the number of sites capable of being the centres of pits' initiation significantly and becomes a dominating factor which determines the number of active pits even in bulk solution where the exhaustion with respect to Cl\(^-\) ions may only have a minor role.

At the potentiostatic polarisation of the preliminary passivated electrodes at \(E_{\text{imp}} > E_{\text{br}}\), the number of active pits generated in the 50\(\mu\)m layers of neutral chloride solutions (\(C_{\text{NaCl}} = 0.1M–1.4M\)) are constant in time (at least at \(t \leq 30\text{min}\)) and show only a slight dependence on concentration of the electrolytes (Figure 6.6, curves 1–3). In the bulk of the corresponding electrolytes, the number of pits is always larger than in 50\(\mu\)m layer (Figure 6.6, curves 1–3). The difference between these two numbers is small and constant in time for 0.1M solution, while for 0.35M and, especially, for 1.4M solution the difference is larger due to increase in \(n_{\text{ap}}\) for bulk solutions during the first 10min of the polarisation. It is apparent that the exhaustion of the electrolyte with respect to Cl\(^-\) ions, which restricts the number of active pits in 50\(\mu\)m layer of 1.0M NaCl solution, can affect the number of the pits in thin layers even at the higher chloride concentrations.
Figure 6.6: Number of active pits formed on the initially passivated steel Cr18Ni10Ti versus time of potentiostatic polarisation at $E_{imp} > E_{br}$; 1 and 1' - bulk and thin ($\delta = 50\mu m$) layer of 0.1M NaCl solution respectively; 2 and 2' - 0.35M NaCl; 3 and 3' - 1.4M NaCl.
The noted peculiarities of pits' generation process under conditions of potentiostatic polarisation in thin electrolyte layers may also affect the growth of the pits with time. The time dependences of the average values of depth (h) and radius (r) of the pits (for $t = 60s$) obtained on the Cr18Ni10Ti steel in 0.1M NaCl solution are presented in Figure 6.7. The character of the time dependences shows that the following power functions may represent the relation of average pit geometric sizes on polarisation time

$$h_{av} = k_h t^a \quad (6.6)$$

and

$$r_{av} = k_r t^b \quad (6.7)$$

where $k_h$, $k_r$, a and b are some empirical constants. For the various thicknesses of the electrolyte layers the magnitude $a = 0.46$, i.e. mean depth of pit in all cases increases with time according to the law $\sqrt{t}$. However, the magnitude of $b$ does depend on the layer thickness, decreasing with the thinning of the layers from 0.53 (bulk solution) to 0.33 ($\delta = 50\mu m$), e.g. at a transition from bulk to the 50$\mu m$ layer the law $\sqrt{t}$ for the time dependence of average radius of the active pits gradually is replaced with the law $3\sqrt{t}$. At $\delta = 300\mu m$ and 150$\mu m$ the values of $b$ are 0.48 and 0.43 respectively.

On differentiation of equations (6.6) and (6.7) with respect to time ($t$), the average rates of the active pit growth may be obtained. Thus the average rate of the pit deepening $\frac{dh_{av}}{dt}$ for all the layers thicknesses decreases with time according to the law $\sim t^{-\frac{1}{2}}$, while the average rate of increase of pit
Figure 6.7: Average depth and radius of active pit formed on Cr18Ni10Ti steel versus time of potentiostatic polarisation in 0.1M NaCl solution at $E_{imp} > E_{br}$: $h_{av}$; $r_{av}$; 1 - bulk; 2 - $\delta = 300\mu m$; 3 - $\delta = 150\mu m$; 4 - $\delta = 50\mu m$. 
radius $\frac{\partial r_{av}}{\partial t}$ in bulk solution and in relatively thick ($\delta = 300\mu m$) layers follows the same law. However, during the transition from bulk electrolyte into $50\mu m$ layer the rate drops, becoming proportional to $\sim t^{-\frac{2}{3}}$. Maximal sizes of the pits ($h_{max}$ and $r_{max}$) exceed the average ones only insignificantly and conform with the analogous laws.

The kinetics of the active pits development under conditions of potentiostatic polarisation at $E_{imp} > E_{br}$ after preliminary passivation both in bulk solution and in relatively thick layers results in a formation of pits with $r > h$. Reduction in the thickness of electrolyte layer leads to lower rates of pit growth with respect to their radii and, consequently, to the formation of pits with $r < h$.

The kinetics of formation and development of pits on Cr18Ni10Ti steel was studied under conditions of galvanostatic anodic polarisation. These conditions are closest to the natural conditions of self-dissolution, when the rate of a cathodic reaction, or, at a given rate of the cathodic reaction, the value of cathodic area determines anodic current in the "conjugate" pits. The resulting data show that upon galvanostatic polarisation the number of active pits depends only on the polarisation current density (Figure 6.8) and practically does not depend on:

- NaCl concentration;
- thickness of the electrolyte layer; and
- duration of polarisation (for $t > 60s$).
Figure 6.8: Number of active pits formed on Cr18Ni10Ti steel versus current density of anodic galvanostatic polarisation in 0.1M NaCl.
The independence of the number of the active pits, generated under galvanostatic conditions, from the polarisation time indicates that the average current density in the pits reduces with growth. Based on the results obtained in this study for the steel Cr18Ni10Ti in 0.1M NaCl ($\delta = 50\mu m$) at current densities of $1.5 \cdot 10^2$, $7.0 \cdot 10^2$, $1.0 \cdot 10^3$, and $3.0 \cdot 10^3 \mu A cm^{-2}$, the calculated (at an assumption on hemispherical shape of pits) current densities of dissolution in pits are $1.19 \cdot 10^5$, $1.78 \cdot 10^5$, $1.41 \cdot 10^5$, and $1.47 \cdot 10^5 \mu A cm^{-2}$, respectively (at polarisation time $t = 30 min$). These are obviously independent of the value of polarisation current and reveal a good agreement with the available literature data [87, 259, 268–270]. These results show that the period of the active pit development can be characterised with the relatively low values of current densities in pits ($\sim 10^5 \mu A cm^{-2}$), while for the period of the pits’ initiation significantly higher values of the current densities are typical ($10^7$–$10^8 \mu A cm^{-2}$ [240, 271]).

Time dependences of the average depth ($h_{cr}$) and radius ($r_{av}$) of pits developing under conditions of galvanostatic anodic polarisation can be described by equations (6.6) and (6.7). For the Cr18Ni10Ti stainless steel in 0.1M NaCl solution the parameters $a$ and $b$ practically do not depend on current density of polarisation ($1.5$–$3.0 \cdot 10^2 \mu A cm^{-2}$) and are equal to 0.3 and 0.15 respectively for both bulk solution and 50$\mu m$ layer. Meanwhile for the Cr-Mn stainless steel Cr25Mn15 at galvanostatic polarisation ($i = 1.5 \cdot 10^2 \mu A cm^{-2}$) the values $a$ and $b$ are significantly lower, 0.05 and 0.04 (0.1M NaCl), and 0.11 and 0.07 (0.01M NaCl) respectively. The reduction of the values $a$ and $b$ with increase in NaCl concentration was also observed for steel Cr18Ni10Ti. During the galvanostatic polarisation ($i = 3.0 \cdot 10^3 \mu A cm^{-2}$) in 0.35M and 1.4M NaCl solutions the $a$ and $b$ assume values 0.15 and 0.09, and 0.04 and 0.03 respectively. Thus, with an increase in the corrosivity of
solution (in an agreement with previous data on influence of temperature [240]) or with a decrease in corrosion resistance of steel the parameters a and b decrease in value. One of the reasons for the observed phenomenon may be due to a significant increase in number of the small repassivated pits, which are not taken into consideration at the $h_{av}$ and $r_{av}$ determination but may affect the kinetics of development of the stable functioning pits, reducing their part of the polarising anodic current.

The average sizes of pits grown in bulk solution and in thin ($\delta = 50\mu m$) layer under conditions of galvanostatic polarisation are approximately the same, whereas the maximal sizes which the pits develop in thin layer exceed the ones in bulk solution and the difference increases with the increase in polarisation current. The shape of the "average" pits developed in bulk solution and in 50$\mu$m layer is also approximately the same and can be described as a hemispheroid with the major semi-axis perpendicular to specimen surface and with a ratio of the minor semi-axis to the major semi-axis usually around 0.7–0.8 (Table 6.1). During potentiostatic polarisation such a shape is characteristic only for the pits grown under sufficiently thin layers with $\delta < 150\mu m$, while both under the thicker layers and in bulk solution the pits are more "cuplike" with $r > h$. This type of morphology for an "average" pit during galvanostatic polarisation is associated with the fact that the constant a in the relationship is two times greater than the constant b.
Table 6.1: Characteristics of "average" pits grown on Cr18Ni10Ti stainless steel under galvanostatic conditions in 50μm layer and in bulk of neutral chloride solutions. Data in the numerators and denominators correspond to 50μm layer and bulk solution respectively.

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<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>r_{av}, μm</td>
<td>28</td>
<td>30</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>32</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>r_{max}, μm</td>
<td>28</td>
<td>30</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>35</td>
<td>52</td>
<td>35</td>
</tr>
<tr>
<td>h_{av}, μm</td>
<td>36</td>
<td>38</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>40</td>
<td>38</td>
<td>40</td>
</tr>
<tr>
<td>h_{max}, μm</td>
<td>39</td>
<td>40</td>
<td>39</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>44</td>
<td>46</td>
<td>44</td>
</tr>
<tr>
<td>r_{av}/h_{av}</td>
<td>0.78</td>
<td>0.87</td>
<td>0.67</td>
<td>0.72</td>
</tr>
<tr>
<td>r_{max}/h_{max}</td>
<td>0.72</td>
<td>1.13</td>
<td>1.16</td>
<td>1.02</td>
</tr>
<tr>
<td>h_{50μm}/h_{bulk}</td>
<td>0.88</td>
<td>1.08</td>
<td>1.43</td>
<td>1.61</td>
</tr>
<tr>
<td>r_{50μm}/r_{bulk}</td>
<td>0.93</td>
<td>1.48</td>
<td>1.66</td>
<td>1.46</td>
</tr>
</tbody>
</table>

The preferential formation under galvanostatic polarisation of the pits with \( r < h \) may be ascribed to the lower corrosivity of the solution in the pit's mouth compared with the solution near the pit's bottom, and to the ohmic
voltage drop inside the pits resulting in the more positive potential of the pit's bottom comparing with the potential of the pit's mouth.

The increase in current density of galvanostatic polarisation or concentration of solution results in a prevalence of sizes of pits grown under thin layer over the sizes of pits grown in bulk electrolyte. Apparently the increase in number of small repassivated pits with increase in concentration of solution (or polarisation current) has stronger influence on process of development of active pits in bulk rather under thin electrolyte layer.

The similar trend of pits' development is also characteristic of the "average" pits grown under the conditions of chemical tests in bulk and in 50μm layer of 10% FeCl₃ + 0.01M HCl solution at 20°C (Table 6.2).

Table 6.2: Characteristics of pits grown on Cr18Ni10Ti stainless steel under conditions of chemical tests in bulk and thin (50μm) layer of 10% FeCl₃ + 0.01M HCl solution at 20°C (test duration 1h).

<table>
<thead>
<tr>
<th></th>
<th>δ = 50μm</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{ap} ), cm⁻²</td>
<td>80–120</td>
<td>80–120</td>
</tr>
<tr>
<td>( r_{cv} ), μm</td>
<td>23.01</td>
<td>19.65</td>
</tr>
<tr>
<td>( h_{av} ), μm</td>
<td>48.04</td>
<td>29.75</td>
</tr>
<tr>
<td>( \frac{r_{av}}{h_{av}} )</td>
<td>0.48</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 6.2 demonstrates that with the same number of active pits generated in thin (δ = 50μm) layer and bulk solution under the conditions of chemical tests, the sizes of "average" pits grown in thin layer are larger than that in bulk.
6.4 Conclusions

(i) It is shown that the number of the repassivated pits with $r < r_{cr}$ increases with an increase in:

(a) time of polarisation;

(b) anodic current density of galvanostatic polarisation; and

(c) concentration of the neutral chloride solutions.

The critical dimension of stable functioning (active) pits within the spread of experimental data was estimated to be $r = 7-8 \mu m$, while the theoretical evaluation of the critical concentration ($C_{cr}$) of the aggressive anions (chlorides) at a pit mouth, which enables the transformation of the pit nucleus into an active pit, gave the value $C_{cr} = 1.64M$.

(ii) The number of active pits generated under conditions of potentiostatic polarisation depends on the thickness of the electrolyte layer. Thinning of the layer and preliminary stabilisation of passive film at $E_{cor} < E_{pas} < E_{rp}$ reduces the number and diminishes its dependence on time. An exhaustion of solution with Cl\(^-\) ions may be the dominating factor limiting the number of active pits in thin electrolyte layers.

(iii) In the potentiostatic polarisation of the initially passivated electrodes the mean depth of pits for all thicknesses of the electrolyte layer increases with time according to the law $\sqrt{t}$, while for the mean radius
of pits the law $\sqrt{t}$ (bulk solution) is gradually replaced by the law $\frac{3}{\sqrt{t}}$ ($\delta = 50 \mu m$). The average rate of the pits deepening $\frac{dh_{av}}{dt}$ for all the thicknesses of electrolyte layer decreases with time according to the law $t^{-\frac{1}{2}}$, while the average rates of increase of pits in radius in bulk and in relatively thick ($\delta > 150 \mu m$) follow approximately the same pattern but on transition to the $50 \mu m$ layer the rate becomes proportional to $t^{-\frac{2}{3}}$. Such a kinetics of the active pits' development under conditions of the potentiostatic polarisation results in a difference in the shapes of pits grown in bulk solution and in the relatively thick ($\delta > 150 \mu m$) layers ($r > h$) and of pits grown under the layers with $\delta = 150 \mu m$ and $50 \mu m$ ($r < h$).

(iv) In the galvanostatic tests the number of active pits depends neither on duration of polarisation for (1min < t < 30min) nor on concentration or thickness of layer of the neutral chloride solutions used, but only on the polarisation current density of polarisation. With increase in the polarisation current density the number of the active pits increases.

(v) The active pits grown both under conditions of galvanostatic polarisation and in chemical tests in 10% FeCl$_3$ + 0.10M HCl preferentially have the shape with $r < h$ which may be associated with the lower corrosivity of solution near the pit's mouth comparing with one near the pit's bottom, and with the ohmic voltage drop inside the pits resulting in the more positive potential of the pit's bottom comparing with the potential of the pit's mouth.
(vi) With increase in the corrosivity of solution or decrease of corrosion resistance of stainless steel, the rates of the active pits propagation drop. One of the reasons for this may be due to a substantial increase in number of the small repassivating pits which consume a part of the current of polarisation. On transition from bulk electrolyte into thin layers the number of the repassivating pits under the conditions of galvanostatic polarisation and chemical tests may drop (due to proposed exhaustion in respect with Cl\textsuperscript{-} ions). Ultimately, this may result in larger sizes of the active pits developed in the thin layers.
Chapter 7

On the possibility of improvement of the corrosion resistance of Cr-Mn stainless steels
For steels as well as some other metals, impurities such as sulphur, oxygen, manganese, silicon, calcium, etc. not only dissolve in the matrix, but also participate in the formation of so-called nonmetallic inclusions. The inclusions (oxides, sulphides, nitrides, etc.) may affect both the mechanical and physical properties, and corrosion resistance of steels. Primary data on nonmetallic inclusions as preferable sites of localisation of corrosion processes were published some time ago [272–274]. Development of such effective methods of surface study as scanning electron microscopy and electron probe microanalysis gave experimental data which show that the boundaries of sulphur-containing inclusion such as manganese sulphide (MnS) or the sulphides associated with oxide inclusions are the preferred sites for the nucleation of pitting corrosion in stainless steels [60–64, 68, 275–279].

Manganese sulphide inclusions in Cr-Ni stainless steels retard passivation of the steels in acid media and reduce their resistance to pitting corrosion in chloride solutions [280–283]. Prevention of formation of such inclusions is possible if the value $P = [\text{Mn}] [\text{S}] < P_{cr} \approx 2.4 \cdot 10^{-3}$ (wt. %), where $P_{cr}$ is close to the value of MnS solubility product in steel $L_{\text{MnS}}$ [280, 282]. There is no difference which way the inequality $P < P_{cr}$ is achieved: with the reduction of manganese [Mn] or sulphur [S] concentrations of both the impurities simultaneously [280].

In Cr-Mn stainless steels prevention of formation of the MnS inclusions is possible only by reducing of the sulphur concentration. However, such desulphurisation resulting in the extremely low concentrations of sulphur (for instance 0.00016% for steel Cr14Mn15) cannot be accomplished with the
existing technologies of melting and refining which are able to reduce the sulphur content to 0.002–0.003% [281]. Nevertheless, even in the region $P > P_{cr}$, reduction in value of $P$ results in decrease with amount of MnS inclusions in Cr-Ni stainless steels and consequently in improvement of the corrosion characteristics of the steels [280–283]. In this work, the possibility of improving the corrosion resistance of Cr-Mn stainless steels by the reduction of sulphur concentration in the steels is investigated.

7.2 Results and discussion

Corrosion-electrochemical behaviour of two meltings of Cr14Mn15 with the concentrations of sulphur 0.02% ("ordinary" steel) and 0.004% ("pure" steel) was studied. The maximum permitted sulphur content in the steel is 0.03% [284]. Chemical compositions of the steels studied is given in Table 7.1.

Table 7.1: Chemical composition of the Cr14Mn15 steel, wt. %.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>ordinary</td>
<td>0.038</td>
<td>13.86</td>
<td>13.44</td>
<td>0.020</td>
<td>0.09</td>
</tr>
<tr>
<td>pure</td>
<td>0.044</td>
<td>14.48</td>
<td>12.35</td>
<td>0.004</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The presence and composition of nonmetallic inclusions in the steels was studied with the aid of scanning electron microscope with the attachment for energy dispersive X-ray microanalysis. Both steels had the MnS inclusions (a typical inclusion spectrum is given in Figure 7.1), however the ordinary steel has significantly larger amount of the inclusions and their mean size ($\approx 1 \mu m$) was approximately twice the ones in pure steel.
Figure 7.1: X-ray energy spectrum recorded from a typical manganese sulphide inclusion in Cr14Mn15 steel.
Electrochemical characteristics of pitting corrosion of the steels studied in 0.1M NaCl solution are very close and similar to that of the same type of steel in Table 5.8. However, the reduction of sulphur content in the steel improves such passivation characteristics in sulphuric acid as critical current density of passivation ($i_{cc}$) and potential of passivation ($E_{pp}$). Values of $i_{cc}$ and $E_{pp}$ for the two steels studied in sulphuric acid solutions are shown in Figure 7.2. As it can be seen the reduction in sulphur content results in corresponding reduction of $i_{cc}$ by not less than half an order of magnitude over the range of sulphuric acid concentrations used (curves 1 and 2) while $E_{pp}$ shifts towards more negative values by 0.02–0.04V (in $5 \cdot 10^{-4}$M H$_2$SO$_4$ the shift is even larger -0.2V). Therefore, the reduction of the sulphur concentration in steel Cr14Mn15 makes the steel, in terms of passivation characteristics, similar to steels with higher content of Cr, e.g. stainless steel Cr25Mn15 (Figure 7.2, curve 3).

The desulphurisation of Cr14Mn15 steel does not prevent formation of MnS inclusions in metal matrix. Nevertheless, the desulphurisation reduces number and sizes of the inclusions and brings passivation characteristics of the steel to steels with higher concentration of Cr. Deep desulphurisation of the steels takes additional refining and remelting which is not expedient economically. However, it is known [209, 280] that alloying of steel with elements (for instance rare-earth metals) which possess stronger affinity to sulphur than manganese and form sulphides with higher corrosion resistance than MnS may result in approximately the same improvement of corrosion resistance of metal as desulphurisation providing the correlation $P < P_{cr} \approx L_{MnS}$. Therefore, the corrosion resistance of Cr-Mn stainless steels possibly may be improved not only by increasing of the content of such
Figure 7.2: Passivation potential ($E_{pp}$) and critical current density of passivation ($i_{cc}$) versus concentration of sulphuric acid: 1 and 1' - "ordinary" Cr14Mn15 steel; 2 and 2' - "pure" Cr14Mn15 steel; 3 - Cr25Mn15 steel.
elements as Cr, Si, etc., but by alloying of the steels with a small amount of strong sulphur-combining elements of the mentioned type.

7.3 Conclusions

Corrosion-electrochemical behaviour of Cr14Mn15 stainless steels with different content of sulphur has been investigated in neutral chloride and acid sulphate media.

(i) It was demonstrated that the reduction of sulphur content in the steel results in a decrease in the number and size of MnS inclusions. This does not affect the resistance of the steel to pitting corrosion in chloride solution, but improves passivation characteristics in sulphuric acid over a wide concentration range.

(ii) A suggestion is made that alloying of the Cr-Mn stainless steels with elements which possess stronger affinity to sulphur than Mn and sulphides of which are more corrosion resistant than MnS may improve corrosion resistance of the steels to the same extent as deep desulphurisation when $P < P_{cr} \approx L_{MnS}$. 

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Chapter 8

Comparison of full-scale corrosion tests and laboratory corrosion-electrochemical studies
8.1 Introduction

The aim of all corrosion tests is the determination of the durability of a metal in a specific corrosive environment, and the elucidation of the mechanism and kinetics of corrosion process, establishment of the limiting stages of the process and factors affecting corrosion rate, etc.

Two types of corrosion tests were carried out in this work:

(i) field tests, aimed at determining the corrosion behaviour of metals studied in natural environment (atmosphere); and,

(ii) laboratory electrochemical and chemical tests, aimed at elucidating the mechanism and kinetics of corrosion processes studied.

The electrochemical tests used in this thesis, due to the relatively short time involved, may be considered as accelerated tests aimed to provide information on long-term durability of a given metal in a natural corrosive medium.

Numerous reports have been produced on full scale outdoor tests and accelerated indoor studies of atmospheric corrosion of metals (i.e. intermittent submersion, climatic chambers). The lack of correlation between these results has been known for years and the corrosion-electrochemical measurements in thin layers of electrolyte are seldom used for this purpose. Yet, the use of this technique, as a supplement or an alternative approach to traditional atmospheric corrosion tests, could be effective. Electrochemical measurements in bulk electrolytes are widely and successfully used for the evaluation of corrosion resistance of metals,
particularly stainless steels, under various solution conditions. In this work, an attempt is made to determine the feasibilities and limitations in the prediction of stainless steels' atmospheric durability, based on the results of electrochemical measurements carried out in thin phase electrolyte layers.

8.2 Results and discussion

In section 4.2, it was shown that stainless steels Cr25Mn15 and Cr17(SS430) in bulk of acid sulphate solutions corrode from active state, while in thin electrolyte layers the steels passivate spontaneously. The self-passivation of the steels is irreversible and the passive state achieved can be retained for a long time even in the bulk solution in which the steels corroded actively prior to the self-passivation. The resulting passivity can only be disturbed by mechanical means (scratching of the metal's surface) or by a sufficiently energetic cathodic reduction. The results obtained suggest that high corrosion resistance of the steels in atmospheres polluted with sulphur dioxide as the corrosion occurs in conditions of intermittent wetting with acid sulphate electrolyte [9, 22, 101, 117, 127, 128, etc.] and subsequent drying. Indeed, a theoretical evaluation of the corrosion rate k of Cr17 steel in such atmospheres based on the data for corrosion current \( i_{\text{cor}} = 0.3 \mu \text{Acm}^{-2} \) of the steel after self-passivation in thin electrolyte layer gives the value \( k = 3.17 \cdot 10^{-3} \text{mmyear}^{-1} \) and, thus, indicates a high atmospheric durability of the steel. The data are consistent with the results of half-year full scale outdoor tests of the steels Cr25Mn15 and Cr18Ni10Ti in an industrial atmosphere (chemical plant, production of bisulphite, city of Rustavi, Republic of Georgia, USSR) highly polluted with sulphur dioxide (1.5–6.0mgm\(^{-3}\)). The corrosion rates obtained for steels Cr25Mn15 and Cr18Ni10Ti are very close; being \( 3.3 \cdot 10^{-3} \text{mmyear}^{-1} \)
and $2.1 \cdot 10^3 \text{mmyear}^{-1}$, respectively. This is in good agreement with the theoretically evaluated values for the self-passivated steel Cr17.

Despite a significant difference in the corrosion-electrochemical behaviour of the steels in bulk acid sulphate solutions (at pH = 1–4 the steels Cr25Mn15 and Cr17 corrode in an active state, while the steel Cr18Ni10Ti corrodes in passive state) the corrosion rates of the steels in a sulphur dioxide contaminated industrial atmosphere (experimental results for the steels Cr25Mn15 and Cr18Ni10Ti, and theoretical assessment for the steel Cr17) indicate that all three steels should corrode in the passive state. Therefore, it would be generally erroneous to predict the atmospheric durability of some stainless steels in industrial atmospheres on the basis of corrosion-electrochemical tests in bulk electrolytes only. Such tests can be unduly severe as they can underestimate the atmospheric durability of the steels, whereas tests performed in thin layers of electrolyte are likely to enable a more accurate prediction.

As it can be seen from Tables 5.7 and 5.8 the electrochemical characteristics of pitting corrosion of the stainless steels in bulk and thin layers of neutral chloride solutions coincide with each other. In section 5.4, it was shown that with respect to electrochemical criteria of resistance to pitting corrosion the steels studied can be ranked equally both in bulk and under thin layers of neutral chloride solutions: Cr14Mn15 < Cr25Mn15 < (Cr18Ni10Ti, Cr22Ni10Ti). According to $\Delta E$-criteria, none of the steels would undergo pitting corrosion in a pure chloride-containing atmosphere. The suggestion is supported by the results of full scale outdoor tests (2.5 years) of the steels in pure marine atmosphere (city of Batumi, atmospheric corrosion station of Institute of Metallurgy, Academy of Sciences, Republic of Georgia, USSR).
The data show that:

(i) the $\Delta E$-criteria are applicable for evaluation of the pitting resistance of stainless steels under atmospheric conditions; and

(ii) the prognosis of the relative resistance of the steels in pure marine atmosphere, in contrast to industrial atmosphere polluted with sulphur dioxide, can be based on conventional electrochemical tests in bulk electrolytes.

The use of the $\Delta E$-criteria determined in bulk electrolytes for the prediction of atmospheric pitting resistance of metals can be further proven with the data of laboratory electrochemical and full-scale outdoor tests (1.5 years, city of Batumi) of aluminium alloys (chemical composition in Table 8.1).

*Table 8.1:* Chemical composition of the aluminium alloys, wt. %.

<table>
<thead>
<tr>
<th>Number</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>0.56</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.27</td>
</tr>
<tr>
<td>2</td>
<td>6.50</td>
<td>0.30</td>
<td>0.50</td>
<td>3.80</td>
<td>0.10</td>
<td>0.10</td>
<td>1.20</td>
</tr>
</tbody>
</table>

According to the results of the tests under conditions of pure marine atmosphere these aluminium alloys undergo severe pitting corrosion. However, the data of laboratory electrochemical measurements in bulk and thin layers of NaCl solutions ($C = 0.01M - 0.001M$) indicate that these alloys give the following $\Delta E$-criteria: $\Delta E_{\text{pit}}^{\text{min}} < 0$, $\Delta E_{\text{br}} \approx 0$ and $\Delta E_{\text{rp}} < 0$ which indicate high probability of pitting corrosion of the alloys in the outdoor test conditions.
8.3 Conclusions

A comparison of the results of full scale outdoor corrosion tests of stainless steels in industrial atmosphere heavily polluted with sulphur dioxide and in pure marine atmosphere with those of laboratory electrochemical tests are given in this chapter. Analysis of the data leads to the following conclusions:

(i) prognosis of corrosion behaviour of some stainless steels in industrial atmosphere polluted with sulphur dioxide based on the results of electrochemical measurements under conventional conditions (bulk acid sulphate solutions) may be erroneous; unduly severe conditions of the test result in an underestimation of the atmospheric durability of the steels, whereas similar electrochemical measurements carried out on electrodes covered with thin layers of the same electrolyte provide more accurate prediction;

(ii) $\Delta E$-criteria of pitting corrosion, which have been developed for the assessment of relative resistance of stainless steels to pitting in bulk electrolytes are applicable to the evaluation of corrosion behaviour of the steels under atmospheric conditions; and

(iii) prognosis of the relative resistance of stainless steels to pitting corrosion in pure chloride-containing atmosphere may be based on electrochemical measurements carried out conventionally in bulk electrolytes.
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Corrosion of Stainless Steels in Bulk and Under Thin Layers of Electrolytes

by

Alexander R. Basman

A Thesis Presented for the Degree of Doctor of Philosophy

Department of Chemistry
Faculty of Science and Technology
University of Western Sydney, Nepean

17 September, 1993
PLEASE NOTE

The greatest amount of care has been taken while scanning this thesis,

and the best possible result has been obtained.
University of Western Sydney, Nepean

Candidate's Certificate

I certify that the thesis entitled "Corrosion of Stainless Steels in Bulk and Under Thin Layers of Electrolytes" submitted for the Degree of Doctor of Philosophy is the result of my own research, and that this thesis (or any part therein) has not been submitted for a higher degree to any other university or institution.

Signed: 

Dated:
Dedicated to my family – for
their love and patience.
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Summary
Passivation, local anodic depassivation and pitting corrosion of stainless steels in bulk and under thin phase layers of acid sulphate and neutral chloride solutions have been studied. A number of electrochemical, chemical, metallographic and physical techniques were employed in this study. The choice of stainless steels, test solutions and methods of investigations was based on scientific expediency and practical availability.

For the first time the electrochemical and corrosion characteristics of passivation, local anodic depassivation and pitting corrosion of stainless steels were obtained in thin layers and compared with those in bulk electrolytes. It was demonstrated that the thickness of the electrolyte layer can influence the passivation process and, under certain conditions, the kinetics of pitting corrosion.

A decrease in the thickness of acid sulphate solution layer facilitates the passivation of stainless steels through the deceleration of the anodic process of ionisation of the metal and acceleration of the cathodic process of oxygen reduction. For stainless steels Cr25Mn15 and Cr17, the possibility of self-passivation in thin layers of acid sulphate solutions has been demonstrated. It was shown that the thickness of electrolyte layer at which the self-passivation occurs (critical thickness of self-passivation $\delta_{cr}$) increases with the increase in pH of the electrolyte. It is, therefore, proposed that the value of $\delta_{cr}$ be adopted as one of the criteria for evaluating the corrosion resistance of stainless steels in atmospheres polluted with sulphur dioxide. Self-passivation of stainless steels in thin phase layers of acid sulphate solutions was responsible for the high corrosion resistance observed in industrial atmospheres polluted with sulphur dioxide, as well as in bulk electrolytes in which the steels corroded in active state, prior to the self-passivation.
The role of the cathodic reaction of oxygen reduction in extending the passivity retention time ($t_p$) of stainless steels in naturally aerated dilute sulphuric acid has been demonstrated. The effect of oxygen reduction on maintenance of passivity, following passivation at a potential corresponding to the middle of the passive region of anodic polarisation curve, is small and diminished with an increase in the passivation time. In contrast, this effect can be particularly significant if the chosen passivation potential is within the cathodic loop region. The cathodic loop region is thus proposed as a preferred region for the implementation of anodic protection for some stainless steels as it provides a prolonged after-effect and, hence, enhances the reliability of the protection.

The electron diffraction patterns of passive film formed on Cr25Mn15 steel in acid sulphate solution have been studied. It was shown that the passive film on the Cr-Mn stainless steel has a lattice of the face-centred cube and consists of Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ which is similar to that found on the Cr-Ni and chromium stainless steels.

Automatic quantitative metallography was used to determine the critical dimension (the critical radius $r_{cr}$) of the pits on stainless steels, i.e. the minimum radius required for the pit nucleus to turn into an active (stable functioning) pit. Within the spread of experimental data, the critical radius $r_{cr}$ was found to be 7-8μm.

The independence of the boundary potentials for the pitting corrosion of stainless steels on the thickness of neutral chloride electrolyte layer has been demonstrated. Hence, it has been proposed that the processes of pits nucleation and repassivation on stainless steels are not affected by the
peculiarities of corrosion in thin electrolyte layers and the stainless steels are ranked equally both in bulk and under thin layers with regard to their relative pitting corrosion resistance.

The kinetics of pits development under conditions of anodic potentiostatic and galvanostatic polarisation was studied. It was shown that the number of repassivated pits with \( r < r_{cr} \) increases with an increase in: (i) time of polarisation; (ii) current density of galvanostatic polarisation; and (iii) concentration of neutral chloride solution. The number of active pits generated under potentiostatic polarisation conditions is reduced as the thickness of the electrolyte layer is decreased, while the number of active pits generated under galvanostatic polarisation conditions depends only on the polarisation current density. Under the potentiostatic and galvanostatic polarisation conditions the time dependence of the average values of depth (\( h_{av} \)) and radius (\( r_{av} \)) of active pits can be described by the following power functions:

\[
h_{av} = k_h t^a
\]

and

\[
r_{av} = k_r t^b
\]

where \( k_h, k_r, a \) and \( b \) are some empirical constants. Under potentiostatic conditions the value of \( a \) is independent on the thickness of the electrolyte layer, and the depth of active pits increases with time according to law \( \sqrt{t} \).

At the same time the value of \( b \) depends on the thickness of the electrolyte layer, and during transition from bulk to the 50\( \mu \)m layer the law \( \sqrt{t} \) for the
time dependence of the active pit's radius is replaced gradually with the law \(3\sqrt{t}\). Under galvanostatic polarisation conditions the values \(a\) and \(b\) do not depend on both current density of polarisation and thickness of electrolyte layer. However, these values decrease with increase in chloride ion concentration in solution and with a decrease in corrosion resistance of the steel.

Sizes of pits developed in thin layers of chloride-containing electrolytes under anodic galvanostatic polarisation conditions or during chemical tests are larger than those obtained in the bulk electrolyte. This difference was associated with the larger number of small \((r < r_{cr})\) repassivated pits formed on the stainless steels in bulk electrolytes.

The possibility of improving the passivation characteristics of Cr-Mn steel in sulphuric acid solution by reducing the sulphur concentration in the steel has been demonstrated. The improvement was associated with the decrease in the number and size of MnS inclusions.

The feasibilities and limitations of accelerated estimates of atmospheric resistance of stainless steels based on corrosion-electrochemical characteristics obtained in thin layers and in bulk electrolytes have been studied. It was shown that the prognosis of corrosion behaviour of some stainless steels in sulphur dioxide contaminated atmosphere based on electrochemical measurements in bulk electrolytes can be erroneous. The same measurements carried out in thin phase layers enable more accurate prediction. However, the prognosis of the relative resistance of the stainless steels to pitting corrosion in the clean chloride-containing atmosphere may
be based on conventional electrochemical measurements in the bulk of corresponding electrolytes.
Aims of the study and brief description of the thesis
The main objectives of this study are to:

- investigate the corrosion-electrochemical behaviour of some stainless steels in bulk and under thin phase layers of acid sulphate and neutral chloride solutions;

- investigate the peculiarities of passivation, local anodic depassivation and pitting corrosion of stainless steels under thin electrolyte layers;

- examine, identify and develop new approaches for the application of stainless steels in different corrosive environments; and

- investigate the feasibilities and limitations of electrochemical accelerated estimates of corrosion resistance of stainless steels under atmospheric conditions.

The work is described in eight chapters. A review of literature on studies of corrosion of stainless steels is given in Chapter 1. The second section of the chapter (1.2) deals with basic principles of electrochemical corrosion of metals and reviews the literature on passivation, breakdown of passivity, and pitting corrosion of stainless steels. Sections 1.3 and 1.4 provide an introduction to the field of wet atmospheric corrosion of metals, reveal some principal characteristics of the process and the literature data obtained in full-scale tests of stainless steels in the different atmospheric environments. Section 1.5 reviews the experimental techniques and results of corrosion-electrochemical studies on metals covered with the thin electrolyte layers.
Chapter 2 deals with all experimental procedures and arrangements used in this study. The electronic circuitries designed for measurements of the thickness of the electrolyte layers and that used for maintaining constant temperature and high relative humidity ($\text{RH}_r = 100\%$) in the cell, used in the study, are described in section 2.3.

Chapter 3 provides a short introduction to the problem of IR-error in electrochemical polarisation measurements. Results of one theoretical and three experimental approaches for the determination of the error as applied to the particular experimental arrangement used in this work are described in section 3.2.

Results on passivation of stainless steels in bulk and under thin layers of acid sulphate solutions are discussed in Chapter 4. Some peculiarities of corrosion-electrochemical processes in thin layers of these electrolytes are brought up and discussed in section 4.2. The phenomenon of cathodic reduction of oxygen in the region of potentials of anodic dissolution of stainless steels in acid solutions along with the different factors influencing this process are considered in section 4.3. Sections 4.4 and 4.5 deal with the effect of oxygen reduction on the retention of passivity by stainless steels in acid sulphate solutions both in the presence and absence of the chloride ions, and describe the way by which the oxygen reduction can be used to enhance the after-action and, hence, the reliability of anodic protection of the steels. Results on composition and structure of passive films, formed on chromium-manganese (Cr-Mn) stainless steel in acid sulphate solutions, obtained by using Aüger electron spectroscopy and electron diffraction techniques are included in section 4.6.
Chapter 5 includes results on chemical and electrochemical tests of stainless steels for resistance to pitting corrosion and examines data on boundary potentials for pitting corrosion of the steels obtained in experiments both in bulk and under thin phase layers of neutral chloride solutions.

Data on critical size of pits on stainless steel obtained by using quantitative metallography, and results on propagation of pits in conditions of chemical tests and under potentiostatic and galvanostatic polarisations are discussed in Chapter 6.

A possibility of improvement of corrosion resistance of Cr-Mn stainless steels by reducing sulphur content is considered in Chapter 7.

Chapter 8 includes a comparison of results of full-scale atmospheric corrosion tests with results of laboratory electrochemical studies and contains discussion of feasibilities and limitations of accelerated estimations of atmospheric durability of stainless steels based on electrochemical measurements in bulk and under thin phase electrolyte layers.

The thesis is based on research material published in 13 papers and reported on at 5 corrosion-electrochemical conferences; and comprises 61 figures, 19 tables and 284 references.
Publications
Papers


Conference presentations


**Other publications**


