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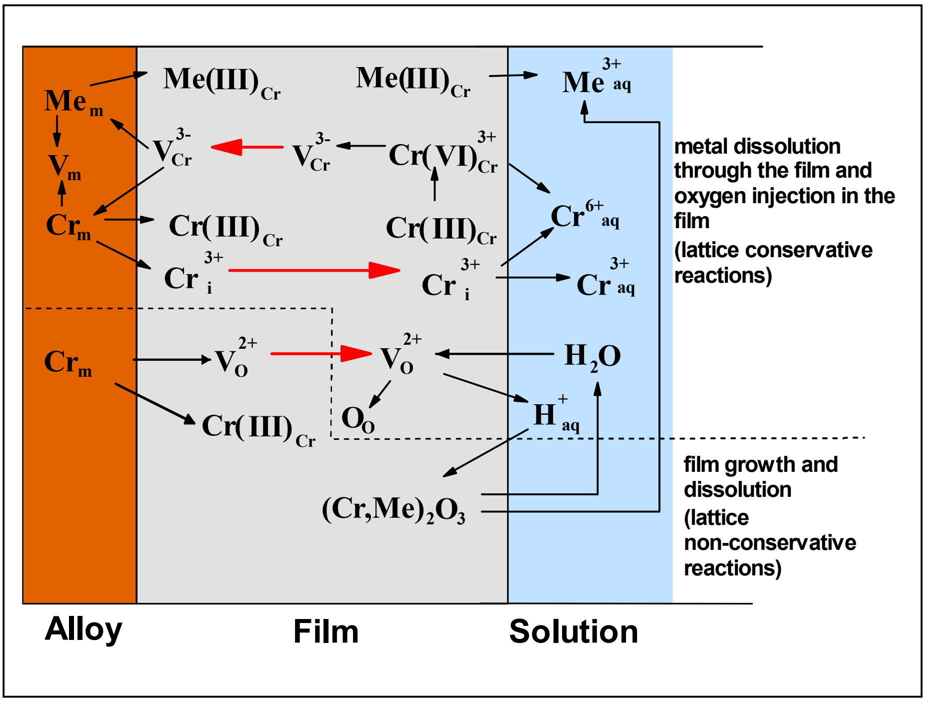

Petri Kinnunen

Electrochemical characterisation and modelling of passive films on Ni- and Fe-based alloys

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Petri Kinnunen

VTT Industrial Systems

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Abstract

The behaviour of oxide films formed on Ni- and Fe-based alloys in different environments has been studied electrochemically. The aim was to study the effect of pH, temperature and Cr content of the alloy on the protectiveness of the oxide film using a wide combination of electrochemical techniques: conventional linear sweep cyclic voltammetry, rotating ring-disc voltammetry, electrochemical impedance spectroscopy (EIS), contact electric resistance technique (CER) and contact electric impedance technique (CEI). The other goal was to develop modelling tools to describe and predict the oxide film behaviour in different conditions.

Increasing pH has been found to decrease oxidation rates in both the passive and transpassive regions. Increasing pH as well as increasing temperature shifts the passive region in the negative direction on the potential scale. A higher amount of Cr in the alloy leads to a more passive oxide film on the metal surface both at low and high temperatures. On the other hand, transpassive dissolution takes place at lower potentials and its rate increases with higher Cr content of the alloy. The potential region of transpassive oxidation and secondary passivation increases and the effect of Cr on the electrochemical behaviour especially on Ni-Cr alloys decreases at high temperatures.

The behaviour of oxide films in the passive state in different environments was simulated using the Mixed Conduction Model (MCM). Using this model the diffusion coefficients of current carriers and reaction rate constants at room temperature and profiles of resistances against ionic transport in the oxide films at 200°C were estimated.

Also the transpassive dissolution of Ni-Cr alloys at room temperature was studied and a kinetic model proposed to determine quantitatively the reaction rates in the transpassive region. The model describes the oxidation and dissolution reactions of metal cations at the film/solution interface. The proposed model can be used to estimate steady-state current densities as well as dependencies of surface fractions of dissolving species on potential.

Preface

This work has been carried out at VTT Industrial Systems (by the end of 2001 VTT Manufacturing Technology), Technical Research Centre of Finland, and at the Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, Finland, in 1998–2002.

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I wish to express my gratitude to supervisor Emeritus Professor Göran Sundholm for his advice and guidance. I also want to thank Professor Kyösti Kontturi for introducing me the interesting world of electrochemistry.

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This work would not have been done without extensive contribution from Dr. Martin Bojinov, Dr. Timo Laitinen and Dr. Timo Saario. These fellows have taught me both the practical and theoretical sides of the phenomena related to corrosion and oxide film studies. Their motivation and help during the work has been invaluable.

The co-authors of the publications as well as the personnel of the Laboratory of Physical Chemistry and Electrochemistry at Helsinki University of Technology and my colleagues at VTT Industrial Systems are acknowledged for their help and support.

Finally, I would like thank my fiancée Riina Tolvanen and my mother Terttu Kinnunen for their patience, support and encouragement during the work and in life on the whole.

List of papers included in the thesis

This thesis contains a summary of the work performed and seven appended papers which are referred to in the text by their Roman numerals (I–VII)

I Bojinov, M., Fabricius, G., Kinnunen, P., Laitinen, T., Mäkelä, K., Saario, T. & Sundholm, G. Electrochemical study of the passive behaviour of Ni-Cr alloys in a borate solution – a mixed conduction model approach. *J. Electroanal. Chem.* **504** (1) (2001) 29–44.

II Bojinov, M., Kinnunen, P., Laitinen, T., Mäkelä, K. & Saario, T. A View of Passive Films on Metals as Mixed-Conducting Oxides. In: *Corrosion and Corrosion Protection*, (edited by Sinclair, J.D., Kalman, E., Kendig, M.W., Plieth, W. & Smyrl, W.H.), PV 2001-22, The Electrochemical Society, Inc., NJ, 2002. Pp. 26–33.

III Bojinov, M., Fabricius, G., Kinnunen, P., Laitinen, T., Mäkelä, K., Saario, T. & Sundholm, G. The mechanism of transpassive dissolution of Ni-Cr alloys in sulphate solutions. *Electrochim. Acta* **45** (17) (2000) 2791–2802.

IV Bojinov, M., Fabricius, G., Kinnunen, P., Laitinen, T., Mäkelä, K., Saario, T., Sundholm, G. & Yliniemi, K. Transpassive dissolution of Ni-Cr alloys in sulphate solutions – comparison between a model alloy and two industrial alloys. *Electrochim. Acta* **47** (11) (2002) 1697–1712.

V Bojinov, M., Kinnunen, P. & Sundholm, G. Electrochemical Behaviour of Ni-Cr Alloys in a High-Temperature Aqueous Electrolyte. *Corrosion Journal*. In print.

VI Beverskog, B., Bojinov, M., Englund, A., Kinnunen, P., Laitinen, T., Mäkelä, K., Saario, T. & Sirkiä, P. A mixed-conduction model for oxide films on Fe, Cr and Fe-Cr alloys in high-temperature aqueous electrolytes. – I. Comparison of the electrochemical behaviour at room temperature and at 200°C. *Corrosion Science* **44** (9) (2002) 1901–1921.

VII Beverskog, B., Bojinov, M., Kinnunen, P., Laitinen, T., Mäkelä, K. & Saario, T. A mixed conduction model for oxide films on Fe, Cr and Fe-Cr alloys in high-temperature aqueous electrolytes. – II. Adaptation and justification of the model. *Corrosion Science* **44** (9) (2002) 1923–1940.

The author of this thesis has been responsible for all the measurements as well as the model simulations, analysis and writing the text of papers I, III, IV and V. He performed the measurements with Ni-20%Cr alloy presented in paper II and also took an active part in writing the text of papers VI and VII. In all papers the authors are presented in alphabetical order regardless of the contribution to the papers.

Contents

Appendices of this publication are not included in the PDF version. Please order the printed version to get the complete publication (http://www.vtt.fi/inf/pdf/)

List of abbreviations and used terminology

a	atomic jump distance (cm)
b_i, $i = 3, 3i, 4$	Tafel coefficients of the interfacial reactions (V^{-1})
$c_O(L)$	concentration of oxygen vacancies in the film at the metal/film interface (mol cm^{-3})
$c_O(0)$	concentration of oxygen vacancies in the film at the film/solution interface (mol cm^{-3})
$c_O(x)$	concentration profile of oxygen vacancies in the film (mol cm^{-3})
D_i	diffusion coefficient of interstitial cations (cm^2 s^{-1})
D_M	diffusion coefficient of cation vacancies (cm^2 s^{-1})
D_O	diffusion coefficient of oxygen vacancies (cm^2 s^{-1})
E	potential (V)
$\boldsymbol{E}$	electric field strength (V cm^{-1})
F	Faraday's constant (96 485 C mol^{-1})
J_{Mv}	flux of cation vacancies in the film (mol cm^{-2} s^{-1})
J_O	flux of oxygen vacancies in the film (mol cm^{-2} s^{-1})
k_3^0	rate constant for cation dissolution at the film/solution interface (mol $cm^{-2}s^{-1}$)
k_{3i}^0	rate constant for interstitial cation dissolution at the film/solution interface (cm s^{-1})
k_4^0	rate constant for the incorporation of oxygen from water at the film/solution interface (cm s^{-1})
L	oxide film thickness (cm)
Me_{aq}^{2+}	dissolved cation
Me_{Me}	cation in the metal position in the anodic film
m	metal atom in the metal phase
O_O	oxygen anion in the oxygen position in the anodic film

R	gas constant (8.314 J K^{-1} mol^{-1})
T	temperature (K)
V_M^{x-}	cation vacancy in the anodic film
V_O^{2+}	oxygen vacancy in the anodic film
x	distance within the film (cm)
y	valence of a cation
z	charge number
α	polarisability of the film/solution interface
UNS N06600	construction material (14–17 wt-% Cr, 6–10 wt-% Fe, ≤ 0.15 wt-% C, ≤ 1 wt-% Mn, Ni bal.)
UNS N06690	construction material (27–31 wt-% Cr, 7–11 wt-% Fe, ≤ 0.05 wt-% C, ≤ 0.5 wt-% Mn, ≤ 0.5 wt-% Cu, Ni bal.)
UNS N10276	construction material (14–17 wt-% Cr, 4–7 wt-% Fe, ≤ 0.02 wt-% C, ≤ 1 wt-% Mn, 15–17 wt-% Mo, 3–5 wt-% W, ≤ 0.35 wt-% V, ≤ 2.5 wt-% Co, Ni bal.)
UNS S30400	construction material (18–10 wt-% Cr, 8–12 wt-% Ni, ≤ 0.08 wt-% C, ≤ 2 wt-% Mn, Fe bal.)
UNS S31600	construction material (16–18 wt-% Cr, 10–14 wt-% Ni, ≤ 0.08 wt-% C, ≤ 2 wt-% Mn, 2–3 wt-% Mo, Fe bal.)
BWR	boiling water reactor
CEI	contact electric impedance
CER	contact electric resistance
EIS	electrochemical impedance spectroscopy
HFM	High-Field Model
MCM	Mixed Conduction Model
PDM	Point Defect Model
SCAHFM	Surface Charge Assisted High-Field Migration Model

1. Introduction

Ni- and Fe-based alloys are widely used construction materials in process industry and energy production in nuclear power plants. Ni-based alloys, e.g. UNS N06600 and UNS N06690, have been found to be suitable construction materials e.g. for steam generators used in nuclear power plants under high temperature and pressure. Ni-based alloys are also often used as filler materials for welds. On the other hand, Fe-based alloys, such as UNS S30400 and UNS S31600, are mostly used e.g. in nuclear power plants as pipework materials in water circulation loops or as corrosion resistive coatings on top of carbon steel with low Cr content. When comparing Ni- and Fe-based alloys with each other, a generally higher degree of resistance against corrosion is observed for Ni alloys. This can be explained partly by the more noble (approx. 0.18 V) corrosion potential of Ni and by the different properties of the oxide films formed on Ni-based alloys in comparison with those on Fe-based alloys [1].

The composition and structure of the oxide film determines how different ions are transported through the oxides. The transport of material, on the other hand, affects the corrosion rate of the material. Knowledge of the transport properties of oxide films is especially important when studying the activity incorporation on primary circuit surfaces in nuclear power plants. Another example of a process environment in which the resistive properties of oxide films against corrosion have to be known is the highly oxidising pulp bleaching process. Operation in such a corrosive process environment makes it essential to characterise the effects of different parameters (pH, temperature etc.) on the behaviour of the protective oxide films and to determine the rate limiting steps for corrosion reactions.

Experimental electrochemical characterisation of the oxide films gives valuable information for understanding the correlations between material behaviour, oxide film composition, structure and process environment. By combining the experimental data with theoretical analysis, several important features, such as rates of transport of ionic species or the effects of different anions on the oxidation rates of construction materials, can be estimated and predictions made concerning the safety and service life of components. So far, analysis of the behaviour of construction materials such as Ni- and Fe-based alloys has been carried out mainly at room temperature. Lack of understanding of the high-temperature electrochemical behaviour of these materials has been partly responsible for unexpected repair actions taken, for example, in nuclear power plants.

This thesis presents the work carried out at Helsinki University of Technology and the Technical Research Centre of Finland (VTT) in 1998–2002. The goal of this work was to study the electrochemical behaviour of Ni- and Fe-based model alloys in different conditions. The main focus was on studying the effects of pH and temperature, as well as of Cr as the major alloying element, on the protectiveness of oxide films formed on such alloys. Experiments were carried out both in solutions with different pH at room temperature and in solutions with slightly alkaline pH at high temperatures 200°C and 300°C. Attention was also paid to the transpassive oxidation of Ni-based alloys including two commercial alloys, UNS N06600 (Alloy 600) and UNS N10276 (Alloy C276). Behind this was the need to find out the effect of the highly oxidising environment typical of e.g. the pulp bleaching process on the protectiveness of oxide films formed on Ni-based construction materials and welds. In order to extract more detailed features of the processes occurring on and in the oxide films, the Mixed Conduction Model (MCM) was further developed in this work and a kinetic model for the transpassive dissolution was proposed. The MCM has made it possible to estimate the electrochemical parameters, rate-limiting steps and transport properties of the oxide films on metal alloys. In the future, the results of this work may go some way to explaining in better detail the material problems faced by the process industry and nuclear power plants, and the modelling approach can be extended to explain the features also observed on other commercial metal alloys.

2. Passivity and transpassivity

The use of many metal alloys having suitable mechanical properties and reasonable prices as construction materials is possible because the alloys passivate, i.e. a protective oxide film is formed on the alloy surface. Without such a film, the alloy would keep on reacting with the environment until it is totally oxidised.

The different states of the metal electrode during oxidation are briefly outlined in terms of the current-potential – i.e. voltammetric – relation shown in Fig. 1. Voltammetry is a common electrochemical method for studying the oxidation of a metal electrode. The potential of the electrode is usually the controlled variable being changed either linearly or stepwise, and the current created by reactions of the electrode material with the environment at different potentials is monitored. In most cases the measurement is started on a bare electrode surface on which no film exists.

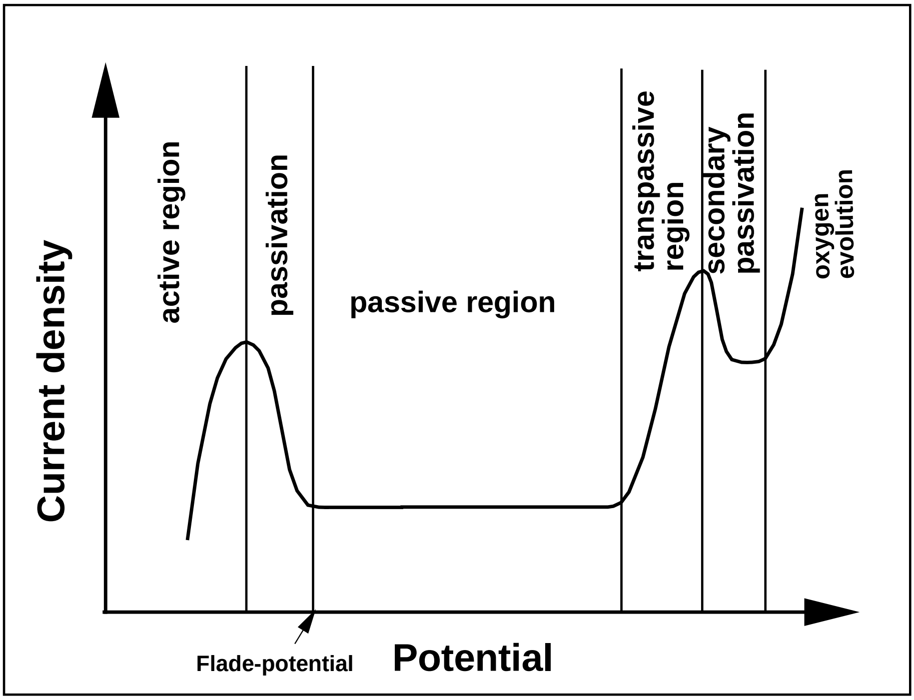

Figure 1. States of a metal electrode (e.g. Ni, Fe) during voltammetric measurement.

When the potential of a bare electrode is increased from very low up to the *active region*, the electrode material starts to oxidise (Fig. 1). The oxidation is seen as an increase in current. By increasing the potential further, at a given potential the current through the electrode starts to decrease and *passivation* begins. During passivation the electrode surface becomes covered with the oxidation product and an oxide film is formed. When the current achieves its minimum value after passivation at the *Flade-potential*, and stays low with increasing potential, the electrode is said to be in its *passive state*. In this state the corrosion current through the electrode is usually considerably lower than in the active state.

If the potential of a passive electrode made of a construction material like Ni- or Fe-based alloy is increased, the oxidation current will finally start to increase again and *transpassive oxidation* begins. In this potential region metal cations are oxidised to higher valences than in the primary passive region. These oxidation reactions may lead not only to a film containing high-valence metal species but also to enhanced dissolution of the metal through the film. Electrode reactions in the transpassive region usually involve several parallel and consecutive steps leading to solid, dissolved or gaseous reaction products. In addition, the corrosion current increases rapidly in the transpassive region and no clear potential thresholds between different reactions can be observed. The valence state of the cations is not well known for all metals at transpassive potentials. For these reasons the transpassive behaviour has been often excluded from studies of the electrochemical behaviour of metals and alloys.

At very high potentials in the transpassive region, the surface of the electrode may either start to passivate again (*secondary passivation*) or the current continues increasing and *oxygen evolution* begins. The existence of the secondary passive region is highly dependent on the solution environment, pH and temperature and cannot be observed on all metals. In the oxygen evolution region the oxide film dissolves from the electrode surface and no new protective oxide film is formed.

The films existing in the passive region can be divided into two groups based on their structure. *Discontinuous films* are porous, have a low protectiveness and a substantial thickness up to 1 mm. They are formed at potentials close to the equilibrium potential of the corresponding $MeO_{y/2}/Me$ electrode, where y is the valence of the cation, via a dissolution-precipitation mechanism. Films of this kind include e.g. sulphate films on Fe and Ni. *Continuous (barrier, passivating) films* have a high resistivity, above 10^6 Ω cm, and a maximum thickness of approx. 1 µm. A barrier film is a continuous film which can prevent current flow and thus support a high electric field in the film. During their formation metal cations do not enter the solution, but rather oxidation occurs at the metal/film interface via a solid state mechanism. Oxide films on Al and Ta are examples of these films. [2]

The metal surface can be covered by both discontinuous and continuous films at the same time. In this case the discontinuous film is the outer and the continuous film the inner layer next to the metal. In fact, this is the case on most metal surfaces where the oxide film has formed in real process conditions.

3. Modelling approaches presented in the literature for oxide film behaviour and transport processes

The behaviour of oxide films on different materials has been tentatively explained via several different modelling approaches in recent decades. Models have been created to explain the energy band structure, chemical composition, structure and growth of oxide films. However, no general agreement has been reached on the applicability of different models.

Growth of the oxide film proceeds either at the metal/film or the film/solution interface. If the growth occurs solely via deposition of species originally present in the solution, no ionic transport through the film is required. In all other cases, the transport of ionic species through the film is necessary to make film growth and the related phenomena possible.

The composition and structure of the oxide film is the factor determining whether the cation or anion species move in the film. Transport of oxygen species from the film/solution interface is needed for film growth. On the other hand, transport of cationic species from the metal/film interface contributes not only to the film growth but also to the dissolution of the film and subsequent formation of further deposits on the metal surface.

In order to enable the transport of ionic species in the oxide film, a certain minimum mobility of the species and a driving force is needed. Mobility is influenced mostly by the oxide film structure. The driving force in most cases is either a potential gradient resulting in the migration of species or a concentration gradient resulting in the diffusion of species. These driving forces can also exert a joint and simultaneous influence.

In summary, to be able to model the behaviour of an oxide film, several parallel processes and factors must be treated simultaneously. The basis for finding a suitable model to describe this behaviour is recognition of the properties or processes most affecting the nature of the film.

The features of the most important and most often cited models for oxide films are summarised briefly in this chapter. Classification of the models can be done in several ways; here it falls into two categories: 1) models explaining the electronic properties of passive films by their composition and structure and 2) models emphasising the transport of mass and charge in the film. In order to keep the amount of selected models processable, only models that have been developed to describe oxide films with crystalline structures are included. This is because in most cases presented in the literature, the oxide film on a construction material like a Ni-based alloy and stainless steel is assumed to have a continuous, crystalline structure including point defects and a thickness of more than only a few monolayers. Finally, the reasons for the development of the MCM used in this work are discussed and the basic assumptions of the model are presented.

3.1 Models explaining the electronic properties of passive films by their composition and structure

3.1.1 Semiconductor models

Energy band structure models have been used to explain the electronic properties of oxide films. Stimming and Schultze [3] derived from capacitance measurements a semiconductor model for a bi-layer type passive film on Fe. The inner Fe_3O_4 layer of the film is thought to have nearly metallic conductivity, but the outer Fe_2O_3 may behave as an n- or p-type semiconductor or insulator depending on the potential. The model takes into account the potential drops in the oxide film and in the Helmholtz layer at the film/solution interface, the energy band structure of the film and the tunnelling probability of electrons. Transfer reactions in the film are divided strictly into electron transfer and ion transfer. The electron transfer reactions are said to take place via the conduction band at low potentials in the active region, and via the valence band at very high potentials in the transpassive region. At intermediate potentials in the passive region the outer layer behaves as an insulator.

As limitations to their model Stimming and Schultze mentioned that if the thickness of the space charge layer becomes too high in comparison with the film thickness, the electrochemical data, e.g. the electrode capacity in the insulator region, becomes constant, which may make the quantitative evaluation of estimated parameters difficult. Also, the stoichiometric changes at the metal/oxide interface may change the rate of production and consumption of ferrous and ferric ions, which in the model are assumed to be produced and consumed at a constant rate. Furthermore, the electronic equilibrium in the film, which is assumed in the model, is reached in thin oxide films but may be disturbed in thicker films if the anodic current exceeds the rate of hole generation at high potentials.

Other examples of semiconductor models are that presented by Gerischer [4] for the passive film on Fe in acidic solutions and that of Delnick and Hackerman [5] for kinetics of the redox reactions on passive Fe. Using his model, Gerischer was able to explain the onset potentials for activation in acidic solutions and for water oxidation. On the other hand, Delnick and Hackerman used their approach to explain the charge transfer mechanisms in the passive film on Fe in the presence of a redox pair and the effect of pH on them.

Semiconductor models in general give important knowledge of the electronic structure of the oxide films. However, they require quite detailed knowledge of the structure and thickness of the oxide film as well as changes in them. Moreover, they explain mostly only the electronic features of the films but do not take into account the contributions of ionic transport and chemical reactions in the film or at its interfaces.

3.1.2 Chemi-conductor model

Chen and Cahan [6, 7, 8] introduced the chemi-conductor model for the passive film on Fe in 1982. It is not a true semiconductor model in the sense that it does not concentrate only on the electronic structure of the oxide film but also takes into account the movement of ionic species in the film and changes in the film composition. According to Chen and Cahan, an oxide film cannot be adequately described in terms of a classical semiconductor with relatively well-defined bandgaps and fixed dopants. Thus a chemi-conductor has been defined as a single phase insulator whose stoichiometry can be varied by oxidative and reductive changes of the valence state. This non-stoichiometry can then modify the local electronic and ionic conductivity of the film. This is equivalent to a variable doping with defects rather than foreign species.

Chen and Cahan have assumed a single phase structure containing trivalent Fe, like FeOOH, for the oxide film. The growth of the oxide film is due mostly to the transport of Fe ions. The local conductivity of the film has been assumed to be determined by a concentration of Fe^{2+} defects at the metal/film interface and the charge neutrality is sustained with protons coming from the film/solution interface. Under the influence of a potential gradient, Fe^{2+} ions migrate outward, establishing a chemical potential gradient which balances the electrostatic potential gradient. This linear chemical potential gradient corresponds to an exponential Fe^{2+} distribution following the predictions of the model by Young [9] derived earlier for niobium oxide films. The model by Young is based on the idea that as a result of non-stoichiometric defect formation at one interface, the conductivity of the film is exponentially dependent on the distance from that interface [10].

In the chemi-conductor model, the closer to the film/solution interface the profile of divalent species extends, the lower is the applied potential. At sufficiently low potentials the profile is described to reach the film/solution interface, leading to dissolution of the film. At higher potentials the profile of Fe^{2+} ions becomes steeper from the metal/film interface by stripping out the excess protons and a very thin layer of Fe^{2+} excess next to the metal surface is assumed to remain. Then virtually all of the film behaves as an insulator and the outer part of the film approaches stoichiometric composition. A further removal of protons will finally induce tetravalent Fe species into the film. As a result, an exponential concentration gradient of Fe^{4+} ions is described to extend towards the film bulk, increasing the conductivity in that part of the film. Finally, at sufficiently high potentials, a significant concentration of Fe^{4+} may reach the region enriched in Fe^{2+} close to the metal/film interface. Then an overlap of the Fe^{2+} and Fe^{4+} rich regions creates a possibility for dc conduction through the whole film and makes oxygen evolution possible.

3.2 Models emphasising the transport of mass and charge in the oxide film

Models emphasising the transport of mass and charge can be classified according to the electric field strength in the oxide film. Depending on the magnitude of the electric field strength the mathematical treatment of the transport has been carried out in different ways. It is worth introducing briefly the main differences in the transport equations for oxide films with different electric field strengths.

The transport of ionic species in a barrier oxide film can be described with a general equation by Fromhold and Cook [11]. For example, for the transport of anion, i.e. oxygen, vacancies the flux has the form

$$J_O(x) = -D_O \frac{\partial c_O(x)}{\partial x} \cosh\left[\frac{zFa\mathit{E}(x)}{RT}\right] - \frac{D_O}{a} c_O(x) \sinh\left[\frac{zFa\mathit{E}(x)}{RT}\right] \qquad (1)$$

In the case of a low ($< 10^6$ V cm^{-1}) and homogeneous electric field in the oxide film, the mathematical treatment can be simplified by assuming that $zFa\boldsymbol{E}/(RT) << 1$, $\tanh(zFa\boldsymbol{E}/(RT)) = zFa\boldsymbol{E}/(RT)$ and $\sinh(zFa\boldsymbol{E}/(RT)) = zFa\boldsymbol{E}/(RT)$. Then equation (1) can be written in the form

$$J_O(x) = -D_O \frac{\partial c_O(x)}{\partial x} - \frac{D_O}{a} c_O(x)\left[\frac{zFa\mathit{E}(x)}{RT}\right] \qquad (2)$$

Equation (2) is analogous to the Nernst-Planck transport equation. By assuming a homogeneous electric field strength the solution to this transport equation in the steady state becomes

$$J_O = \frac{zFD_O\mathit{E}}{RT} \frac{\left\{c_O(0)\exp\left[-\frac{zF\mathit{E}L}{RT}\right] - c_O(L)\right\}}{1-\exp\left[-\frac{zF\mathit{E}L}{RT}\right]} \qquad (3)$$

showing a linear dependence of the flux on the electric field strength.

If the electric field strength in the film is high ($\geq 10^6$ V cm^{-1}), the general transport equation (1) can be simplified by assuming that $(zFa\boldsymbol{E}(x)/(RT) >> 1$, $\tanh(zFa\boldsymbol{E}(x)/(RT)) \approx 1$ and $\sinh(zFa\boldsymbol{E}(x)/(RT)) \approx \exp(zFa\boldsymbol{E}(x)/(RT))/2$. By assuming homogeneous electric field strength, the steady state solution of equation (1) will be in the form

$$J_O = \frac{D_O}{2a} \exp \frac{zFaE}{RT} \left\{ c_O(0) \exp\left[-\frac{L}{a} \right] - c_O(L) \right\} \tag{4}$$

Equation (4) shows that the flux of the ionic species is exponentially proportional to the electric field strength in the film and to the oxide film thickness.

In most models presented in this chapter some value for the electric field strength has been assumed. The equations above show in a compact way the basic effect of differences in electric field strength on the treatment of the transport problem. However, these equations for the transport of ionic species under the influence of an electric field have not been used as such in all the models presented below.

3.2.1 High-Field Model

The first model for explaining the growth of oxide films on metals and semiconductors was developed by Verwey [12] already in 1935 and has been briefly summarised by e.g. Macdonald *et al.* [13] and Brusic [14]. Verwey assumed in the model that the driving force for the transport of charge carriers in the film is a high electric field, and thus the model is generally called the High-Field Model (HFM). The entire potential drop in the metal/film/solution system is assumed to occur across the film. Thus the electric field strength in the film decreases as the film thickens under potentiostatic conditions. The HFM also predicts that no steady state exists for the film thickness or for the current. Further, Verwey assumed that the rate determining step for film growth is the transfer of cations between adjacent lattice sites within the film.

Macdonald *et al.* [13] have criticised the HFM, because the model does not take into account the existence of steady states in the current and film thickness, which existence they have experimentally proven by studying tungsten, W, in phosphate buffer solutions.

3.2.2 Mott-Cabrera model

Another example of the early models for oxide film growth is the model proposed and developed by Mott and Cabrera [15, 16, 17], which has been reviewed for example by Macdonald *et al.* [18].

In the Mott-Cabrera model the film growth is assumed to be due to the transport of metal cations across the oxide film to the film/solution interface where they react with the electrolyte. Furthermore, the penetration of cations through the films is assisted by a high, $> 10^6$ V cm^{-1}, and constant electric field existing within the oxide film. The potential drop across the film is assumed to be constant and hence independent of the film thickness. The rate-limiting step for film growth is assumed to be the emission of metal cations from the metal into the film at the metal/film interface. Resulting from this model an inverse logarithmic rate law for film growth has been obtained.

Macdonald *et al.* [18] criticised the Mott-Cabrera model on the basis that the model does not take into account the passive film dissolution at low pH or anion transport, which also plays an important role in film growth according to experimental results. Kirchheim *et al.* [19, 20, 21] considered the assumption of Mott and Cabrera concerning a constant potential drop at the film/solution interface under non-stationary conditions to be an obvious limitation of the model. The criticism was based on measurements by Vetter and Gorn for Fe in an acidic sulphate solution [22]. Further, Castro [23] criticised the Mott-Cabrera model for assuming that the concentration of diffusing ionic species in the film does not vary with distance in the film, the ionic movement being determined only by the influence of the electric field. According to Castro this is not the case in oxide films formed on transition metals, like Fe and Ni, and on their alloys.

3.2.3 Models developed by Vetter and Kirchheim for the formation of passive films

Kirchheim *et al.* [19, 20, 21] have described the formation of passive layers on Fe and its alloys based on the concepts of Vetter [24]. In the Vetter-Kirchheim model the kinetics of the formation of the passive layer is described with regard to the processes at the metal/film and film/solution interfaces and the potential gradient within the film. The electric field strength in the film is assumed to be high, of the order of 10^6–10^7 V cm^{-1}, in accordance with the Mott-Cabrera model [15, 16, 17]. Further, Vetter explained the electric field strength to be a function of the oxide composition and the ionic current density or the applied potential. This means that when a certain current is applied, the oxide film composition at any distance is uniquely determined. In the Vetter-Kirchheim model the nature of the moving species has not been exactly defined, but the transport is proposed to occur either by a cation vacancy, an anion vacancy or an interstitial cation mechanism. The total ionic current in the film can be divided into two parts: the current due to the dissolution of the metal cations from the film to the electrolyte, and the current responsible for the formation or decomposition of the film both taking place at the film/solution interface. According to Macdonald *et al.* [25], the occurrence of film formation and dissolution at the film/solution interface requiring at the same time injection and removal of the same species, O^{2-}, is physically impossible. Thus it is likely that the formation or decomposition of the film do not both occur at the film/solution interface.

Good features of the Vetter-Kirchheim model are that it couples the ionic current densities through the film with those through the film/solution interface and takes into account the relaxation effects, i.e. the possibility of transient phenomena in the film. This means that, if the current through the passive film changes, the system can react either via a change in the electric field strength or via a change in the concentration of moving species. The latter case means that during non-stationary periods the concentrations of moving species may change at the interfaces of the film, giving rise to enrichment or depletion of some of the species. A finite relaxation time is needed to level the changes in concentration of these species within the film after perturbations. According to Castro [23] the use of the description of Mott and Cabrera (Chapter 3.2.2.) for the ionic flux in the film during relaxation is an imperfection in the Vetter-Kirchheim model.

Gabrielli *et al.* [26] considered the relaxing parameter to be the density of mobile Fe^{3+} in the barrier film on Fe. Accordingly, they included the effect of the concentration of Fe^{3+} in the expression for the total passive current. Gabrielli *et al.* used the electrochemical impedance spectroscopy to measure the electrochemical responses and extract more detailed analysis of the behaviour of Fe. They derived a model for the impedance response, which has been found to reproduce quite well the features of the experimental impedance spectra of the passive film on Fe. Also Carranza *et al.* [27] modified the Vetter-Kirchheim model by deriving more exact equations for the potential drops at the interfaces of the oxide film.

3.2.4 Castro's model for the impedance response of passive films on transition metals and alloys

Castro [23, 28] used an impedance technique to extract data concerning the transport properties of passive Fe in borate buffer solutions. On the basis of the measurement results, Castro developed a model in which the ionic transport in the film is coupled to the electrochemical reactions taking place at both metal/film and film/solution interfaces. Castro assumed in the model that

1. The oxide film on Fe consists of non-porous Fe_2O_3 and the ionic transport in the film is assisted by the high, $\sim 10^6$ V cm^{-1}, and homogeneous electric field.

2. The contribution of the induced electric field during measurement to the total field is small in comparison to that required for film growth.

3. The perturbing ac signal used in impedance measurements does not affect the oxide thickness

4. The applied potential is consumed in the film and at both interfaces.

5. The passive current on Fe as well as the concentration of oxygen atoms in normal lattice positions, close to the film/solution interface, is independent of the applied potential.

By using a similar kind of notation for reactions to that used by Macdonald in PDM (Chapter 3.2.6), and by applying the general transport equations of Fromhold and Cook [11], Castro derived a transfer function showing that the impedance response is determined not only by the charge transfer reactions at the interfaces but also by the transport of Fe vacancies through the film. This means that the electrochemical behaviour of oxide films on Fe cannot be described solely by concentrating on the reactions at the interfaces, but the role of the transport of ionic species in the film must also be taken into account.

3.2.5 Grain boundaries-pores model of aqueous solutions at high temperatures

Robertson [29, 30] was one of the first researchers to develop a model for high temperature aqueous corrosion. He constructed a model for the growth of duplex layers like Fe_3O_4 during corrosion of ferrous alloys. The model assumes that the inner oxide layer of the film grows by *in situ* oxidation of the metal following the ingress of water along micropores in the oxide while the outer layer grows by outward diffusion of metal ions along grain boundaries. The micropores are created in the oxide as a result of growth stresses due to mismatch of molar volumes of the oxide and the metal. The Fe ion flux in the oxide is carried as vacancies under alkaline conditions and as interstitials under acidic conditions. The corrosion rate is dependent on pH and increases in acidic and in alkaline conditions because the concentrations of these defects increase as pH changes. On the other hand, the corrosion rate of the material is independent of the presence of the outer layer, of the degree of saturation of the water with the corrosion product, and of the water flow rate.

One criticism of Robertson's model could be that the preferential paths and driving forces for ion transport, as well as the nature of mobile defects, have not been thoroughly clarified. The egress of cations from the metal/film interface also needs further confirmation: if micropores in the film extend to the metal, as Robertson assumes, the outward transport of metal ions along these pores cannot, in all likelihood, be totally excluded.

3.2.6 Point Defect Model

The Point Defect Model (PDM) developed by Macdonald *et al.* [18, 31–36] is perhaps the most well-known oxide film model nowadays. It was originally developed to explain the growth [18], breakdown [31] and impedance characteristics [32] of passive films on Ni, Fe and Fe-based alloys. It was later extended to consider the properties of barrier passive films under steady state conditions and finite-rate interfacial kinetics [34, 35]. The basic features of the PDM are presented in Fig. 2.

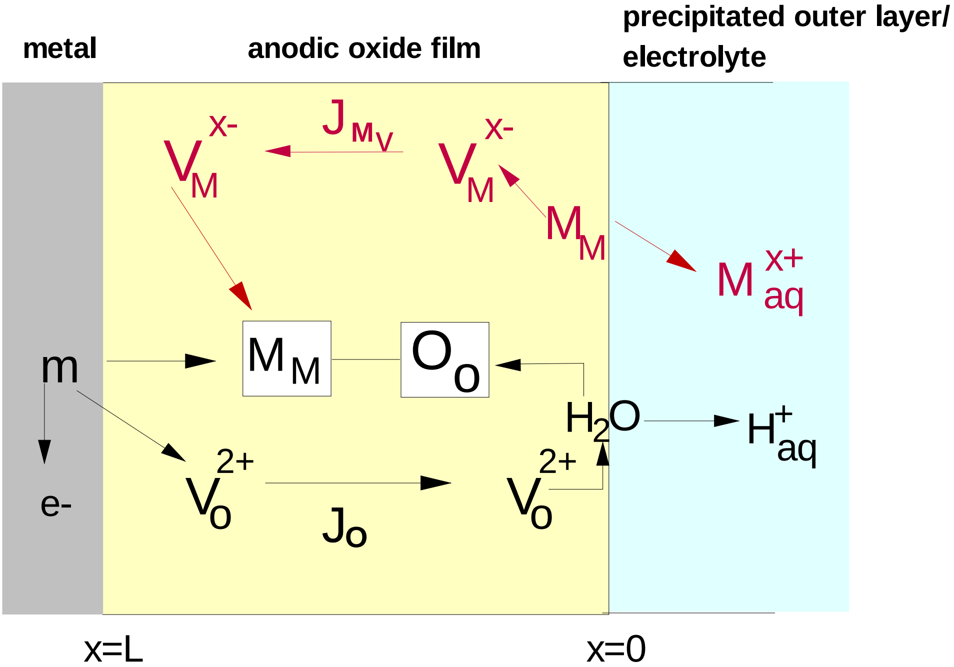

Figure 2. Schematic representation of the processes taking place in a barrier oxide film according to the Point Defect Model [36, modified]. The fluxes of ionic species, J_O *and* J_{M_V}*, can be described using the Nernst-Planck equation shown above (Eq. 2 for oxygen vacancies).*

The PDM emphasises the role of mobile charged point defects in conducting the current through the film. The main assumptions of the PDM can be summarised as follows:

1. When the external potential is more noble than the Flade-potential, i.e. the potential at which the current achieves its minimum value after passivation (Fig. 1), a continuous oxide film with composition $MeO_{y/2}$, where y is the valence of the cation, is formed on the metal surface.

2. This oxide film contains high concentrations (> 10^{20} cm^{-3}) of point defects such as cation vacancies, V_M^{x-}, and anion vacancies, V_O^{2+}, electrons and electron holes.

3. Anion vacancies, V_O^{2+}, injected at the metal/film interface and annihilated at the film/solution interface, contribute to the film growth.

4. Cation vacancies, V_M^{x-}, injected into the film at the film/solution interface and annihilated at the metal /film interface, contribute to metal dissolution through the film.

5. The transport of ions through the film is described using the Nernst-Planck equation (Eq. 2).

6. The transport of different charge carriers is independent of each other in the oxide film.

7. The rate determining step for processes involving cation and anion vacancies was originally assumed to be the transport of vacancies through the film. This means that the cation and anion vacancies are in their equilibrium states at the corresponding interfaces of the oxide film. Afterwards, Macdonald *et al.* assumed the rate determining step to be located at the metal/film interface.

8. The oxide film sustains a high electric field (~ 10^6 V cm^{-1}), which is characteristic of the film composition and structure and independent of the film thickness and the applied potential. The band-to-band tunnelling of electrons and holes generates a counter-electric field that buffers the field within the oxide. The buffering prevents the electric field strength in the oxide from exceeding the breakdown field strength and the destruction of the film.

9. The applied potential is distributed as interfacial and bulk potential drops, and the potential drop at the film/solution interface is proportional to the applied potential and the pH of the solution.

Based on these assumptions, Macdonald *et al* derived diagnostic criteria and an impedance model to explain the properties of different oxide films at a quantitative level. The PDM has been found to account successfully for the linear dependence of the oxide film thickness on the potential and for the exponential dependence of the steady state current on the potential found experimentally for many systems. Also the impedance responses of e.g. Ni in phosphate and borate buffers have been successfully simulated using this model [32, 33].

However, several assumptions made in the derivation of the PDM need to be re-evaluated. The most important discrepancy in the theory is the use of the Nernst-Planck equation for the transport of defects, observed and criticised also by Guo *et al.* [37]. Macdonald *et al.* have stated several times that the assumed electric field strength in the film is of the order of 10^6 V cm^{-1}. Such a high electric field does not fulfil the requirement $zFa\boldsymbol{E}/(RT) << 1$ included in the derivation of the Nernst-Planck equation (Eq. 2, on page 22). Thus the use of the exponential dependence of the flux on the electric field strength due to high-field assisted migration of defects would be more correct.

Furthermore, the PDM states explicitly as an assumption that the oxide film is electronically conductive, but seems to be experimentally proven valid mainly for electronically insulating and wide band-gap semiconducting films. Also, the concept of independence of the electric field strength on applied potential and film thickness is not straightforward, although its influence on quantitative results is probably rather insignificant. Macdonald *et al.* [13, 32, 33, 38–41] made a great deal of experimental effort to prove this assumption as well as the assumptions concerning the existence of steady state current and thickness in the film using W, Zr, Ta, Ni and Fe in different environments. According to them all these assumptions are the major differences between the PDM and the early high-field models of Verwey (Chapter 3.2.1), Mott and Cabrera (Chapter 3.2.2) and Vetter and Kirchheim (Chapter 3.2.3)

The PDM assumes also that the reactions at both the metal/film and film/solution interfaces are in electrochemical equilibrium, which means that the reactions at the interfaces are reversible. Further, the model assumes that the build-up of the potential drops at these interfaces is instantaneous, i.e. no relaxation of the charge carrier concentration is taken into account. This means that the model cannot take full account of the transient processes during passive film growth and dissolution.

Considering the transport processes of charge carriers, Macdonald *et al.* first neglected the possibility of interstitial cations being charge carriers for any other material studied but Zn [42] for several years. However, in their recent papers on Fe [43, 44] they have recognised this possibility. The presence of interstitials has been concluded to be possible due to the oxide structure, and thus interstitials have been selected for one possible type of charge carriers also by Betova *et al.* [45] and Davenport *et al.* [46].

3.2.7 Modifications of the PDM

The basic concepts of the PDM are widely used. Several researchers have, however, modified the model in order to explain more complex phenomena than the original model does and, on the other hand, to clarify the discrepancies between the model and the experimental results. Pyun and Hong [47] and De Wit and Lenderink [48] have proposed that the transport of metal cations contributes not only to the metal dissolution as assumed in the PDM but also to the film growth. In the opinion of Pyun and Hong [47] also the adsorption of water molecules at the film/solution interface has to be included in the PDM. Based on these additional features Pyun and Hong have calculated the electric field strength for passive films on Fe and Ni in acidic solutions to be between $7\times10^4 \ldots 9\times10^5$ V cm^{-1}. This is not, however, in line with the assumption No. 8 on page 29 that the electric field strength in the film is very high.

Battaglia and Newman [49] have used the concepts of the PDM to derive a comprehensive general model including any number of species that may react homogeneously and heterogeneously, and also including both high-field and low-field transport in the oxide film. The model also treats the effects due to variations in the adjacent solution phase and can be used to explain film growth and dissolution. On the basis of their model, Battaglia and Newman have been able to explain passivation features of Fe in a borate solution and calculate the diffusion coefficient for Fe^{3+} interstitials (2×10^{-16} cm^2 s^{-1}). However, only the low-field transport has been numerically simulated, because the equations for the high-field case turned out to be too difficult to be implemented. This drawback means that the model is most probably too complicated to be used more generally.

Krishnamurthy *et al*. [50], on the other hand, have extended the PDM to a continuum model for time-dependent formation of passive oxide films on metal surfaces. The model extends the steady-state analysis of the PDM to explicit time dependence and treats oxide film growth more extensively than the model of Battaglia and Newman [49]. The model also introduces boundary conditions based on jump mass balances in order to describe the film formation as a moving boundary problem. The jump mass balances relate the fluxes of ionic species to interfacial reaction rates and the motion of the film boundary. The predictions of the model have been found to be satisfactory at a qualitative level with the experimental data on Ni.

Summarising on the PDM and its modifications, it can be said that the model includes many general features that are widely accepted. However, as can be seen from the list of deficiencies given above and from the modifications to the model, the PDM does not explain comprehensively all the features observed in the behaviour of oxide films on different materials, and it includes several features which need further justification.

3.2.8 Development of the Mixed Conduction Model

The Mixed Conduction Model (MCM) is used in this work to extract quantitative data on the electrochemical behaviour of Ni- and Fe-based alloys. The MCM is based on the features introduced in the PDM. The motivation for developing the MCM from the PDM has been to obtain more quantitative estimations for the transport parameters of oxide films than those obtained with the PDM, and also to couple the electronic and ionic properties of an oxide film. The steps of development of the MCM are introduced briefly in the following.

As mentioned above in Chapter 3.2.6, the build-up of the potential drops at the metal/film and film/solution interfaces is assumed to be instantaneous in the PDM. Thus no existence of possible space or surface charges and their effects on the behaviour of the passive film have been included in the model. For example, König and Schultze [51] and Fromhold [52], Lohrengel [53] and Kanazirski *et al.* [54] discussed the effects of the space charge on film growth kinetics. The space charge can be in the form of immobile charged impurities or immobile trapped carriers, or in the form of mobile ions in the bulk of the film. The ideas of König and Schultze and Lohrengel seem capable of explaining the non-steady state growth of passive films on a range of metals. However, their models do not take into account the possible influence of space charge on the kinetics in steady state conditions. Kanazirski *et al.* [54] proposed a space charge approach, in which this influence is included, to model the film growth in galvanostatic and potentiostatic conditions.

The major deficiencies in the existing theories including the concept of space charge presented so far are that

1. they neglect the role of the interfacial reactions and interfacial potential drops in film growth,

2. they assume that both positive and negative defects move through the growing film, but usually only the formation of a space charge of a single sign is considered,

3. the effect of space charge formation on the structure of the oxide film has not been theoretically or experimentally explored in detail, and

4. none of these models considers the possibility of coupling between the ionic and electronic conduction within the oxide and at the interfaces with the substrate and the solution.

The next step towards a more complete model was the Surface Charge Assisted High-Field Migration Model (SCAHFM) for anodic film growth originally proposed by de Wit *et al.* [55] and later developed by Bojinov *et al.* [56–58]. The nature of the oxide film and the reactions taking place in the film in the SCAHFM are based on the concepts introduced in the PDM (Chapter 3.2.6), but the concept of accumulation of defects creating surface charges close to the metal/film and film/electrolyte interfaces has been added. This has been done in order to explain the response of metal/oxide film/solution systems to perturbations in the current or potential. Also the time dependence of the surface charges was taken into account. Further, differently to the PDM the general transport equations of Fromhold and Cook [11] are used instead of the Nernst-Planck equation under the influence of the high electric field in the oxide film.

In the SCAHFM the high rate of injection of oxygen vacancies at the metal/film interface results in the formation of an n-type semiconductive interfacial region, and the corresponding injection of cation vacancies at the film/solution interface results in the formation of a corresponding p-type semiconductive interfacial region. Thus the passive film can be presented as having a highly-doped n-type/insulator/p-type structure. At steady state, the transport of oxygen vacancies is assumed to be much faster than that of cation vacancies. In the transient regime following a perturbation of potential or current around the steady state, the migration of oxygen vacancies towards the film/solution interface is enhanced by a negative surface charge formed by the accumulation of cation vacancies generated at the film/solution interface.

Even though it is able to predict the electrochemical behaviour of several materials, the SCAHFM takes into account only the contribution of ionic charge carriers to the total conductivity, but not that of the electronic charge carriers. For this reason the development of the model has been continued and the model used in this work, i.e. the MCM, can be considered to remove also this deficiency when the prevailing electrochemical conditions are known.

The theory of the MCM has been introduced thoroughly in Papers I and VII for room temperature and in Paper VII for the first time for high temperatures. The MCM is at the conceptual level quite similar to the PDM. However, some basic assumptions made in these models differ to some extent and thus it is worth summarising the assumptions made for the MCM:

1. The film consists mainly of homogeneous single-phase oxide and the amount of hydroxide in the film is negligible. Thus the possible doping of the layer with incorporated hydrogen e.g. playing the role of electron donor

is not taken into account. The stoichiometric composition of the oxide varies gradually with potential without abrupt structural changes.

2. Possible ionic charge carriers in the film are anion, i.e. oxygen, vacancies, interstitial cations and cation vacancies.

3. A certain concentration of oxygen vacancies is maintained in the film, in order to explain the growth of the film via the inward-motion of oxygen ions.

4. The electric field strength in the film is assumed to be homogeneous and independent of potential, while the film thickness is assumed to be proportional to the applied potential. However, very recent thickness measurements indicate that the latter assumption may not be fulfilled at high temperatures.

5. For the transport of ionic species, the high-field approximation (Eq. 4, page 23) is used at room temperature and the low-field approximation (Eq. 3, page 22) at high temperatures, i.e. the electric field strength is assumed to decrease as the film becomes thicker and/or more defective at high temperatures.

6. An exponential dependence on the local potential drops is assumed at both interfaces for the interfacial rate constants.

7. Each ionic point defect in the film plays the role of an electron donor or acceptor. This means that it is accompanied by an electronic defect that contributes to the electronic conductivity in the film.

8. The main contribution to the measurable film resistance comes from the part of the film in which the defect concentration and thus also the conductivity of the film is at its minimum.

The major differences between the PDM and MCM are included in assumptions 5 and 8, i.e. according to the MCM the Nernst-Planck equation can be used only to describe the low-field assisted transport processes (5) and the local electronic conductivity is linearly dependent on the local ionic defect concentration (8).

In the MCM the impedance of the metal/film/solution system is a combination of the impedances of the interfaces and that of the bulk film. For the passive film in the steady state the interfacial impedances can be usually neglected, because the reactions at the interfaces are either very fast compared with the transport in the oxide film, or the capacitances corresponding to these reactions are very large so that the impedances are not distinguishable. The film impedance consists of the electronic and ionic contributions. Using the general transport equations given by Fromhold and Cook [11] and defining the appropriate boundary conditions, the concentration profiles for different ionic charge carriers in the film can be defined. Further, the electronic conductivity is proportional to the concentration of defects, and equations describing the electronic conductivity can be derived for both low and high potentials according to the type of charge carriers having the strongest effect. The transfer function for the electronic contribution to the total conductivity and to the film impedance depending on the film thickness and potential can be derived from an explicit physico-chemical model, being mathematically equivalent to the formal model of Young [9] for insulating layers with defect induced conductivity. The ionic part of the film impedance, on the other hand, often reduces to a resistance, if the apparent diffusion coefficient is high, or to a Warburg impedance in the case of a low diffusion coefficient.

The MCM has been successfully used previously to explain the features of several metals and alloys in the passive region at room temperature [59–62]. In this work the model has been used to obtain estimates of kinetic and transport parameters from the electrochemical behaviour of Ni-Cr and Fe-Cr alloys both at room temperature and, for the first time, at high temperatures. In addition to the steady state oxide films, the MCM can be also modified to describe processes either during anodic oxidation and passivation at low potentials or during transpassive oxidation and dissolution at high potentials. In these cases the oxidation and dissolution reactions at the metal/film and film/solution interfaces, respectively, are the major reactions that determine the electrochemical response. The effect of the transport processes in the film on the electrochemical response depends on the material and need not be taken into account in the transpassive model for all materials. The model describing the oxidation and dissolution in the transpassive region has been applied previously to several materials [63–65], and in this work the model has been further developed and applied to Ni-Cr alloys for the first time. In its complete form the model includes the oxidation of Cr, dissolution of metal cations from the outermost film, the adsorption of intermediates at the film/solution interface and their self-catalytic effect on dissolution. The detailed theory behind the model and the scheme of processes occurring during transpassive dissolution are given in Papers III and IV.

4. Experimental

The aim of this work has been to study the effect of different environments on the electrochemical behaviour of several Ni- and Fe-based alloys. Mostly binary alloys have been used in order to find out also the effects of the amount of alloyed Cr on the electrochemical responses.

The materials used in this study are shown in Table 1. The contents of the alloys have been given in percent by weight (wt-%). Alloys UNS N06600 (Alloy 600, 14–17 wt-% Cr, 6–10 wt-% Fe, ≤ 0.15 wt-% C, ≤ 1 wt-% Mn, Ni bal.) and UNS N10276 (Alloy C276, 4–17 wt-% Cr, 4–7 wt-% Fe, ≤ 0.02 wt-% C, ≤ 1 wt-% Mn, 15–17 wt-% Mo, 3–5 wt-% W, ≤ 0.35 wt-% V, ≤ 2.5 wt-% Co, Ni bal.) were used to study the effect of pH on the passive and transpassive behaviour in acidic solutions. On the other hand, Fe-12%Cr was used to study the effect of temperature in a slightly alkaline solution. Other materials were used for all the measurements, i.e. to study the effects of both pH and temperature.

Table 1. Materials used in measurements.

PURE METALS	Ni-BASED ALLOYS	Fe-BASED ALLOYS
Ni	Ni-10%Cr	Fe-12%Cr
Fe	Ni-15%Cr	Fe-25%Cr
Cr	Ni-20%Cr	
	UNS N06600	
	UNS N10276	

The effects of pH were studied by comparing the results obtained at pH 0, 5 and 9.3. The electrolytes used to study the effect of pH were 1 M H_2SO_4 (pH 0), 1 M Na_2SO_4, the pH value of which was adjusted to 5 with sulphuric acid, and 0.1 M $Na_2B_4O_7$ (pH_{25} 9.3). The effect of temperature on Ni-Cr alloys was studied in 0.1 M $Na_2B_4O_7$ solution at 200°C (pH_{200} 8.7) and 300°C (pH_{300} 9.1). For Fe-based materials the high temperature measurements presented in Paper VI were carried out only at 200°C. All the measurements presented in this summary and in the appended papers have been repeated at least three times.

The measurement techniques used in this work were conventional linear sweep cyclic voltammetry (Papers I, III–VI), rotating ring-disc voltammetry (Papers I, III, IV), electrochemical impedance spectroscopy (EIS) (Papers I–VII), contact electric resistance (CER) technique (Papers I–VII) and contact electric impedance (CEI) technique (Papers VI, VII). The basic ideas of the CER and CEI techniques can be summarised as follows:

The CER technique is based on the measurement of the electric resistance across a solid – solid contact surface using direct current. During the measurement the surfaces are brought together and pulled apart at regular intervals. While the probes are apart their surfaces are exposed to the influence of the environment. The potential of the probes can be controlled by a potentiostat. When the controlled probes are brought into contact, a direct current is passed through the contact surfaces and the resulting potential is measured in order to determine the resistance of the surface film. With respect to the mode of signal acquisition, the CER technique can be regarded as a slow pulse technique, i.e. a transient technique in the time domain. A more detailed description of the CER technique is given in Refs 66 and 67.

In the CEI technique the oxide film is formed as in the CER technique. The electric and electrochemical properties of the oxide film are measured while it is in contact with two electronic conductors, i.e. with the substrate metal and an inert noble metal probe. The CEI technique can be regarded as an analogue of the CER technique in the frequency domain. In the CEI technique, different solid-state processes taking place at different rates in oxide films can be distinguished, because the measurement configuration of the CEI emphasises the transport processes in the film itself in respect to the interfacial charge transfer reactions. The CEI technique is introduced more thoroughly in Refs 45 and 68.

5. Results

5.1 Effect of pH and Cr content on the electrochemical behaviour on Ni-Cr and Fe-Cr alloys at room temperature

5.1.1 Electrochemical behaviour of oxide films on Ni-Cr and Fe-Cr alloys in the passive region

The aim of the measurements performed in solutions with different pH values was to find out how the pH and Cr content of the alloy affect the protectiveness of the oxide films on Ni- and Fe-based alloys in the passive region.

Effect of pH

The basic effects of increasing pH can be summarised by showing the results for Ni-20%Cr and Fe-25%Cr (Figs 3 and 4). The results are compiled from Papers I, III, VI and Refs 60 and 65. The resistance curve for Ni-20%Cr at pH 9.3 measured during the positive-going potential sweep in Fig. 3b is shown here for the first time. On Ni-20%Cr the non-stationary currents measured using voltammetry decrease in the passive region when pH increases from 0 to 5, and the oxidation currents in the active region before passivation diminish (Fig 3a). The passive and transpassive regions also shift in the negative direction on the potential scale with increasing pH. The voltammetric behaviour of Ni-20%Cr at pH 5 is quite similar to that at pH 9.3 except that the passive region is wider at pH 9.3. In the transpassive region at pH 9.3 a plateau is observed on Ni-20%Cr. This has been concluded to be due to an accumulation of oxidation products on the electrode surface (Paper I). In general, the voltammetric behaviour of Ni-20%Cr is in agreement with thermodynamic equilibrium calculations [69].

An interesting effect of pH on the behaviour of Ni-20%Cr is seen in resistance measurements (Fig. 3b) carried out with the CER technique as the increase of resistance at pH 5 takes place at lower potentials than at pH 0 or 9.3. This feature may be due to fact that at pH 0 the dissolution of the metal through the oxide film is stronger and the film does not grow at low potentials as easily as at pH 5. On the other hand, the film structure and also the dependence of the resistance on potential at pH 9.3 are most probably quite different from those at pH 5. These assumptions are supported by simulations using the MCM at different pH (see Table 2 on page 47). Moreover, the resistance measurements (Fig. 3b) indicate that the resistance values in the passive region are not very stable, but the resistance starts to decrease right after reaching the maximum value. The resistance maxima are also located at potentials at which the current in voltammetric measurements (Fig. 3a) starts to increase indicating the onset of transpassive oxidation.

The voltammetric behaviour of Fe-25%Cr (Fig. 4a) changes almost in a similar way with increasing pH to that of Ni-20%Cr; the passive state current decreases and the potential region indicating active-passive-transpassive behaviour shifts in the negative direction on the potential scale. The latter observation is an expected result on the basis of thermodynamic equilibrium calculations [69]. At pH 5 the passive region on Fe-25%Cr, according to voltammetric measurements, starts at lower potentials and is remarkably wider than at higher or lower pH. At pH 9.3 secondary passivation takes place at high potentials, which is not observed at lower pH.

Judging from the resistance measurements (Fig. 4b) the passive region indicating high resistance values is noticeably narrower at pH 0 than at higher pH, which is in agreement with the voltammetric results (Fig. 4a). However, no big differences in the dependency of the resistance on potential at low potentials can be observed between the results obtained at pH 5 and 9.3. The passive region starts roughly at the same potential at both pH values, which is a different result from those obtained with voltammetry (Fig. 4a). At pH 9.3 the secondary passivation is also observed in the resistance measurements, as the resistance of the oxide film stays high up to potentials at which the current in voltammetric measurements increases strongly in the transpassive region.

The differences in shapes of the voltammetric curves between Ni-20%Cr and Fe-25%Cr in the passive region are quite small. However, the resistance curves of these materials are quite different in shape compared with each other: the resistance values of Fe-25%Cr are higher and more stable than those of Ni-20%Cr in the passive region. Also the potential region of the increased resistance level from the value of the bare electrode surface measured at low potentials is wider on Fe-25%Cr than on Ni-20%Cr. These observations can be taken as a proof that in order to compare materials with each other thoroughly, a combination of several measurement techniques is needed.

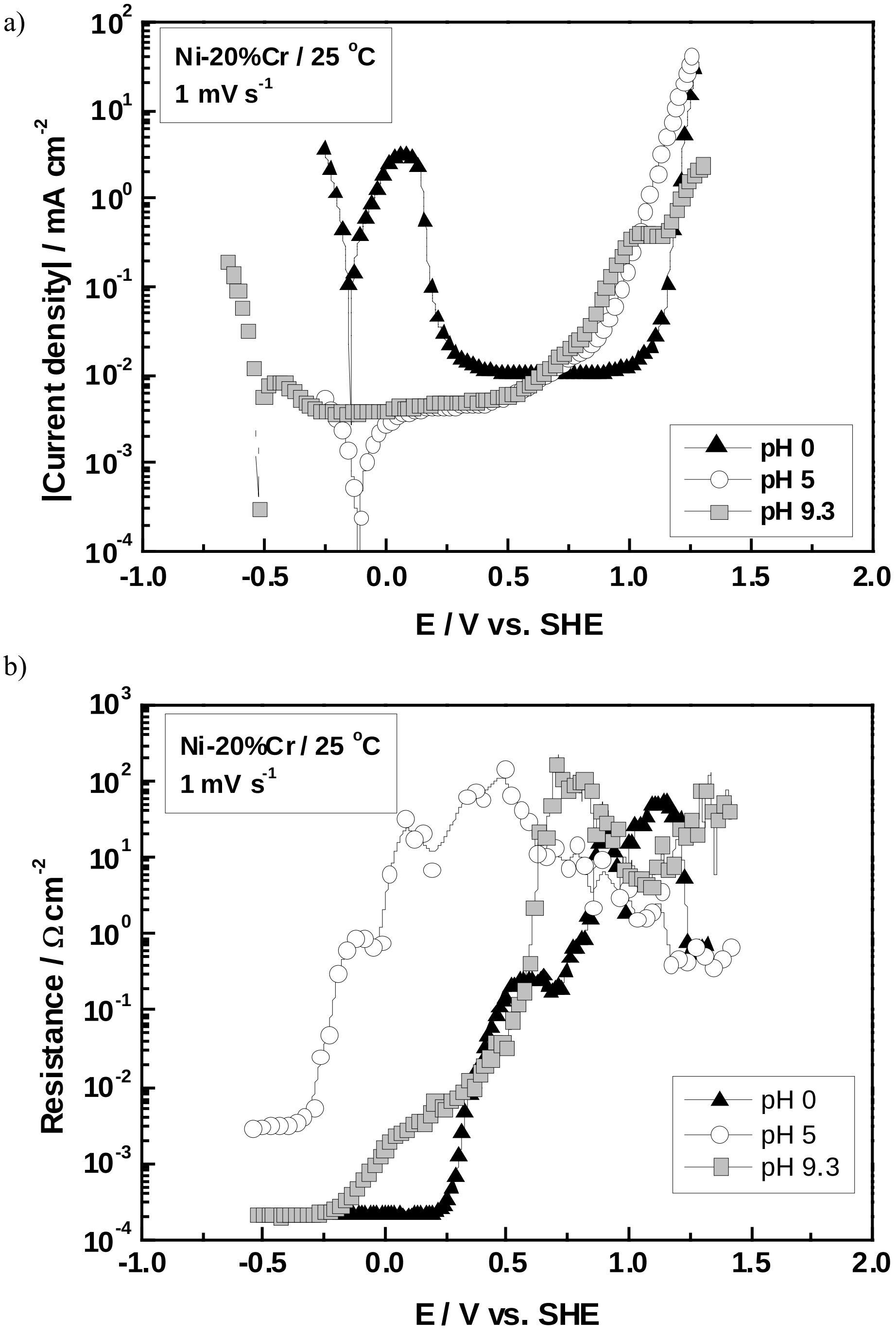

Figure 3. Effect of pH on a) the voltammetric and b) the resistance behaviour of Ni-20%Cr.

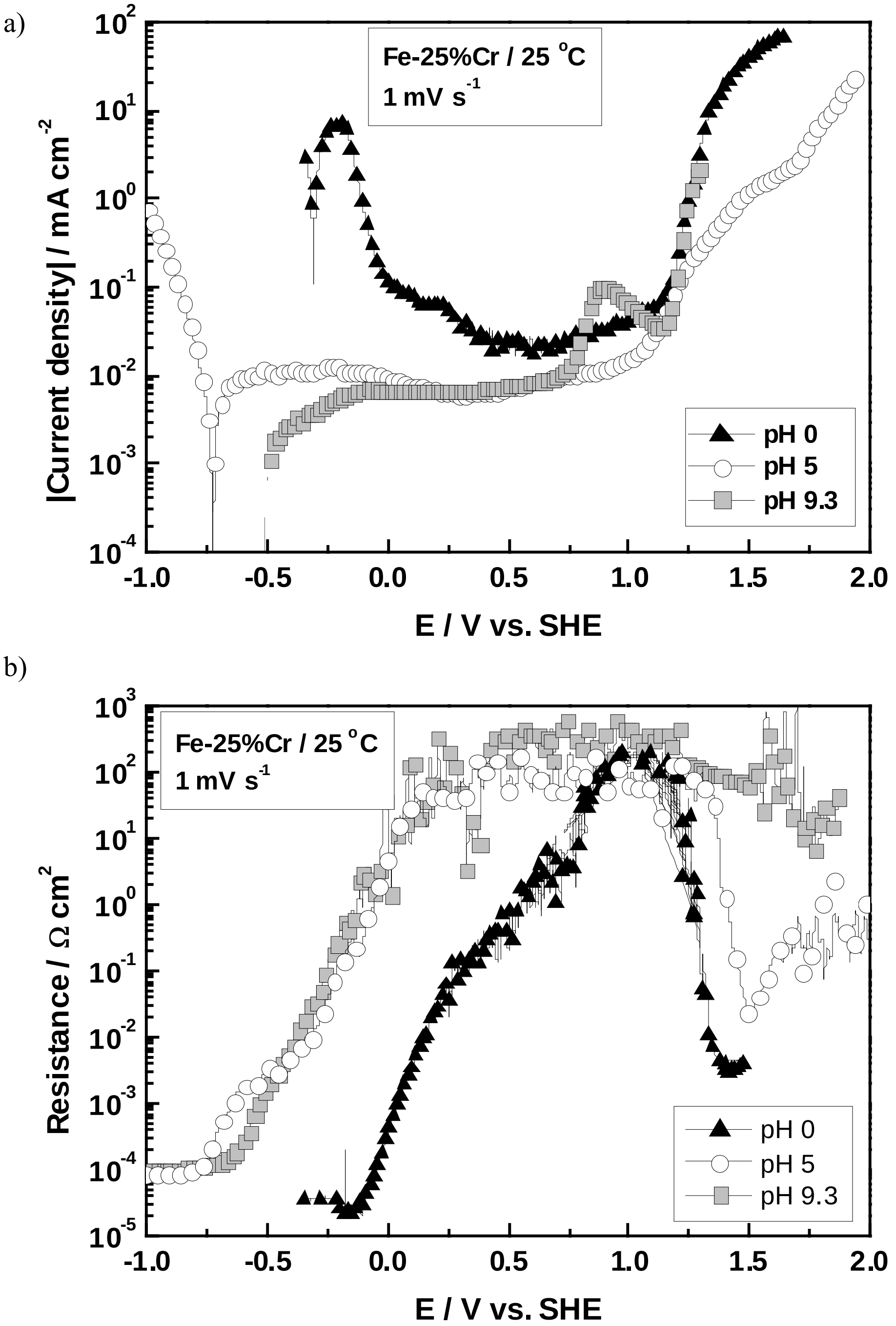

Figure 4. Effect of pH on a) the voltammetric and b) the resistance behaviour of Fe-25%Cr.

Effect of the amount of alloyed Cr in the passive state

The effect of the amount of alloyed Cr at low potentials and in the passive state on the electrochemical behaviour of Ni-Cr and Fe-Cr alloys is best observed in the voltammetric and resistance measurements (Papers I, III, IV and VI and Ref. 65).

On Ni-based alloys, already 10 wt-% Cr has been found sufficient to shift the passive region in the negative direction on the potential scale, as well as to decrease the current density and increase the resistance level in the passive region from the values of pure Ni. The effect is almost the same at all pH values studied. Also, the dependence of the increase in resistance on potential is higher the higher the amount of Cr in the alloy. The electrochemical responses measured with Ni-20%Cr are already quite Cr-like, and the effect of Ni on the electrochemical behaviour is quite small on this alloy. Furthermore, on the commercial UNS N06600 and UNS N10276 containing also other alloying elements than Cr, the passivation in acidic environments has been found to be more complete than on the binary Ni-15%Cr alloy (Paper IV).

An interesting feature emerging from the measurements is that the Ni-15%Cr alloy has been found to show electrochemical responses that often differ from those of other Ni-Cr alloys or pure Ni and Cr. This observation can be considered to confirm the suggestion of Oblonsky and Ryan [70, 71] that at a threshold content between 8 and 16 wt-% Cr the structure of the film changes, leading to higher reaction rates.

On Fe-Cr alloys the higher amount of Cr also leads to decreased current in the active and passive regions and to lower onset potential of the transpassive region. However, the effect of Cr on the resistance levels is twofold (Paper VI and Ref. 65). If the resistance is measured using probes both made of the studied alloy, the resistance levels of the films on Fe-Cr alloys in the passive region become higher the higher the amount of Cr in the alloy. On the other hand, if the other probe for the CER measurement is made of an inert material, e.g. Ir, the measured resistance of the oxide film in the passive region is lower the higher the amount of Cr in the alloy. This difference in resistances has been observed also on pure Cr, but is not so well pronounced on pure Fe. This feature has been explained by Bojinov *et al.* [62] to be due to an decreased probability of direct tunnelling of electrons when using CER probes made of the same material. When such probes are used, the thickness of the oxide film formed on the surface of the alloy is double the film thickness in a resistance measurement using an inert probe together with a probe made of the studied material. In addition, the exponential decay of the concentration of point defects acting as donors or acceptors with distance from the respective interface greatly diminishes the probability of resonance tunnelling, which is inversely proportional to the distance between resonance centres [62]. A similar comparison between the results obtained with different CER measurement methods cannot be performed on Ni-Cr alloys because the resistance measurements on Ni-Cr alloys in this work were performed only using probes made of the studied material.

In summary, the effect of alloyed Cr seems to be quite similar on both Ni- and Fe-based alloys in the passive region. In the passive region the resistance levels of oxide films, however, are higher on Fe-Cr alloys (Figs 3b and 4b and Paper II) at all pH values studied. The main difference in voltammetric measurements between Ni-Cr and Fe-Cr alloys is observed in the transpassive region where the current drop towards secondary passivation decreases on Ni-Cr alloys and increases on Fe-Cr alloys the higher the amount of Cr in the alloy.

Simulations using the MCM

Although the voltammetric behaviour of Ni- and Fe-based alloys has been found to be rather similar in the passive region, the resistance measurements have shown that differences in the film conductivity between Ni-20%Cr and Fe-25%Cr can be several orders of magnitude (Figs 3b and 4b and Paper II). In order to extract more detailed data on the differences between Ni-Cr and Fe-Cr alloys, the impedance results measured at different pH were simulated using the MCM. One possible set of the most relevant parameters collected from Paper II and Ref. 45 for steady state oxide films on Ni-20%Cr and Fe-25%Cr at different pH is shown in Table 2. The parameter values for Ni-20%Cr at pH 9.3 were evaluated by assuming the dissolution rate of metal ions in the transpassive region to be the same as on Fe-25%Cr. This was done because more exact values for Ni-20%Cr cannot be calculated, since the CEI data used in calculations for ferrous alloys at pH 9.3 does not show any frequency dependence on Ni-based alloys. The films on Ni-based alloys behave as pure resistances in the CEI measurements and the electrons tunnel through the film. This means that the model cannot be used as such to predict the transport properties of oxide film on Ni-based alloys at high pH at room temperature. Furthermore, the resistance of ionic transport through the film on Ni-20%Cr cannot be calculated from the conventional impedance data either. On the other hand, the CEI data is not needed at low pH due to the fact that the resistance of the ionic transport through the film can be calculated from the conventional impedance spectra. Thus the fitting procedure can be also performed for Ni-based alloys at low pH.

The simulations using the MCM have shown that the diffusion coefficient of cation vacancies in the film formed on the Ni-20%Cr alloy at pH 0 is roughly two orders of magnitude higher than for the film on the Fe-25%Cr alloy. The diffusion coefficient of cation vacancies is also higher than the diffusion coefficient of oxygen vacancies in the film formed on Ni-20%Cr. Thus the passive films on Ni-based alloys can be considered to be predominantly cationic conductors, as discussed also by Macdonald and Smedley [33] for pure Ni. At higher pH the difference in diffusion coefficients between the alloys is smaller. On Ni-20%Cr also the difference between cationic and anionic diffusion coefficients has diminished, and most probably both cationic and anionic species are responsible for the film conduction on this material. The diffusion coefficient of ionic species on Fe-based materials seems on the whole to increase with increased pH (Table 2, Paper VI and Ref. 61). At pH 9.3 the ionic transport has been found as a Warburg impedance only on pure Ni and Ni-10%Cr, but not on Fe-Cr alloys or on the rest of the Ni-Cr alloys (Papers I and VI and Ref. 61).

The Tafel coefficient for the dissolution of metal through the oxide film, αb_3, is higher than that for the growth reaction, αb_4, at acidic pH (Table 2). This means that the importance of the dissolution of metal increases the higher the applied potential. Furthermore, the rate constant for the cation dissolution at the film/solution interface, k_3^0, is several orders of magnitude higher but the Tafel coefficient, αb_3, is considerably smaller at pH 9.3 than at lower pH. This feature suggests that the film structure is different at different pH. By using the values given in Table 2 and the thermodynamic equilibrium potentials for the oxidation of Cr(III) to Cr(VI) obtained from Ref. 69, the rate constant for the dissolution of metal through the oxide film on Ni-20%Cr, k_3, can be calculated to be lowest at pH 5. These simulation results may explain, at least partly, the different resistance behaviour of Ni-20%Cr at pH 5 seen in Fig. 3b and discussed on page 40.

Table 2. Parameters determined by simulating data with the MCM.

Parameter	**Ni-20%Cr**			**Fe-25%Cr**		
	pH 0	pH 5	pH 9.3	pH 0	pH 5	pH 9.3
D_M / cm^2s^{-1}	$2 \bullet 10^{-18}$	$2 \bullet 10^{-19}$	$\sim10^{-19}$ *	$3 \bullet 10^{-20}$	$2 \bullet 10^{-18}$	$2 \bullet 10^{-18}$
D_O / cm^2s^{-1}	$2 \bullet 10^{-20}$	$1 \bullet 10^{-20}$		$2 \bullet 10^{-19}$	$2 \bullet 10^{-19}$	
D_i / cm^2s^{-1}						$2 \bullet 10^{-18}$
k_3^0 / mol $cm^{-2}s^{-1}$	$3 \bullet 10^{-21}$	$1 \bullet 10^{-21}$	$4 \bullet 10^{-12}$ *	$3 \bullet 10^{-20}$	$3 \bullet 10^{-21}$	$4 \bullet 10^{-12}$
αb_3 / V^{-1}	14	12	7 *	14	14	6
k_{3i}^0 / cm s^{-1}						$3 \bullet 10^{-10}$
αb_{3i} / V^{-1}						10
k_4^0 / cm s^{-1}	$1.5 \bullet 10^{-11}$	$1 \bullet 10^{-11}$		$4 \bullet 10^{-15}$	$3 \bullet 10^{-11}$	
αb_4 / V^{-1}	9	14	17	11	10	
$\boldsymbol{E}(1-\alpha)^{-1}$ / Vcm^{-1}	$3 \bullet 10^6$	$4 \bullet 10^6$	$\sim10^6$ *	$8 \bullet 10^6$	$5.5 \bullet 10^6$	$6.6 \bullet 10^6$

* Rough estimate based on the assumption that the dissolution rate of metal ions in the transpassive region is the same as on Fe-25%Cr.

Calculations have also shown that the diffusion coefficient of electronic charge carriers is greater for Ni-20%Cr than for Fe-25%Cr (Paper II). It can be argued that Ni(II) enters the Cr(III)-based film as a substitute ion and increases the degree of non-stoichiometry, thus making the film a better electronic conductor. This result is to some extent corroborated by the lower values of the field strength for the films formed on the Ni-20%Cr alloy at pH 0 and 5 in comparison to those for Fe-25%Cr (Table 2). On the other hand, for Fe-based alloys, the diffusion coefficient of electronic charge carriers has been shown to be several orders of magnitude higher than that of ionic charge carriers at all pH values. This supports the assumption of the predominance of electronic mobility over ionic mobility in the passive film on Fe-Cr alloys (Paper II and Refs 45 and 68).

5.1.2 Transpassive dissolution on Ni-Cr alloys

The goal in studying transpassive dissolution was to discover the role of oxide films in corrosion in highly oxidising environments, such as those encountered in pulp bleaching processes or in BWR nuclear power plants where the operation potentials e.g. in the primary water circuit may be near the transpassive region. Transpassive oxidation takes place in the oxide films on alloys containing Cr, as Cr(III) is oxidised to Cr(VI). The transpassive dissolution is said to occur when Cr(VI) is dissolved from the oxide film. In this work, the transpassive oxidation and dissolution were studied in detail using binary Ni-Cr alloys and commercial UNS N06600 and UNS N10276 in acidic solutions (Papers III and IV). The corresponding results for Fe-Cr alloys are given in Ref. 65. Before concentrating purely on the transpassive behaviour of Ni-based alloys, the general features of the results in the transpassive region on both Ni-Cr and Fe-Cr alloys are briefly summarised.

In general, the onset potential of transpassive oxidation has been found to decrease with increasing pH on both Ni- and Fe-based materials (Figs 2a and 3a), which is in agreement with the pH dependence of the thermodynamic equilibrium potential of the Cr(VI)/Cr(III) couple [69]. On the other hand, the rate of transpassive oxidation increases with increasing Cr amount in the alloy (Papers III, VI, V and VII and Ref. 65), except in the case of Ni-Cr alloys where the oxidation rate at low pH is highest on the commercial UNS N10276 alloy (Paper IV). This has been proposed to be due to the accelerating effect of Mo on dissolution of Cr [62]. The tendency towards secondary passivation decreases with increasing Cr amount in both Ni- and Fe-based alloys in acidic solutions. On Ni-Cr alloys no secondary passivation at pH 9.3 is observed (Paper I). For Fe-based materials in a borate environment at pH 9.3 the decrease of the current due to secondary passivation seems to be more pronounced the higher the amount of Cr in the alloy (Paper VI).

The rotating ring-disc electrode measurements made in this work using Ni-Cr alloys in acidic solutions (Papers III and IV) indicate that transpassive dissolution results in the release of high-valence Cr species from Ni-Cr alloys, and possibly also high valence Mo species from UNS N10276. A kinetic model for the transpassive dissolution processes of Ni-based alloys is proposed in order to distinguish between different reactions and estimate the rate limiting steps for transpassive dissolution (Papers III and IV). The model takes into account the most important processes occurring at the film/solution interface in the transpassive region. The model proposed in this work is based on the model for the active-to-passive transition of Fe-Cr alloys employed by Annergren et al. [72] and on the earlier model proposed for the transpassivity of Fe-Cr alloys [65]. In this work the model has been further developed and in its complete form it includes not only the oxidation of Cr and dissolution of metal cations from the outermost film, but also the adsorption of reaction intermediates at the film/solution interface and their self-catalytic effect on the dissolution.

The simulations using this model have given one possible set of parameters for each alloy describing the reactions on Ni-based alloys in the transpassive region. The simulation results indicate that increasing pH slows the reactions and diminishes the differences between the rates of individual reactions on Ni-based alloys (Papers III and IV). Furthermore, especially the rate of dissolution of Cr(VI) seems to decrease and become less dependent on potential with increasing pH.

For most alloys studied, the rate constants corresponding to the dissolution of Ni, Fe or Mo from the oxide film and to the oxidation of Cr(III) to Cr(VI) in the outermost layer of the oxide film are higher than for the other reactions at the film/solution interface. The calculated surface fractions for Ni-10%Cr and Ni-20%Cr indicate that the fraction of Cr(VI) in the outermost layer of the oxide film in the transpassive region is the higher the higher the amount of alloyed Cr. However, the decrease in the surface fraction of Cr(VI) is steeper at very high potentials when the amount of alloyed Cr is increased. This is in agreement with the voltammetric results, which show higher transpassive oxidation rate for Ni-20%Cr in comparison with Ni-10%Cr. The adsorption phenomenon at the electrode surface has been found to play an important role for UNS N10276 containing Mo at high potentials at pH 5, which is in line with observations with other Mo bearing Ni-based materials [73]. Thus the mechanism of transpassive dissolution of UNS N10276 in these conditions is different from that at lower potentials and at lower pH.

Comparison of the results presented in this work with those determined previously for Fe-Cr alloys [65] is not straightforward, because in the model used for Fe-based material the impedance of the film has been taken into account as well, and different species are considered as intermediates in Cr dissolution reactions in Ref. 65. In the model for Ni-Cr alloys presented in this work, the contribution of the film impedance has been assumed to be negligible because of the more pronounced electronic and ionic conductivity of the films formed on these alloys.

The main deficiency in the present model is that at low overpotentials in the transpassive region it predicts too low impedances and accordingly too high currents. This discrepancy probably arose because no reverse reactions occurring at the film/solution interface were taken into account in the model but they may affect the electrochemical processes at low overpotentials.

5.2 Effect of temperature and Cr content on the electrochemical behaviour on Ni-Cr and Fe-Cr alloys at high temperatures

The aim of studying the effect of temperature was to understand and model the initial part of passive film formation in aqueous environments simulating real high-temperature conditions, especially in nuclear power plants. The increased film thickness and different film structure e.g. on stainless steels [74–77] at high temperature also affect reaction rates and corrosion phenomena in oxide films on such construction materials. Thus also the experimental electrochemical analysis on these materials has to be carried out at high temperatures and theoretical approaches have to be developed to include features of oxide films observed possibly only at elevated temperatures. In this work the high temperature corrosion of Ni- and Fe based binary alloys has been studied in a slightly alkaline aqueous environment. For the first time, the features observed on alloys have been simulated using the MCM modified for elevated temperatures.

Effect of temperature

The effects of temperature on the electrochemical behaviour of Ni-20%Cr and Fe-25%Cr are summarised in Figs 5 and 6. The results are compiled from Papers V and VI and Ref. 78. The resistance measurements in Fig. 6 differ from the measurement results shown in Paper VI in the sense that the results in Fig. 6 were obtained using two similar CER probes. The results shown in Paper VI were obtained using Ir as second probe material.

According to the voltammetric measurements (Figs 5a and b), the active, passive and transpassive regions shift towards more negative potentials with increasing temperature on both Ni-20%Cr and Fe-25%Cr. This is expected from thermodynamic calculations [79–81]. The increasing temperature also leads to increased current levels in the oxide film and to narrower passive regions on both alloys (Fig. 5 and Papers V and VI). Furthermore, on Fe-25%Cr an oxidation peak is observed in the passive region at $E = -0.6\ldots-0.4\ V_{SHE}$ at high temperatures. This is most probably due to oxidation of Fe(II) to Fe(III) (Paper VI). The transpassive oxidation starts at lower potentials and the secondary passivation is observed on both Ni-20%Cr and Fe-25%Cr alloys at high temperatures. At 300°C the passive region is very narrow especially on Ni-20%Cr and the potential region of transpassive oxidation and secondary passivation has increased from that at lower temperatures.

The resistance measurements on these alloys together with the results obtained with pure metals indicate that the films form in quite a narrow potential region at low potentials on all materials, which is seen as a steep increase in resistance (Fig. 6). The dependence of the increase in resistance on potential seems to be slightly higher on Ni-based materials. Overall, the resistance measurements on alloys are in good agreement with the voltammetric measurements in the sense that the passive region showing the highest resistance values becomes narrower with increasing temperature. The shift of the passive region in the negative direction is also seen in the resistance measurements. No big differences in maximum resistance values can be observed between Ni-20%Cr and Fe-25%Cr, which may be, however, partly due to the fact that the maximum resistance values on both alloys are already near the resolution limit of the measurement device.

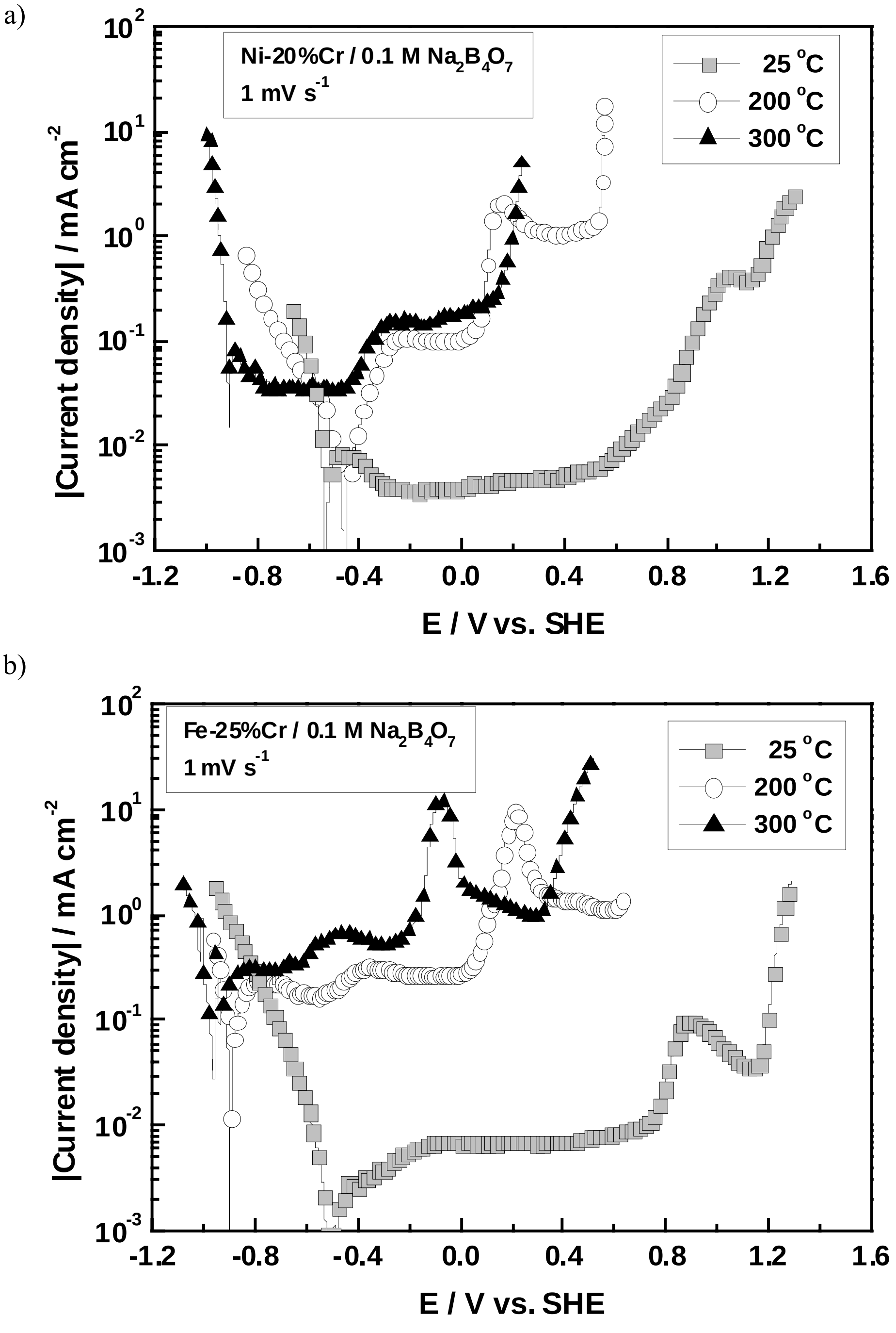

Figure 5. Effect of temperature on the voltammetric behaviour of a) Ni-20%Cr and b) Fe-25%Cr.

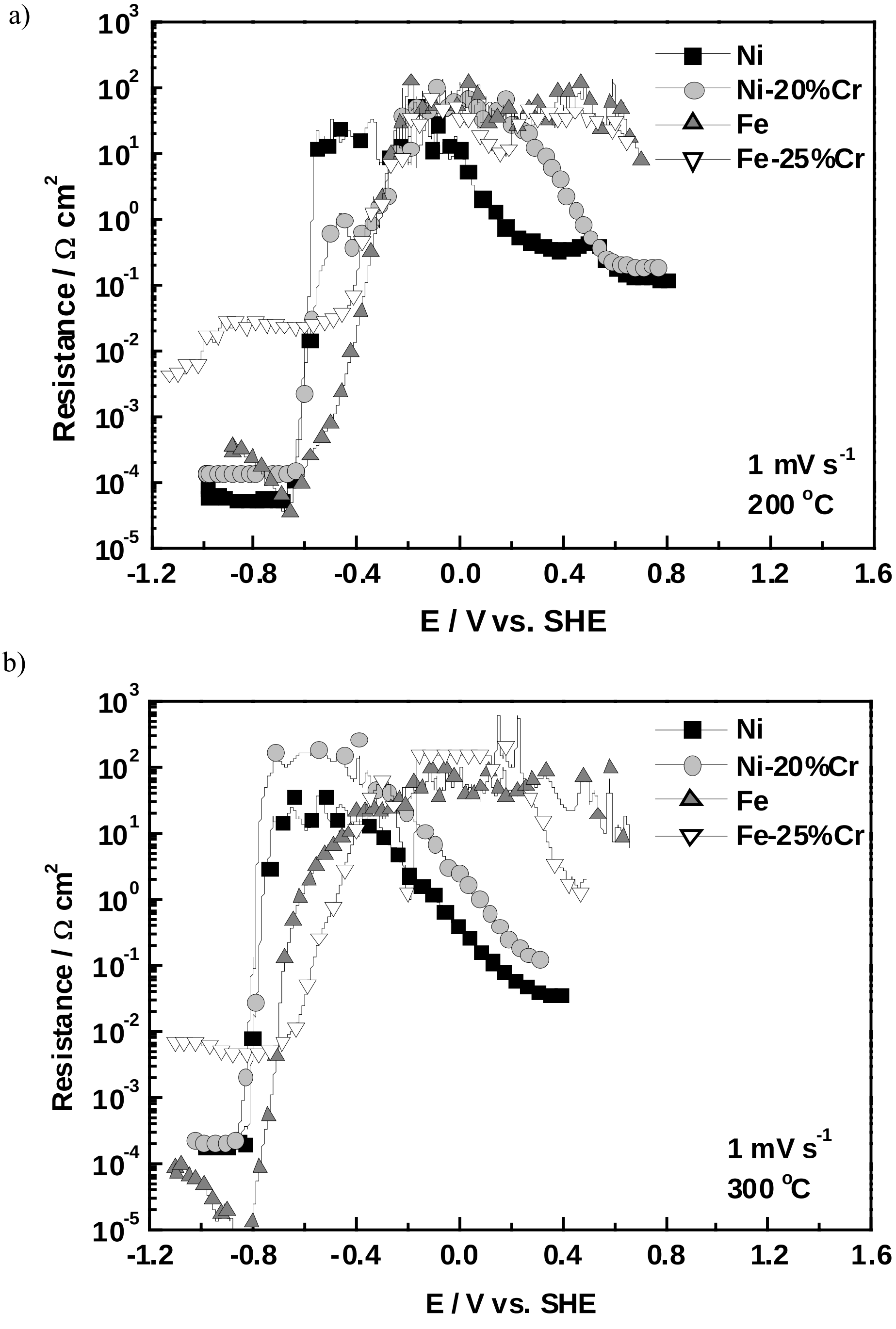

Figure 6. Comparison of the resistance vs. potential behaviour of Ni, Ni-20%Cr, Fe and Fe-25%Cr in 0.1 M $Na_2B_4O_7$ at a) 200ºC and b) 300ºC.

An interesting feature observed from voltammetric and resistance measurements is that both techniques show the onset of transpassivity, seen as an increase in current and a decrease in resistance, for Ni-20%Cr roughly at the same potential at both 200°C and 300°C (Figs 5 and 6). However, on Fe-25%Cr the increase in current due to transpassive oxidation takes place at lower potentials than the decrease in film resistance. Transpassive oxidation does not seem to lead to dissolution of the oxide films on Fe-25%Cr, but the film is transformed from the Cr-rich primary passive film to the Fe-rich secondary passive film, the resistance of which is even higher than that of the primary passive film (Figs 5 and 6 and Paper VI).

Effect of the amount of alloyed Cr at high temperatures

In general, the effect of Cr at high temperature, according to voltammetric measurement, is almost the same as at room temperature; i.e. the current of the passive state decreases, transpassive oxidation starts at lower potentials, and its rate increases with higher Cr content of both Ni-Cr and Fe-Cr alloys (Papers V and VI). The voltammetric measurements together with impedance measurements have shown that the behaviour of Ni-Cr alloys and of Fe-Cr alloys at 200^{o}C is intermediate between pure Ni or Fe and pure Cr and becomes more Cr-like the higher the Cr content of the alloy. On the other hand, the resistance measurements indicate that the resistance behaviour of both Ni-Cr and Fe-Cr alloys resembles more that of pure Ni or Fe than pure Cr (Fig. 6 and Papers V and VI). The maximum resistance levels of both Ni-Cr and Fe-Cr alloys at high temperatures are almost the same as those at room temperature (Figs 3, 4 and 6).

On Ni-based alloys some differences in the passive state behaviour between the alloys can be observed at 200°C. First of all, on Ni-15%Cr oxidation peaks have been observed in the passive region (Paper V). Secondly, Ni-20%Cr has been observed to be the only Ni-Cr alloy, which shows tendency towards secondary passivation at 200°C. These features refer to same kind of changes in the film structure at the threshold in Cr content as suggested by Oblonsky and Ryan [70, 71] for room temperature behaviour of Ni-Cr alloys. When the temperature is increased from 200°C to 300°C the passive region diminishes and the potential region of transpassive oxidation and secondary passivation increases on all Ni-Cr alloys. At 300^{o}C all Ni-Cr alloys used in this work show secondary passivation and the tendency towards it seems to decrease the higher the Cr content of the alloy. The differences between alloys with different Cr contents are not as visible at 300°C as at 200°C.

The voltammetric behaviour of Fe-Cr alloys is quite similar to that on Ni-Cr alloys, except that Fe-Cr alloys show secondary passivation at both 200°C and 300°C (Paper VI and Ref. 78). The current drop towards the secondary passivation seems to increase with a higher amount of Cr in the alloy. On Fe-based alloys different results are obtained for the effect of Cr in resistance measurements depending on how these have been carried out. The results shown in Fig. 6 measured with two similar CER probes show no big difference between the resistance behaviour of pure Fe and Fe-25%Cr. This may be partly because the resistance values on both these materials are near the resolution limit of the measurement device. However, the results in Fig. 2 in Paper VI, measured using Ir as a second probe material, show that the behaviour of Fe-Cr alloys is more Cr-like in the passive region. The most probable reason for the differences in the resistance results is different film thicknesses depending on what kind of combination of CER probes is used, as discussed in Chapter 5.1.1. When the potential is increased to the transpassive region and dissolution of Cr takes place, the resistance values of Fe-Cr alloys increase steeply in a narrow potential region, due to the formation of an Fe-rich film in this region (Paper VI).

Simulations using the MCM at high temperatures

In order to extract more data on the properties of oxide films on Ni- and Fe-based alloys formed at high temperatures, the impedance spectra for the oxide films were measured and then simulated using the transfer functions obtained from the modified MCM for high temperatures. The high-temperature MCM was applied for the first time in this work. The theory behind the model is given in Paper VII.

Impedance measurements have shown that the transport of ionic species at 200°C is higher than at room temperature in oxide films on both Ni- and Fe-based materials (Papers V, VI and VII). The transport of ionic species has been observed as a Warburg-like impedance on Ni and Ni-10%Cr (Chapter 5.1.1.) at room temperature, but has not been observed on Fe-Cr alloys. At 300°C the contribution of the transport of ionic defects as a Warburg impedance has not been observed on Ni-Cr alloys. The analysis of the transport properties of oxide films on Fe-Cr alloys at 300°C is in progress, but preliminary results indicate that the rate of transport of ionic species driven by a concentration gradient in the films on these materials increases with increasing temperature [78].

The increased rate of ionic transport at 200°C is likely to lead to the formation of thicker oxide films on these materials. Further proof for this assumption is obtained from the CER measurements on Fe-Cr alloys. The measurements using inert Ir as a second probe in the CER measurements have shown that the maximum resistance values of the films formed on Fe-Cr alloys are noticeably higher at high temperatures than at room temperature (Paper VI). On the basis of the relatively low values of the activation energies for electronic conduction in Fe- and Cr-based oxides below 400°C (max. < 0.5 eV) [82, 83] the resistivity of the oxide film can be assumed to slightly decrease with increasing temperature. This assumption leads to the conclusion that the films formed on Fe-based alloys at high temperature are most probably thicker than those formed at room temperature. On Ni-Cr alloys, however, no such conclusion can be drawn because the resistances have not been measured using Ir as a second probe and the results obtained with probes made of the material studied show that the values measured at room temperature do not differ much from those at high temperatures on these alloys. This fact combined with the low activation energies for Ni-based oxides (≤ 0.6 eV) [84, 85] indicates that neither the resistivity nor the thickness of the highly resistive (barrier) parts of the oxide films formed at high temperatures changes significantly with temperature.

To sustain a comparatively high rate of ionic transport, the oxide films formed at high temperatures most probably contain an appreciable amount of defects. Thus they are not likely to support the high-field conditions in the film and the low-field approximation for the electric field strength has to be used (Chapter 3.2.). This has also been the basis for modifying the MCM from room temperature to higher temperatures, meaning that the ionic transport at high temperatures is described using the Nernst-Planck equation (Eq. 2 in Chapter 3.2.) in the model.

Simulations of the impedance data using the high-temperature MCM have shown that on Ni-Cr alloys the resistance to ionic transport, i.e. the Warburg constant, is higher the higher the amount of Cr in the alloy. The Warburg constant exhibits a maximum roughly at the same potentials at which the maximum resistance values were observed in the CER measurements. (Paper V). The maximum value of the Warburg constant on Ni-20%Cr is even higher than on pure Cr. As the Warburg coefficient is inversely proportional to the concentration of defects in the film, the conclusion can be drawn that this concentration becomes smaller the higher the amount of Cr in the alloy. On Fe-Cr alloys the Warburg constant also shows the maximum but its value seems to be smaller on Fe-25%Cr than on Fe-12%Cr and pure Cr (Paper VII).

The extraction of absolute values for the parameters from simulations requires data concerning the thickness of the film and the steady-state concentrations of defects. Due to the lack of such data measured at high temperatures, only rough estimates of the parameters can be given. By combining the contact impedance data with the conventional impedance data, the ratio of the electronic and ionic diffusion coefficients for pure Fe has been calculated to be roughly 30 at 200°C, while at room temperature the ratio is of the order of 10^5 (Paper VII). Such a large difference in ratios explains the considerably higher growth rate and thickness of films formed on Fe due to a higher transport rate of ionic defects at the higher temperature. The diffusion coefficient of ionic current carriers on Fe has been estimated to be of the order of 10^{-13} cm^2 s^{-1} at 200°C using an electric field strength of 2×10^4 V cm^{-1} (Paper VII). Furthermore, the estimates of the diffusion coefficient for Fe-Cr alloys indicate that alloying with Cr lowers the ionic mobility in the passive film on a Fe-based alloy.

On Ni-Cr alloys the contact impedance measurements do not show any frequency dependence at high temperatures and thus the calculation of diffusion coefficients becomes even more uncertain. Very rough estimates calculated from the time constants obtained from the conventional impedance data shows that the diffusion coefficients on all Ni-Cr alloys at 200°C are of the order of 10^{-16}–10^{-15} cm^2 s^{-1} (Paper V). These values are 5–6 decades higher than on Ni at room temperature [33] and lower than on Fe at 200°C. The electric field strength has been assumed to be 10^5 V cm^{-1}. However, on the basis of the simulations the diffusion coefficients on Ni-Cr alloys seem to vary with the potential.

Summarising the results concerning the electrochemical behaviour of Ni-Cr and Fe-Cr alloys at high temperatures, it can be said that even though the voltammetric behaviour is quite similar on these alloys, the resistance and impedance results together with simulations reveal that the oxide films on Fe-based alloys are more resistant to highly oxidising conditions. The transport of ionic species seems to be higher on Fe-Cr alloys than on Ni-Cr alloys in the passive region, which probably also leads to thicker films on Fe-based alloys. The effect of the Cr content of the alloy is quite similar on both Ni-Cr and Fe-Cr alloys.

6. Summary of the main results

This thesis presents the work done at Helsinki University of Technology and the Technical Research Centre of Finland (VTT) to characterise and model the electrochemical behaviour of oxide films formed on Ni- and Fe-based alloys. The main objective of this work has been to study the effects of pH, temperature and the Cr content of the alloy on the conduction mechanism in the oxide films on these materials. The main results can be summarised as follows:

Effect of pH at room temperature

- Increasing pH decreases the current in the passive region and shifts the passive region in the negative direction on the potential scale. The latter observation is an expected result on the basis of thermodynamic calculations.

- Resistance measurements have indicated that the resistance of the oxide film increases at lower potentials at pH 5 than at other pH.

- Simulations using the Mixed Conduction Model (MCM) have shown that the dissolution rate of the metal through the oxide is, in fact, lower at pH 5 than at pH 0 or pH 9.3.

- Simulations have also shown that the diffusion coefficient of cation vacancies in the film on Ni-20%Cr at pH 0 is higher than for the film on Fe-25%Cr. The diffusion coefficient of cation vacancies on Ni-20%Cr is also higher than the diffusion coefficient of oxygen vacancies.

- The diffusion coefficient of electronic charge carriers is higher on Ni-20%Cr than on Fe-25%Cr.

- The diffusion coefficients of ionic species on Fe-based materials increase and the difference in diffusion coefficients between Ni-Cr and Fe-Cr alloys, as well as between the cationic and anionic defects, diminish with increasing pH.

Effect of Cr content of the alloy at room temperature

- A higher amount of Cr in the alloy causes more rapid passivation of the metal surface.

- The current in the passive region decreases and transpassivity starts at lower potentials with a higher Cr content of the alloy.

- Ni-15%Cr alloy has been found to show electrochemical responses which often differ from those of other Ni-Cr alloys, pure Ni or Cr.

- The resistance levels of oxide films in the passive region are higher on Fe-Cr alloys than on Ni-Cr alloys at all pH values studied.

Transpassive dissolution

- The onset potential of transpassive oxidation decreases with increasing pH on both Ni- and Fe-based alloys, which is an expected result on thermodynamic grounds.

- The rate of transpassive dissolution increases the higher the Cr content of the alloy, but decreases with increasing pH on both Ni- and Fe-based alloys.

- Transpassive dissolution results in the release of high-valence Cr species from Ni-Cr alloys and possibly also high-valence Mo species from UNS N10276 at acidic pH.

- The current drop towards the secondary passive region decreases on Ni-Cr and Fe-Cr alloys with a higher amount of Cr in the alloy at acidic pH. At pH 9.3 the current drop, however, increases on Fe-Cr alloys with a higher amount of Cr in the alloy. On Ni-Cr alloys no secondary passive region is observed at pH 9.3.

- Simulations using the kinetic model developed for the transpassive dissolution have indicated that increasing pH slows the reactions and reduces the differences between rates of individual reactions on Ni-based alloys.

- Simulations have shown that dissolution of Ni, Fe or Mo from the oxide film and the oxidation of Cr(III) to Cr(VI) in the outermost layer of the oxide film are the fastest reactions at acidic pH. Especially the rate of dissolution of Cr(VI) seems to decrease and become less dependent on potential with increasing pH.

- The mechanism of transpassive dissolution of Mo bearing UNS N10276 alloy at high overpotentials at pH 5 is different from that at lower potentials and of other Ni-Cr alloys.

Effect of temperature

- Increasing temperature shifts the passive region in the negative direction on the potential scale in accordance with thermodynamic predictions.

- The increasing temperature leads to increased currents in the oxide film and to narrower passive regions on both Ni-Cr and Fe-Cr alloys.

- The potential region of transpassive oxidation and secondary passivation increases with increasing temperature.

- On Fe-Cr alloys the resistance of the films stays high or even increases in the transpassive region at the same potentials at which the current in the voltammetric measurements increases. On Ni-Cr alloys the decrease in resistance and the increase in current start roughly at the same potential.

- Simulations of experimental impedance spectra using the MCM have shown that the transport rate of ionic species in the film increases with increasing temperature and is higher on Fe-Cr alloys than on Ni-Cr alloys.

Effect of Cr content of the alloy at high temperatures

- The passive currents decrease, the transpassive oxidation starts at lower potentials and its rate increases with a higher Cr content of both Ni-Cr and Fe-Cr alloys.

- The effect of Cr on the electrochemical response of Ni-Cr is smaller at 300°C than at lower temperatures.

- Fe-Cr alloys show a tendency towards secondary passivation at 200°C, whereas Ni-20%Cr is the only Ni-Cr alloy that has shown this tendency. Secondary passivation is observed on both Ni-Cr and Fe-Cr alloys at 300°C.

- Simulations at 200°C show that the resistance to ionic transport increases the higher the amount of Cr in Ni-Cr alloys. On Fe-Cr alloys the effect is the opposite.

7. Conclusions

Oxide film electrochemistry has been an important field of study for several decades already, due to the fact that oxide films provide necessary protection against the corrosion of metals and alloys. Electrochemical measurements and their analysis give valuable insight into the possible reactions taking place in the oxide film and at its surfaces. In this work a wide combination of electrochemical techniques has been used to obtain information of oxide films on Ni- and Fe- based alloys and to build up electrochemical kinetic models (the Mixed Conduction Model and the model for transpassive dissolution) to explain their behaviour.

On the basis of the experimental results and model simulations done in this work the following conclusions can be drawn:

- The conductivity of oxide films on Ni-based alloys is higher than on Fe-based alloys at room temperature.

- Amounts of 10% Cr for a Ni-based alloy and 12%Cr for a Fe-based alloy are enough to change the electrochemical properties of the oxide film on the alloy from Ni- or Fe-like to Cr-like in the passive state.

- For Ni-Cr alloys the amount of 15% Cr is a threshold content at which the oxidation behaviour may be different in comparison to other Ni-Cr alloys. This feature is interesting in the sense that many commercial alloys like UNS S31600 and UNS N10276 contain roughly 15% Cr.

- Cr oxidises and dissolves strongly in the transpassive region irrespective of temperature. This fact is worth taking into account in material selection for e.g. high-temperature nuclear power plant applications, in which the operation potentials in aqueous environments are near or in the transpassive region.

- The protectiveness of oxide films on Ni-based alloys is lower than that of oxide films on Fe-based alloys, especially in highly oxidising conditions. The oxide films on Fe-based alloys are not destroyed in these conditions but are transformed from Cr-rich primary passive films to Fe-rich secondary passive films.

- Higher ionic transport on Fe-based alloys most probably leads to the formation of thicker films on these materials in compared with Ni-based alloys at high temperatures.

- At high temperatures above 200°C, the behaviour of oxide films on Ni-based materials is mostly determined by the reactions of Ni, and the effect of Cr is smaller than at lower temperatures.

The Mixed Conduction Model applied in this work is able to explain several important features of the processes taking place in the oxide films on several materials at both room temperature and high temperatures. Using the MCM estimates of diffusion coefficients of current carriers and reaction rate constants can be obtained and the coupling between electronic and ionic conduction in the passive film is quantified. The MCM provides a useful tool for predicting the electrochemical behaviour of construction materials used in process industry and energy production.

Furthermore, the model developed to explain the transpassive dissolution of Ni-Cr alloys has proved capable of describing the most relevant reactions in detail. The model has also proved capable of explaining the transpassive dissolution on alloys with more than two alloying elements, and it provides a useful tool for predicting the stability of alloys in highly oxidising conditions. This model has already been extensively used to compare several commercial alloys. In the future, it would be useful to extend this model to explain transpassive dissolution also at high temperatures.

Even though the models used in this work have given satisfactory predictions for the behaviour of oxide films, they still need to be developed. In order to obtain fully quantitative results for reaction parameters, data concerning especially the thickness, composition and structure of the films at high temperatures are needed. This is one of the primary tasks ahead. Furthermore, the model for transpassive dissolution has to be improved by taking also reverse reactions into account, so that more accurate predictions can be made for rate constants and oxidation currents at low overpotentials.

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Errata to papers

The following corrections have to be taken into account for appended papers:

Paper I, pages 34–35 (I/6–I/7):

The more correct forms for the concentration of oxygen vacancies at the metal/film interface in equations (25)–(32) are $\dot{c}_{\mathrm{O}}(L\text{-}x=0,\omega)_{\mathrm{ac}}$ and $c_{\mathrm{O}}(L\text{-}x=0)$ and at the film/solution interface $\dot{c}_{\mathrm{O}}(L\text{-}x=L,\omega)_{\mathrm{ac}}$.

Paper II, page 27 (II/2):

The correct form of Equation (10) is

$$Z_{\mathrm{MFE}} = \mathrm{R_{el}} + \{\{(a / \mathrm{j}\omega\varepsilon\varepsilon_0)\ \ln [(1 + \mathrm{j}\omega\rho_{\mathrm{d}}\varepsilon\varepsilon_0 \exp (\mathrm{L} / a)) / (1 + \mathrm{j}\omega\rho_{\mathrm{d}}\varepsilon\varepsilon_0)]\}^{-1} + \mathrm{R_{ion}}^{-1}\}^{-1}$$

i.e. $\tau = \rho_{\mathrm{d}}\varepsilon\varepsilon_0$

Paper II, page 31 (II/6):

The correct unit for diffusion coefficients in Table 1 is $cm^2\ s^{-1}$.

Paper V, page V/21:

The correct form of Equation (12) is $\tau_{\mathrm{W}} = (2\mathrm{K}^2\,\mathrm{D_O})^{-1}$

Paper VII, page 1929 (VII/7):

The correct form of Equation (8) is

$$Z_{\mathrm{MFE}} = \mathrm{R_{el}} + (a / \mathrm{j}\omega\varepsilon\varepsilon_0)\ \ln [(1 + \mathrm{j}\omega\rho_{\mathrm{d}}\varepsilon\varepsilon_0 \exp (\mathrm{L} / a)) / (1 + \mathrm{j}\omega\rho_{\mathrm{d}}\varepsilon\varepsilon_0)]$$

i.e. $\tau = \rho_{\mathrm{d}}\varepsilon\varepsilon_0$

Paper VII, page 1932 (VII/10):

The correct form of Equation (15b) is $\tau_{\mathrm{MFE}} = (2\mathrm{K}^2\,\mathrm{D_O})^{-1}$

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Author(s)
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Title

Electrochemical characterisation and modelling of passive films on Ni- and Fe-based alloys

Abstract

The behaviour of oxide films formed on Ni- and Fe-based alloys in different environments has been studied electrochemically. The aim was to study the effect of pH, temperature and Cr content of the alloy on the protectiveness of the oxide film using a wide combination of electrochemical techniques: conventional linear sweep cyclic voltammetry, rotating ring-disc voltammetry, electrochemical impedance spectroscopy (EIS), contact electric resistance technique (CER) and contact electric impedance technique (CEI). The other goal was to develop modelling tools to describe and predict the oxide film behaviour in different conditions.

Increasing pH has been found to decrease oxidation rates in both the passive and transpassive regions. Increasing pH as well as increasing temperature shifts the passive region in the negative direction on the potential scale. A higher amount of Cr in the alloy leads to a more passive oxide film on the metal surface both at low and high temperatures. On the other hand, transpassive dissolution takes place at lower potentials and its rate increases with higher Cr content of the alloy. The potential region of transpassive oxidation and secondary passivation increases and the effect of Cr on the electrochemical behaviour especially on Ni-Cr alloys decreases at high temperatures.

The behaviour of oxide films in the passive state in different environments was simulated using the Mixed Conduction Model (MCM). Using this model the diffusion coefficients of current carriers and reaction rate constants at room temperature and profiles of resistances against ionic transport in the oxide films at 200°C were estimated.

Also the transpassive dissolution of Ni-Cr alloys at room temperature was studied and a kinetic model proposed to determine quantitatively the reaction rates in the transpassive region. The model describes the oxidation and dissolution reactions of metal cations at the film/solution interface. The proposed model can be used to estimate steady-state current densities as well as dependencies of surface fractions of dissolving species on potential.

Keywords
Ni-based alloys, Fe-based alloys, Ni-Cr alloys, Fe-Cr alloys, oxide films, passive films, electrochemistry, kinetic models, pH, high temperature, dissertations

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VTT PUBLICATIONS 472 Electrochemical characterisation and modelling of passive films ...

Petri Kinnunen

Corrosion of Ni- and Fe-based construction materials is a serious problem in process industry and energy production. The corrosion properties of these materials can be explained partly by the properties of the oxide film formed on material surfaces. The composition and structure of the oxide film determines how different ions are transported through the oxides. The transport of material, on the other hand, affects the corrosion rate of the material. In this work the oxide films on Ni- and Fe-based materials were studied and characterised using a combination of electrochemical techniques. The aim was to study the effect of pH, temperature and Cr content of the alloy on the protectiveness of the oxide film.

The behaviour of oxide films in the passive state in different environments was simulated using the Mixed Conduction Model (MCM). This model takes into account the contributions of both ionic and electronic charge carriers to the total conductivity. Several important features, such as rates of transport of ionic species were estimated by combining the experimental data with the MCM.

Also the transpassive dissolution of Ni-Cr alloys at room temperature was studied and a kinetic model proposed to determine quantitatively the reaction rates in the transpassive region. The model describes the oxidation and dissolution reactions of metal cations at the film/solution interface. The proposed model can be used to estimate steady-state current densities as well as dependencies of surface fractions of dissolving species on potential.

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