Stellingen

behorende bij het proefschrift

_Electrochemical Characterisation of Metallic Thermally Sprayed Coatings_


2. Het resultaat van metingen met behulp van diëlektrische sensoren op het oppervlak van organische dekklagen is dubieus aangezien de geometrie van de gemeten capaciteit niet is gedefinieerd. (Bv. D.H. van der Weijde Thesis TU Delft 1996, pagina 69.)

3. Voor de analyse van elektrochemische ruis voor corrosiemonitoring systemen is het gebruik van wavelet of Fourier transformatie alleen niet zinvol. Het is namelijk niet de frequentieverdeling van de corrosiepotentiaal of -stroom, maar de totale getransporteerde lading, die de mate van corrosie weergeeft.

4. De ASTM Zoutproeitest mag, net als iedere andere test, alleen gebruikt worden voor evaluatie van de materiaal-milieu combinatie waarvoor hij is ontworpen. Het feit dat deze test alom geaccepteerd wordt voor de evaluatie van allerlei materialen en omstandigheden (inclusief organische coatings) berust op een misvatting.


6. In-situ scanning technieken zijn alleen nuttig voor de studie van relatief stationaire situaties. (Dit proefschrift.)

7. Vanuit wetenschappelijk oogpunt is het refereren aan literatuur zonder deze daadwerkelijk voor een publicatie te gebruiken verwerpelijker dan het maatschappelijk ongeaccepteerde, omgekeerde geval. (Discussie "Diekstra" oktober 1996.)

8. Door de voortdurende input van Engels in de Nederlandse taal verdient het aanbeveling om bij het oplezen van nummerreeksen (bijvoorbeeld telefoonnummers) deze ook daadwerkelijk als nummerreeksen op te lezen in plaats van de door veel mensen gebruikte combinaties van getallen. Dus: "zes-twee-zeven-acht-een" in plaats van "tweeën zestig-zeven-eenentachtig".

9. Om een betere maat van het door een snelheidsovertreding ontstane gevaar te verdeneren zou de hoogte van de boete gebaseerd moeten worden op de mate waarin de geconstateerde snelheid afwijkt van de snelheid van het overige aanwezige verkeer. (Wet administratiefrechtelijke handhaving verkeersvoorschriften, juli 1994.)
10. De in Nederland recent ingevoerde wetsconstructie die tot doel heeft de relatief kwetsbare fietsters te beschermen in het verkeer zou ook van toepassing moeten zijn op motorrijders (en bromfietsen).
(Wetsvoorstel verkeersveiligheid december 1997.)

11. Snelheidscontrolecamera’s gericht tegen de rijrichting van het verkeer in hebben vrijwel geen effect op het weggedrag van motorrijders.
Propositions

belonging to the dissertation

*Electrochemical Characterisation of Metallic Thermally Sprayed Coatings*


2. The result of measurements with dielectric sensors on the surface of organic coatings is dubious since the geometry of the measured capacitance is not defined. (E.g. D.H. van der Weijde Thesis TU Delft 1996, pagina 69.)

3. Wavelet or Fourier transform for the analysis of electrochemical noise in corrosion monitoring systems is not useful by itself. The amount of corrosion is not determined by the frequency distribution of corrosion potential or current signals, but by the total amount of transferred charge.

4. The ASTM salt spray test, as any other test, may only be used to evaluate material-environment combinations for which it was designed. The fact that this test is widely accepted for the evaluation of numerous materials and conditions (including organic coatings) is based on a misconception.

5. Separate study of corrosion prevention and anti-fouling regarding copper containing materials may lead to unwanted results in practice. (E.g. N. Warren, Corrosie van metaal op schepen, ISBN 9064101892, 1992.)

6. In-situ scanning techniques are only useful for the study of relatively stationary situations. (This thesis.)

7. Referencing literature without actually using it for a publication is, from a scientific perspective, more objectionable than the socially unacceptable opposite case. (Discussion “Diekstra” October 1996.)

8. Because of the continuing input of English into the Dutch language it can be recommended when reading out series of figures (for example a telephone number) to indeed express these as figures instead of the commonly used combination of numbers. So: “zes-twee-zeven-acht-een” instead of “tweeënzesestig-zeven-eenentachtig“.
9. To better discount the danger that arises from a violation of the speed limit, the height of the penalty should be based on the amount in which the witnessed velocity differs from the velocity of the other traffic present. (Wet administratiefrechtelijke handhaving verkeersvoorschriften, July 1994.)

10. The recently introduced law in The Netherlands that aims to protect the relatively vulnerable cyclists should also be applicable to motorcyclists (and mopeds). (Wetsvoorstel verkeersveiligheid December 1997.)

11. Traffic control cameras pointed against the direction of the traffic flow have almost no effect on the driving behaviour of motorcyclists.
ERRATA

Electrochemical Characterisation of Metallic Thermally Sprayed Coatings

Page 36 Figure 6  Chapter 2 Quality Control of Thermally Sprayed Coatings for Corrosion Protection Electrochemical Behaviour

![Figure 6: Schematic impression of the potential monitoring cell arrangement.](image)

Page 37 Figure 8  Chapter 2 Quality Control of Thermally Sprayed Coatings for Corrosion Protection Electrochemical Behaviour

![Figure 8: Schematic impression of the polarisation measurement cell arrangement, showing the anti-crevice corrosion assembly as a detail in section A.](image)
Electrochemical Characterisation of Metallic Thermally Sprayed Coatings

TNO Institute of Industrial Technology
Potential map using Kelvin probe of freshly applied thermally sprayed Al99.7 coating on steel (thickness approx. 150 μm, surface 4x4 mm)
Electrochemical Characterisation of Metallic Thermally Sprayed Coatings

Elektrochemische karakterisering van metallische thermisch gespoten deklagen

(met een samenvatting in het Nederlands)

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof.ir K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College voor Promoties aangewezen,
on vrijdag 20 november 1998 te 10.30 uur.

door

Mark Paul Waldemar VREIJLING

materiaalkundig ingenieur,
geboren te 's-Gravenhage.
Dit proefschrift is goedgekeurd door de promotor:
Prof.dr. J.H.W. de Wit

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
Prof.dr. J.H.W. de Wit, Technische Universiteit Delft, promotor
Prof.dr.ir. J. van Turnhout, Technische Universiteit Delft
Prof.dr. G. den Ouden, Technische Universiteit Delft
Prof. P.L. Bonora, Università degli Studi, Trento, Italië
Prof. W. F. Bogaerts, Katholieke Universiteit Leuven, België
Prof.dr. J.M.J.M. Bijen, Technische Universiteit Delft
Mighty ships upon the ocean  
Suffer from severe corrosion.  
Even those that stay at dockside  
Are rapidly becoming oxide.  
Alas, that piling in the sea  
is mostly Fe₂O₃.  
And when the ocean meets the shore,  
You'll find there's Fe₂O₄.  
Cause when the wind is salt and gusty,  
Things are getting awfully rusty.

We can measure it. We can test it.  
We can halt it or arrest it.  
We can gather it and weigh it.  
We can coat it. We can spray it.  
We examine and dissect it.  
We cathodically protect it.  
We can pick it up and drop it,  
But heaven knows we'll never stop it.  
So here's to rust! No doubt about it.  
Most of us would starve without it.

Anon.

Met dank aan Allen.
Preface

The purpose of this thesis is to demonstrate the usefulness of electrochemical measurements for the characterisation of the corrosion and corrosion protection properties of thermally sprayed coatings.

The presented results are a selection of the data obtained during the investigation of thermally sprayed coatings over the period from spring 1994 to the summer of 1998 at the TNO Laboratories for Corrosion Prevention in Den Helder, The Netherlands. Inevitably, during a demonstration of the usefulness of a technique, also its limitations will become clear. A purely electrochemical investigation proved to be too limited for practical use. For this reason also other investigation techniques were used (e.g. mechanical tests and microscopy). Nonetheless, in some cases it became clear that it would be impossible to achieve a complete understanding of the corrosion reaction mechanisms. In fact, the in-depth study of some of the encountered phenomena could well result in new research projects. However, the usefulness of electrochemical measuring techniques was demonstrated clearly.
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1 Introduction

Summary

The purpose of this chapter is to provide a broad introduction to the field of corrosion protection using thermally sprayed coatings that may be used as a background to illustrate the relevance of the presented research in this thesis. The first section concludes that the use of thermally sprayed coatings for corrosion protection is relatively modest, compared to the use of organic coatings despite their potentially superior protection properties. This might result from the more complex protection mechanism. The second section explains this well-defined mechanism by discussing the electrochemical interactions involved. The third section shows that the combination coating/substrate determines the qualification criteria for corrosion protection in specific cases. Basics of the thermal spraying application techniques that were used for this thesis are introduced in section four. General considerations on the economics of thermal spraying are discussed in section 1.5. It is argued that for many applications a thermally sprayed coating may well be the most economical solution. However, in general a clear view of the relevant cost considerations is very difficult to obtain, since the cost can only be evaluated reliably for each specific case. The final section discusses the environmental aspects of thermal spraying. Regarding human safety, these can be compared to the general considerations valid for cutting and welding. Regarding the implications of environmental restrictions, it is argued that organic systems will be subjected to more stringent restriction, which indirectly can be expected to stimulate the use of thermally sprayed coatings for corrosion protection.

1.1 General Introduction to Thermally Sprayed Coatings

Thermal spraying is defined as the method of coating application by the deposition of molten or semi-molten particles onto a substrate. A thermally sprayed coating is a coating deposited by thermal spraying. Metallising is defined as the thermal spraying of a metallic coating.

Metallising is not a new technology. From the invention of the process early in this century, thermal spraying has developed into an important industrial process nowadays of which the total turnover still rapidly grows. In fact, the total value of the thermal spraying market in the US alone is expected to increase from 650 million US dollars a year to more than 2 billion in the year 2000 [41].

Generally, a thermally sprayed coating, as any coating, is applied to meet specific requirements for the surface properties of an object. For the majority of all thermal spraying applications these requirements are either wear resistance or corrosion resistance.

Typical examples of mainly wear resistant applications for thermally sprayed coatings are found in aircraft and turbine industry for the coating of rotor and stator vanes. The behaviour of thermally sprayed coatings in these applications is relatively well researched, and the industrial acceptance of these systems is good. Although generally the degradation mechanisms in these applications also involve corrosion phenomena, they will not be discussed in this thesis.

This thesis is limited to the discussion of corrosion resistant thermally sprayed coatings for aqueous corrosion at relatively low (ambient) temperatures.

Under these conditions, corrosion protection by thermal spraying is far less accepted. Although thermally sprayed coatings are ever more recognised as a suitable alternative for conventional organic corrosion protection systems (i.e. "paints"), their actual use remains modest as compared to the organic coating market. Despite the potentially superior corrosion protection, organic coatings appear to be favoured for most applications. [1]

This is reflected by, and perhaps resulting from, the limited attention that thermal spraying for corrosion protection has had from the research community. The amount of available research
data on this subject is relatively small. Most publications describe the result of case studies, some spanning as many as 80 years. However, mechanistic studies towards the protective processes are very few.

Thermally sprayed coatings can, regarding the anodic reaction in a given environment, be divided into effectively inert coatings (gold, ceramics) and electrochemically active coatings. The latter group can be classed as corroding or passivating and when their substrate material is exposed, as cathodic or anodic to their substrate. For each of these situations a different set of considerations needs to be evaluated in order to achieve the desired corrosion protection.

An additional difficulty stems from the morphology of thermally sprayed coatings. The properties of a sprayed coating can differ considerably from their compositional bulk equivalent. Consequently, knowledge of the behaviour of bulk materials in a particular environment might lead to inaccurate expectations when applied to thermally sprayed coatings applied from feedstock material of nominally the same composition.

The reason why the properties of thermally sprayed coatings can be so different is caused by the application technique. A thermally sprayed coating is deposited by (partially) melting of small particles that are projected on to the substrate. The lamellar build-up of melted and partially unmelted particles, together with oxide inclusions and the inevitable pores leads to the typical coating morphology. The exact morphology depends on the coating material, the deposition temperature, speed of application etc. which is partially dictated by the choice of the thermal spraying method and by the applicator’s settings and skill.

![Image of thermally sprayed coating](image)

**Figure 1:** Schematic impression of the build-up of a thermally sprayed coating, showing the lamellar coating build-up with pores, oxides and unmelted particles. [62].

The immediate result is that both chemical and structural properties of the sprayed coating will differ considerably from their bulk equivalent. For mechanical properties it was shown that the sprayed coatings do not need to be inferior, e.g.: pores can effectively act as crack stoppers, thus considerably raising the fracture toughness [2] or favour the integration of foreign objects with living tissue in sprayed coatings on medical implants [3]. However, for corrosion protection, the inherent morphology of thermally sprayed coatings (the presence of pores and oxide inclusions) is generally regarded as a considerable disadvantage.
Whether this is in fact true, depends heavily on the corrosion mechanisms and conditions present in actual service. For instance, for coatings that are anodic to their substrates, the presence of pores in the coating does not need to lead to corrosion damage of the substrate at all, as will be discussed in chapter 4 of this thesis. Assumptions on the effectiveness or expected service life of a thermally sprayed coating in a specific environment are relevant only when the electrochemical interaction of the total coated system with its corrosive environment is known.
1.2 Corrosion of Metals

This section provides a brief introduction into the theory of metallic corrosion. In the first part of this section, three main concepts are introduced. First, the definition of an electrochemical reaction is explained, followed by an introduction of the concept of corrosion potential and polarisation curves. The second part of this section describes the main corrosion mechanisms that are encountered during the discussion of the results in chapters three and four of this thesis.

1.2.1 Electrochemical Reactions

Electrochemical reactions are reactions in which electrical charge is transferred in order to change the valence of the reacting species. An important example of an electrochemical reaction is the corrosion reaction by which a metal is transferred into a higher valent oxidation state. The products may be ionic solutions or solid products like oxides and hydroxides or even sulphides. The driving force for these reactions is provided by nature. In thermodynamical terms: The change in Gibbs free energy is negative for the reaction between the metal and its surrounding.

This process always involves at least two separate reactions: at least one anodic (oxidation) reaction, and at least one cathodic (reduction) reaction. The anodic reaction may involve the formation of a metal ion, increasing the valence of the atom and consequently freeing a number of electrons:

$$Me \rightarrow Me^{n+} + ne^-$$  \hspace{1cm} (1)

Electrochemical (corrosion) reactions at a metal/electrolyte interface involve the exchange of electrical charge over this interface. The charge carriers in the aqueous environment are ions; electrons carry the charge in the metal. The anode is defined as the location where positive charge carriers (ions) enter the electrolyte. The remaining electrons travel through the metal to the cathode. The cathodic reaction takes up the electrons, reducing the reactant to a lower valence:

$$O + ne^- \rightarrow R$$ \hspace{1cm} (2)

Examples of common cathodic reactions for neutral and basic aqueous solutions are:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$ \hspace{1cm} (3)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$ \hspace{1cm} (4)
Examples for acidic solutions are:

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (5)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm} (6)

In these examples the solvent (H₂O) is actively involved. However, also other cathodic reactions are possible, such as the reduction of dissolved components as Cr₂O₇²⁻, Fe³⁺ etc.

1.2.2 Electrode Potential, Polarisation Curve of Singular Electrode

On a uniformly corroding metal, the anodic and cathodic areas will be separated by only a few nanometers and shift with time so that the surface reacts evenly. Since the anodic and cathodic reactions take place on the same metal, the metal is called a multiple electrode. However, to explain the concepts of corrosion potential and polarisation it is necessary to simplify the issue and first discuss a singular electrode.

On a singular electrode only one electrode reaction takes place; For instance the metal dissolution reaction of equation 1. Assuming a dynamic equilibrium state of this metal in an electrolyte means that the oxidation reaction (the formation of the metal ion) and the reduction (the reverse reaction) will take place at the same rate.

Since these reactions involve the separation of positive and negative charge over an interface (the phase boundary between metal and electrolyte) an electrical field will result. The electrons resulting from reaction 1 will remain in the metal. The resulting electrical field will influence the electrolyte consisting of polar water molecules and dissolved ions resulting in a configuration of metal ions along the electrode surface, not unlike a charged capacitor. This configuration is called the electrochemical double layer. The presence of this double layer poses a barrier against further charge transfer and maintains the difference in potential between the metal and the surrounding electrolyte.

![Figure 2: Schematic impression of the electrochemical double layer at a singular metal electrode.](image-url)
The relationship between the current that passes through the interface and the resulting potential of the two reactions (reaction 1 and its reverse reaction) that maintain the dynamic equilibrium can be plotted in a polarisation curve for a singular electrode (Figure 3). Polarisation is defined as the change in the potential of an electrode. The equilibrium electrode potential is indicated in the graph at the position where the anodic and cathodic current magnitudes are equal.

For comparison of polarisation curves of different metals, often the logarithmic (Tafel) representation is preferred. Also in this thesis, the majority of the polarisation curves is shown in this format. A logarithmic version of the graph in Figure 3 is shown in Figure 4.

1.2.3 Corrosion Potential, Polarisation Curve of Multiple Electrode

As discussed before, a corroding metal consists of at least two electrode reactions. One reaction (the one with the lowest electrode potential) will be the anodic reaction. The other one will be the cathodic reaction. This situation is illustrated in Figure 5. The polarisation curve for the multiple electrode (the corroding metal) can be determined by the linear sum of the two singular electrode reactions. The resulting potential of the electrode will be determined by the situation where the anodic current will be equal to the cathodic current. This potential is the corrosion potential of the corroding metal in this specific environment. The corresponding anodic and cathodic current values are a direct measure of the corrosion rate of the electrode. Unfortunately, since the electrode reactions cannot be measured separately, the current values cannot be determined directly.

The resulting corrosion potential can be used to obtain information on the electrochemical behaviour of the corroding metal. However, also this potential value cannot be measured directly. The magnitude can only be determined by comparing the value to a reference potential, using a reference electrode. A reference electrode maintains a constant electrode potential.
virtually regardless of the experimental conditions, within a specified operating window (temperature, pressure etc.). The reference electrode used for the work described in this thesis is the saturated silver/silver-chloride reference electrode.

![Graphs of polarization curves](image)

**Figure 5:** Schematic of a polarization curve for a multiple electrode.

**Figure 6:** As Figure 5 (logarithmic representation)

The detection of the amount of polarisation (shifting of the potential of the metal) is a powerful method to obtain information on the electrochemical behaviour of the metal in a specific environment.

The polarisation can also be applied by an external power source. In practice this is performed by using a potentiostat. This apparatus is capable of maintaining a fixed potential difference between a reference electrode and the metal sample of interest, the working electrode. The resulting current, which can be either anodic when the metal is polarised positive to its corrosion potential, or cathodic when the opposite is true, flows through an inert platinum electrode. An example of the polarisation technique is described in section 2.6.

1.2.4 Corrosion Mechanisms

The previous part of this section assumed no preferential site for the cathodic or anodic reaction on the corroding metal. This is the prerequisite for uniform or general corrosion. This type of corrosion is not often a problem in practical situations. The reason for this is the generally gradual and relatively slow corrosion rate from which the time to critical material loss can easily be predicted.

Far more dangerous are the localised corrosion phenomena. These involve situations where, for a number of reasons, the location of the anodic metal dissolution is fixed. This will result in localised metal loss that may severely compromise the mechanical strength of metal structures, and may even lead to perforation within a relatively short time. This section will discuss two localised corrosion mechanisms that are important for the results discussed in this thesis.
First the mechanism of galvanic corrosion is discussed. The presence of defects and pores in a metallic thermally sprayed coating on an also metallic substrate, that are often unavoidable in practical situations, will expose both metals to the same electrolyte. When these metals differ significantly in corrosion potential, galvanic corrosion may well occur.

Table 1 lists the corrosion potential in artificial seawater for a number of metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Corrosion potential (mV vs. Ag/AgCl)</th>
<th>Metal</th>
<th>Corrosion potential (mV vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>(+43)</td>
<td>Pb 99.9</td>
<td>-459</td>
</tr>
<tr>
<td>Ag</td>
<td>-51</td>
<td>Sn 98.5</td>
<td>-484</td>
</tr>
<tr>
<td>Ni 99.6</td>
<td>-154</td>
<td>C-steel</td>
<td>-535</td>
</tr>
<tr>
<td>Cu</td>
<td>-190</td>
<td>Al 99.5</td>
<td>-867</td>
</tr>
<tr>
<td>18/8 RVS</td>
<td>-245</td>
<td>Zn 98</td>
<td>-1009</td>
</tr>
<tr>
<td>Ti</td>
<td>(-311)</td>
<td>Mg</td>
<td>-1555</td>
</tr>
</tbody>
</table>

Note: Brackets indicate a gradual increase of potential during exposure. Values are measured in artificial seawater to preclude the influence of biological fouling activity on potential values.

The relative value of the corrosion potential of a metal is a measure of its tendency to corrode when coupled to another (different) metal. The metal with the highest corrosion potential is relatively noble compared to the other metal.

The effect of the coupling of two dissimilar metals (A and B) is shown in Figure 7. Before coupling metal A was corroding at rate \( \text{i}_{\text{corr, metal A}} \), at a corrosion potential of \( \text{E}_{\text{corr, metal A}} \). Metal B was corroding at a significantly lower potential, \( \text{E}_{\text{corr, metal B}} \). In this example, metal B is less noble than metal A.

Coupling of metal A to metal B has the following effect (see also the numbers in Figure 7).

1. The total cathodic current increases. Since metal A and B are connected, the total size of the corroding sample (metal) is increased and therefore also the cathodic current. Note: the effect of the coupling on the cathodic reaction is exaggerated in the graph.

2. The total anodic current increases. Since metal A and B are coupled, the sum of their separate anodic reactions will determine the resulting anodic current.

3. The intersection of the total cathodic current and the total anodic current will determine the new corrosion potential. \( \text{i}_{\text{e}} = \text{i}_{\text{c}} \)

4. At the new corrosion potential, metal A corrodes with a rate of \( \text{i}_{\text{corr, metal A (A+B)}} \). Note that this rate is lower than the corrosion rate of metal A before the two metals were connected.

5. Metal B corrodes with a rate of \( \text{i}_{\text{corr, metal B (A+B)}} \). Note that this rate is higher than the corrosion rate of metal B before the two metals were connected.
In the resulting situation metal B corrodes more rapidly by the mechanism of galvanic corrosion. Metal A however, is protected from (rapid) corrosion. The method of corrosion protection is known as galvanic protection.

As was observed from Figure 7 the result of the galvanic interaction depends directly on the following parameters:

- Difference in corrosion potential of the separate metals.
- The cathodic reaction rates on the separate metals.
- The anodic reaction rates of the separate metals.

The resulting effects of galvanic corrosion for thermally sprayed coatings are discussed further in the next section.

Next to galvanic interaction, another important corrosion mechanism when dealing with metallic thermally sprayed coatings is occluded cell corrosion or crevice corrosion. This mechanism is mainly of importance for passivating metals. Passivating metals are metals that obtain their corrosion resistance through the formation of a dense, tightly adherent oxide film. The oxide shields the metal from the corrosive environment, thus significantly reducing the corrosion rate.

Examples of passivating metals are aluminium and titanium in seawater and stainless steels (steels with a chromium content above 12%) in most natural waters. Although all passive films significantly restrict the corrosion rate, the nature of the film may vary considerably. Stainless steels show a passive film of 1 to 10 nm whereas the passivating oxide on aluminium may reach a thickness of 10-20 nanometers and the protective oxide scale on copper alloys may reach values up to tenths of millimetres.

The polarisation curve of a passivating metal is shown in Figure 8. Generally, the anodic current density (current per unit area) needs to reach a critical value before the passivating layer becomes effective. At potentials below this value the material behaves as a common corroding metal. The value at which the passivation starts is called "critical current density" ($i_{\text{critical}}$). After passivation the current density drops to very low values, the passive current density ($i_{\text{passive}}$). A
general order of magnitude for a well passivating system is a passive current density below 100 \( \mu A/cm^2 \).

The potential region in which the current remains relatively constant around the passive current density is called the passive region. A successful use of a passivating metal in a technical application depends (among others) on the condition that the material is not polarised to values outside this passive region.

![Figure 8: Schematic impression of the result of aeration on the corrosion rate of a passivating metal.](image)

The corrosion protection of a passivating metal depends on the effectiveness of the build-up and maintenance of the passive oxide layer. For this reason a main prerequisite is the availability of oxygen. When a passive film is damaged in the presence of oxygen, either by chemical attack (the passive film on stainless steel is mainly susceptible to attack by halides, especially Cl\(^-\)) or mechanical damage, the film will repair and the metal will remain protected (the "well aerated" situation A in Figure 8).

However, in narrow pores and crevices of a thermally sprayed coating, the availability of oxygen may well be impeded. This drastically limits the cathodic current. Damage to a passive film in such a poorly aerated location may lead to the situation B shown in Figure 8. The cathodic current cannot sustain the required current density for the formation of a passive layer. Consequently the metal will become active and the corrosion rate increases from \( i_{passive} \) to \( i_{corrosion} \).

Furthermore in stainless steel coatings, the local anodic activity may lead to acidification in the narrow pore or crevice. The release of metal ions, especially chromium in the crevice produces the acidic condition as a result of a series of hydrolysis reactions [53]. This also will prevent any repassivation and further accelerates the corrosion process. Another important factor when discussing this type of corrosion is the electrical conductivity of the intact passive layer. Passive films that are capable of conducting electrical current (as on stainless steels) are even more susceptible to crevice corrosion. In this case the localised anodic reaction in the crevice can be sustained by a cathodic reaction anywhere on the outside surface of the metal. Poorly
conducting passive films (as on titanium and pure aluminium) require a cathodic reaction close to the crevice that may well decrease the rate of the corrosion reaction.
1.3 Corrosion Protection Using Thermally Sprayed Coatings

In principle there are two ways to protect a metallic substrate against corrosion by using a metallic thermally sprayed coating.

The first method depends on completely shielding (sealing) the substrate from the corrosive environment by using a coating with an acceptable service life in the specific environment. This can be attempted by using a (more or less) inert (immune) coating, or a coating with a good passive oxide layer.

An immune coating has no thermodynamic driving force to dissolve into the corrosive environment. Examples are gold or platinum in seawater. A passive material does corrode, but, as discussed in section 1.2, the result of the corrosion reaction is a tightly adherent, dense oxide layer that completely covers the metallic material. The presence of the oxide layer prevents any further corrosion of the passivating metal. Examples are AISI316 stainless steel or titanium in seawater. These types of coatings are called barrier coatings.

However, these coatings are (by definition) more noble than their substrate. Therefore a (small) defect in the coating may result in rapid localised corrosion of the substrate. For this type of coatings it is very important to minimise defects and porosity of the coating.

The effect of pores in a noble barrier coating is schematically shown in Figure 9. The figure shows the decrease of the anodic current resulting from the coating material at the expense of the material in the pores (the substrate).

![Figure 9: Schematic representation of the effect of pores in a metallic coating that is more noble than the substrate.](image)

The second way to prevent the corrosion of a metallic substrate by a metallic coating is to use the mechanism of cathodic protection. This requires the substrate to be coupled, or (partially) covered by a less noble material. When the less noble material is applied as a coating, it is not absolutely necessary to cover the substrate entirely. Defects and pores that expose the
substrate do not lead to corrosion of the substrate since the substrate will be protected at the expense of the coating. The anodic reaction will take place primarily on the coating and the metallic substrate will mainly support the cathodic reaction. This behaviour is shown in Figure 10.

![Figure 10: Schematic representation of the effect of pores in a metallic coating that is less noble than the substrate.](image)

The increase of the rate with which the coating will be consumed depends on the total anodic current resulting from the exposed substrate material, which is directly related to the number and size of the pores. For this reason a defect free coating is still preferred over a porous coating.

Considering the two described possibilities for corrosion protection, it is possible to formulate the basic qualification criteria in order to achieve acceptable corrosion protection. The first considerations would be:

- **Is the coating more noble or less noble compared to the substrate in the service environment?**
- **Is the coating inert, immune, passivating or cathodically protecting?**

When the coating is inert or immune, the quality of the corrosion protection depends on the question whether the surface is completely covered or not.

For passivating systems, (i.e. systems that form a tightly adherent layer of corrosion products) the corrosion quality depends on:

- **What is the dissolution rate of the passive layer?**
- **How rapidly does the coating repassivate at defects?**

The term passivation should be taken in the broadest sense, including all corrosion retarding anodic deposits that are not, strictly speaking passive film (for instance the protective scale on copper alloys).
For coatings that cathodically protect the substrate material, the corrosion protection quality is determined by:

- What is the corrosion rate of the coating?
- How effective is the cathodic protection in terms of protecting the exposed substrate area?

These considerations are also presented in the diagram shown in Figure 11.

![Diagram showing the evaluation of corrosion protection quality](image)

*Figure 11: Schematic representations of quality evaluations for corrosion protection using a metallic coating on a metallic substrate.*

Standard, or non-electrochemical corrosion tests, based on exposure of a sample to a more-or-less controlled surrounding as, for instance the "air-oxidation test", the "Kesternich test" and the "hot salt spray" test, cannot answer these questions. The result of these accelerated ageing tests is a ranking of the amount of corrosion attack that has occurred during the test duration but does not include information on the mechanisms involved. Still these tests are used extensively, especially by industrial users for selection purposes [60].

It is claimed that, although no information other than "the panel shows little rust, or the panel shows a lot of rust" is obtained, they can be used to compare various systems. For instance, materials that have proved to perform well during service are compared with new or cheaper alternatives. In this case the tests are used as a qualitative reference test.

The main concern when using accelerated ageing tests is that the corrosion mechanisms in the test environment must be identical to the mechanisms that are encountered during actual use of the corrosion protection system. Care should be taken not to invoke corrosion rates or even completely new mechanisms in the test environment that would have no significant influence on the service life during actual use. Even when the test is used solely for qualitative ranking of coating systems, a sufficiently "alien" test environment can completely distort the qualification of any corrosion protection coating.
1.4 Thermal Spraying Technique

Thermal spraying is the generic name of a range of coating processes in which finely divided molten particles are sprayed onto a substrate. Thermal spraying techniques vary according to heat source, spray velocity and feedstock material. A useful overview of this is given in [7]. The application techniques are constantly being developed with respect to coating efficiency and layer build-up. Although there are some characteristic advantages using any one of these techniques, from a corrosion point of view, the properties of the resulting layers are essentially the same [9].

The relevant techniques for the large-scale application of relatively thick (50-200 μm) corrosion resistant coatings (which are also used to apply the coatings for the experiments described in this thesis) are flame spraying, arc spraying, atmospheric plasma spraying and high velocity oxygen fuel spraying. These techniques will be described very briefly below. A more extensive overview of these and more thermal spraying techniques can be found elsewhere [41].

![Diagram of thermal spraying techniques](image)

*Figure 12: Simplified schematic impression of the various spray techniques used.*

Flame spraying uses the energy of combustion of a fuel gas to heat the spray material. The most used fuel gases are oxy-acetylene and oxy-propylene with flame temperatures from 2800 °C to 3200 °C. The flame spray gun is relatively inexpensive and is typically used for spraying of aluminium and zinc, but it can be used for any metal with a melting point below 2800 °C. Figure 12 depicts a powder flame spray principle, but also flame spray guns that use wire feedstock material are commercially available.

Arc spray uses the energy of an electric arc discharge between two feedstock wires. The molten metal is subsequently propelled to the substrate by compressed air. This method can only use wire shaped, electrically conductive feedstock material, and is typically used for the spraying of aluminium and zinc, but also core wires are being developed enabling the use of non-conductive
materials. The voltage between the electrodes is typically in the range of 20 to 40 V which may lead to arc temperatures up to 6000 °C at a current of 280 A.

Atmospheric plasma spraying, as opposed to low pressure plasma spraying, uses the plasma energy to heat the spray material. The plasma is maintained between a circular anode near the tip of the gun and a cathode in the base of the gun. The plasma gas typically consists of argon or a mixture of argon and hydrogen. The temperature of the plasma can reach up to 20000 °C. These high temperatures enable this technique to melt any material that can be injected in powder form.

High velocity oxygen fuel spraying combines a relatively low melting temperature of about 3000 °C with an extremely high particle speed. This speed may reach values of 2000 m/s as opposed to about 100 m/s (flame spraying) to 1000 m/s (plasma spraying). This can result in very dense, tightly adherent coatings with little or no oxidation during the application. The HVOF technique is most used for hard, abrasion resistant coatings where adhesion is the main concern, but it can be used for any material available in powder form.

For all coating procedures, the surface preparation is regarded essential for the quality of the resulting coating. Substrate surfaces should be grit blasted at least to a "near white metal finish" or Swedish standard SA2½, to ensure a minimum of oxides and contaminants under the coating. For the same reason, the time between grit blasting and spray coat application should be reduced to the absolute minimum. However, for galvanically protecting coatings that are not subjected to a mechanical load during service, some lesser degree of surface preparation may well be allowed. This would facilitate the in-situ application of the coatings since optimal grit blasting conditions in these circumstances are not easily created.

For applications that demand specifically high adhesion strength of the coating, using a sharp grit to ensure an "anchor tooth" profile of the substrate can enhance the mechanical bonding. Also, pre heating the substrate (60-90°C) to remove condensation and minimise residual stresses caused by shrink differences is reported to be beneficial. [4]

The popular practice of sealing the thermally sprayed coating using an organic resin or even the application of a fully formulated top coating remains a point of discussion. Supporters of this practice claim considerable improvement of the corrosion resistance [6,15,18,35] together with the obvious improvement of the outward appearance of the structure. However, there are two arguments against this practice:

First, the effect on galvanic protection: Naturally this point is only valid for coatings that are less noble than the substrate. Since the organic coating will prevent the flow of electrical current (ions), the galvanic protection at a defect in the thermally sprayed coating may be drastically limited. [22] Instead of having the entire sprayed surface as a sacrificial anode, only the small area of spray coating at the sides of the defect will rapidly corrode. This is extensively discussed in section 4.3.3.

Second, the effect on the time to first maintenance: Since organic coatings, and especially un-pigmented resins, will generally deteriorate (bubbling, cracking and delamination) much more rapidly than the thermal spraying metal, the time to first maintenance will be significantly decreased. In fact, most probably the first maintenance will consist of the repair or removal of the organic system. [24]. Maintenance of the thermally sprayed coating itself is not expected to be required during its normal service life, apart from perhaps the removal of biological fouling by water jetting for specific marine immersion applications. [19]

Touch-up and on site repair of, for instance areas damaged during construction, is also possible. In fact, thermal spraying of zinc is recognised as the most suitable repair method of hot-dip or electrochemically galvanised structures. [21] However, care should be taken primarily for a sufficient surface preparation under these circumstances to avoid contamination that may lead to
accelerated attack of the repaired sites. Also the environmental consideration with regard to contaminated grit blast debris and over-spray material should be considered.
1.5 Economics of Thermal Spraying

The main goal of an economical corrosion protection system is to minimise total cost over the service life of the structure. In addition to initial expenditure, total cost includes both future maintenance and “loss of use” cost. In general, a true calculation of the cost involved in the application of a corrosion system should involve all related cost, including cost of material, energy expenditure and the effect on the environment. However, mainly high initial cost is the primary deterrent against the widespread use of thermal spraying for corrosion protection.

A reliable value for the initial cost of a thermal spraying layer can only be obtained by examining the different quotations for an actual project. All other values will either be biased in favour of organic coatings or metal spraying according to the calculating method. For instance, rough estimates of thermal spraying initial costs vary from 40% to 200% of the initial cost of an organic system. [20,24] Depending on the estimated life times, costs for maintenance, interest rate during service life and inflation level over next 40 years, the outcome can be very different.

Also the current economical climate will affect the selection of a system with either high or low initial cost. Theoretically, when the inflation rates are (relatively) low and the interest rates are (relatively) high it is better to invest in a system with low initial costs. In the opposite situation it would be more prudent to choose a high cost, high quality system that will require little or no maintenance during its service life. [20]

Another factor is the risk to the installation that would result from severe substrate corrosion. High risk will generally be in favour of the high quality system. Especially if this would be combined with high repair costs since the savings of one maintenance campaign over the service life would generally more than compensate for the higher initial cost. [27]

An estimation of the service life of thermally sprayed coatings is also very difficult. Especially for noble materials, there is not enough experience and information available in international literature to enable a meaningful estimate. For aluminium and zinc, the general experience in literature is reflected by the American Welding Society guide C2.18 that covers the application of thermally sprayed coatings for the protection of steel with aluminium and zinc. In this document a more or less linear relationship between layer thickness and service life is used, assuming general corrosion to be the lifetime determining factor.

Rural atmosphere is recognised as the least severe environment, only requiring 100 μm zinc or aluminium for 10 years of service to 200 microns for 40 years. Salt-water immersion is classed as the most severe service condition. This environment requires 350 μm of zinc or 250 microns of aluminium for 10 years of service. 40 years service in salt-water immersion is expected from either 500 μm of zinc or 350 μm of aluminium [5].

Using these values together with the cost per unit weight of aluminium and zinc to determine the cost of a coating system, one should take into account that the specific density of zinc is about three times higher than that of aluminium: zinc 7.1 g/cm³ to aluminium 2.7 g/cm³. In other words, the required amount of aluminium is less than half the amount of zinc, to obtain a coating of the same thickness.

It can be concluded that, although it is impossible to be exact about life cycle costs, given the variables of specific service conditions, general trends as reported in literature confirm that corrosion protection using thermal spraying of aluminium or zinc can offer a significant economical advantage over conventional organic coating systems. [20]
1.6 Environmental Aspects of Thermal Spraying

Regarding a possible harmful effect on the environment by the use of thermally sprayed coatings, as with the life cycle cost discussed in section 1.5, the complete cycle of production, application, service and recycling should be considered.

During the production of spray materials, the resulting environmental loads will vary considerably depending on the specific metal. However, whether the environmental load will be significant for the discussion about the use of thermal spraying will probably be determined by the fact whether any harmful effect on the environment is incorporated in the cost of the feedstock material as a result of legislation. An important example of this is zinc that is currently being recognised as a heavy metal and restrictions to its use are expected in the near future.

But because of environmental regulations becoming more rigorous, the use of traditional high performance organic systems is also progressively more discouraged. Currently, active legislation and codes of practice already cover the reduction of volatile organic compounds emission, restrictions on chromate and lead compounds, isocyanates, aromatic amine curing agents and the ability to use coal tar based paint formulations. Therefore, since thermally sprayed coatings contain none of these substances and the protective properties in many applications can be at least comparable, any new legislation in this field will be an additional incentive towards the use of thermally sprayed coatings.\[12,27\]

Regarding human safety during application, the basic precautions for thermal spraying are similar as for welding and cutting. Thermal spraying operators should protect themselves with clothing to cover all exposed skin, respirators, face shields and ear protectors. The main health hazards are a high level of noise (up to 120 dB(A)), respirable dust, ultraviolet and infrared radiation, and the formation of ozone and nitrogen oxides.\[11,28\]

In addition, airborne metal dust, finely divided solids or accumulations should be treated as explosives. Adequate ventilation in the thermal spraying work area and collection of over-spray should be made to minimise the explosion and fire hazards and release of controlled and hazardous material [5].

Furthermore, to reduce the need for disposal of contaminated blast debris, the use of recyclable grits is necessary. Ferrous abrasives are more efficiently recycled than non-ferrous abrasives because they can be magnetically removed from contaminated debris. For this reason chilled iron or fractured steel grit should be used since this also is sufficiently sharp to provide the necessary profile required for good adhesion of the thermally sprayed coating.\[18\] However, since direct contact of dissimilar metals should be avoided (as discussed in section 1.5), in practice this can only be used for steel substrates.

Once the coating is in place, no harmful effect on the environment will be expected other than can be expected from a solid structure of the same composition. For example, as discussed in section 4.3.1, the effect of fouling on the integrity of an aluminium coating has indicated no harmful effect of the coating on the condition of the fouling organisms [38]. Although extended exposure to metallic aluminium will affect the nervous system; the outside layer of the aluminium coating will consist primarily of aluminium oxide, which is abundantly encountered in many natural environments and behaves quite passively.
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2 Quality Control of Thermally Sprayed Coatings for Corrosion Protection

Summary

This section gives an overview of the most used techniques for the assessment of the five most important issues that determine the quality of thermally sprayed coatings for corrosion protection: coating thickness, adhesion, porosity, composition and electrochemical behaviour. The purpose of this section is to show that the assessment of each of these items, (except for coating thickness) poses significant problems when applied to thermally sprayed coatings. Electrochemical measurements are recognised to be able to reveal the most relevant information on corrosion protection quality of the coating. It is concluded that an electrochemical investigation is the only available reliable fast method to obtain an indication of the behaviour in service conditions. Therefore, simplified modification of electrochemical test methods will be the most promising alternative to supplement the existing quality tests (based on coating thickness, adhesion etc.) for corrosion resistant thermally sprayed coatings.

2.1 Introduction

This section gives an overview of the most used techniques for the quality assessment of thermally sprayed coatings for corrosion protection. The purpose of this section is to investigate the currently available testing methods and to reveal possible opportunities for the development of novel techniques.

Many of the techniques described in this section have been used for the experiments described in chapter 3 and 4 of this thesis. However, this section is not primarily intended as a description of the used experimental techniques. The overview in this section should be regarded as a general survey of available techniques that are presently used for the qualification of thermally sprayed coatings. Details on the conditions and techniques used during the experiments is provided in chapter 3 and 4.

Perhaps the most pressing problem opposing an increase of the use of thermally sprayed coatings for corrosion control is the need for reliable coating qualification methods [43,44]. A thermally sprayed coating of good quality is defined as a coating that provides adequate corrosion protection for the desired service life of the coated object, without the need for unscheduled maintenance.

Qualification tests for the separation of good coatings from bad coatings are only of use when they are combined with well defined specifications: a set of instructions how the test should be executed and criteria for the interpretation of the quality parameters [1]. In this respect the descriptions in this section are incomplete. However, since the criteria for qualification tests are determined by the materials and the conditions for each specific application, a complete description would be virtually impossible [2]. Nevertheless, an overview of qualification methods is required at this stage to demonstrate the available techniques and position the use of electrochemical qualification techniques for thermally sprayed coatings.

Most testing methods that are currently in use consist of modified and adapted versions of traditional organic paint tests. Paint tests and testing procedures were designed to meet the requirements for organic systems and have evolved to produce the most reliable and reproducible results possible. Consequently, the use of these tests for a significantly different system will lead to an increase of both systematic and random errors in the measurement. This results in a great deal of confusion about the reliability of the coating, although it most probably is the test method that is of poor quality.
An illustrative example is the coating adhesion measured by tensile adhesion testing. For an organic coating the adhesion value is of prime importance since the main protective mechanism is the insertion of a barrier between the substrate metal and the corrosive environment. The tensile adhesion test provides information on the structural integrity of the polymer as well as the integrity of the coating to metal interface. Clustering of moisture in pores and on the coating/metal interface or even the development of osmotic pressures by dissolved salts at the interface will strongly affect coating adhesion. For this reason, the tensile adhesion test is a valuable tool to determine the corrosion protection quality of the organic coating.

As discussed in section 1.3, thermally sprayed coatings do not always rely on a purely barrier type protection mechanism. Although adhesion is important for noble coatings, for metallic coating that are less noble than their substrate, coating adhesion is far less critical. The galvanic protection mechanism is generally well capable of maintaining an adequate corrosion protection regardless of the adhesion of the coating. Naturally, the adhesion of the coating should be sufficiently high to ensure the physical presence of the thermally sprayed layer, but it does not have the same primary role in the degradation mechanisms of the corrosion protection system as for organic coatings. [1]

Nonetheless, many industrial users demand very high adhesion values for galvanically protecting coatings, and even refrain from using them when the arbitrarily requested adhesion value can not be realised.

Including coating adhesion, from experience, five main items can be recognised that are used to define a thermally sprayed coating as being of good or bad corrosion protection quality. These items are thickness, adhesion, porosity, composition and electrochemical behaviour. The next sections provide an overview of the most popular techniques that are currently available to determine these parameters.
2.2 Thickness

Measurement of the coating thickness is probably the first test that is used on a freshly applied thermally sprayed coating. This section gives an overview of the most frequently used techniques for this measurement. The described techniques can roughly be divided into direct (more or less absolute) methods and the indirect but more flexible methods. Specifically, the non-destructive "probe" methods are very easy to use and can be used directly next to the spray gun without any sample preparation.

The main disadvantage of these "probe type" thickness gauges is that their accuracy relies on careful calibration. The highest accuracy can be achieved when the calibration is carried out using material of the same composition as is used for the actual measurement. The thickness of calibration samples is often determined using the direct methods described in the first two subsections.

2.2.1 Screw Gauge Micrometer

A relatively simple and familiar method for the determination of layer thickness is by means of a micrometer screw gauge. A coated specimen is clamped using a low but well-defined force between the spindle and the frame of the micrometer. The distance between the spindle and the frame can be read on a measurement scale and must be compared to the result of a measurement on the uncoated sample. Subtraction of the two values yields directly the thickness of the coating.

The most important drawback of this method stems from the fact that the thickness is measured from tip to tip. Since thermally sprayed coatings have a relatively high surface roughness, this technique will generally indicate significantly higher values when compared to the results of other methods. Also the shape and size of the coated sample is limited since the depth of the frame of a standard micrometer does not exceed about 10 cm.

2.2.2 Microscopy

Probably the most reliable measurement technique for the determination of coating thickness is by using a visual measurement on the cross section of the coating. After embedding, cutting and polishing of the sample, the coating thickness can directly be measured using optical microscopy. The sample preparation does not need to be of the highest quality since the typical coating structure can easily be discriminated from the substrate metal.

The drawback of this method is the number of preparation steps, which makes the method relatively time consuming.

2.2.3 Non Destructive (Probe) Methods

As stated in the introduction of this section, these methods share a very high degree of flexibility. They can be used directly next to the spray gun and do not need any preparation of the sample surface. The reliability of the measurement strongly depends on the correct calibration of the probe for the combination of the coating and substrate.

The most frequently used methods are briefly discussed below [4-7]:

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Magnetic Induction Method
A low frequency alternating current generates a magnetic field of which the flux density (strength) is determined by the distance of the probe tip to a ferro magnetic material. Placing the probe tip on the surface of a non-magnetic coating on a ferro magnetic substrate enables the calculation of the coating thickness by measuring the strength of the magnetic field using a detection coil.

This method can only be used for a combination of a non-magnetic coating on a ferro magnetic substrate.

Eddy-Current Method
A high frequency alternating current generates a high frequency magnetic field that induces "eddy-currents" (induction currents) in the ferro magnetic substrate material. The magnitude of these currents is strongly dependent on the type of material and the amount of that specific material (thickness) that is present under the probe. The signal that is ultimately measured is the change in impedance of the original signal as a result of the generated eddy-currents. This signal can, after calibration, be used to calculate the thickness of a layer.

This method is very well suited for non-conductive coatings on ferro magnetic substrates. However, modern instrumentation enables this measurement on almost any combination of materials provided that the difference in magnetic permeability between a coating and its substrate is sufficiently large.

Ultrasonic (Acoustic) Method
This method determines the thickness of a coating from the time it takes an ultrasonic pulse to travel through it. The pulse is emitted from a probe at the surface, travels through the coating, is reflected at the bottom of the substrate, and returns to the probe tip.

Advanced signal analysis enables in principle a measurement on a coated substrate. Using the relative speed of sound in the coating and the substrate, the thickness of the coating can be calculated. However, in practice a coating thickness is mainly measured by comparing a coated sample to uncoated substrates, but even this measurement needs careful calibration.
2.3 Adhesion

This section briefly describes the most suitable methods for the assessment of the adhesion of a thermally sprayed coating. First some considerations on the definition of adhesion are given, to illustrate the true adhesion value of the coating as compared to the results of the described measurements.

The minimal requirement for the adhesion of a coating can be defined as the required force to remain attached to the substrate during the entire service life of the structure [1,8].

In theory, the adhesion of two materials can be described as a function of their respective surface energies. During an adhesion test, generally two materials (the coating and the substrate) are mechanically separated and the required force is measured. The reversible work required to separate two materials follows from:

\[ W_{AB} = Y_A + Y_B - Y_{AB} \]  

(1)

with:
\[ W_{AB} = \text{reversible work of adhesion} \]
\[ Y_A = \text{specific surface energy A} \]
\[ Y_B = \text{specific surface energy B} \]
\[ Y_{AB} = \text{specific surface energy interface} \]

In practice however, also a certain degree of deformation will occur when the adhesion is measured. This requires the introduction of an extra term in equation (1). The amount of energy related to the deformation of the coating and substrate generally exceeds the surface energies by far.

The amount of work required to separate a completely level surface coating from an also level substrate follows from equation 2. The directions (x,y,z) constitute a standard ordinate system.

\[ W_{AB} = F_{AB}(x)dx + F_{AB}(y)dy + F_{AB}(z)dz \]  

(2)

with:
\[ W_{AB} = \text{reversible work of adhesion} \]
\[ F_{AB} = \text{total adhesive force} \]

Registering the amount of work required for the separation of the sprayed coating would be the most appropriate way to describe the adhesion of the coating. However, generally during an adhesion test, only the peak force required during the test will be registered. No information on the behaviour of \( F_{AB} \) combined with the direction of loading will be available, and hence, no information on the amount of work can be obtained. Furthermore, the magnitude of the registered peak load may be poorly reproducible since the magnitude will depend on the exact direction of load and on the rate with which the load is applied.

This is the main problem when comparing adhesion tests results. It poses severe practical problems for the users of thermally sprayed coatings since adhesion testing is the main qualification technique that is currently used.

The reason why adhesion is popular as a qualification check stems not from the important role of adhesion during actual service of the coating, but from the fact that adhesion is mainly determined by the conditions and procedures during application. An adhesion measurement on the freshly sprayed coating enables the end user, to some extent, to determine whether the
applicator has followed the proper procedures with regard to surface preparation etc. But nonetheless, the adhesion values remain extremely sensitive to experimental conditions and are generally poorly reproducible.

The adhesion of thermally sprayed coatings is mainly based on mechanical anchoring. The surface roughness plays an important role in this mechanism. For this reason most technical specifications demand a SA3 blast clean surface and a 75 to 130 µm peak to valley roughness. More recent studies however, suggest that mainly the shape of the roughness determines the adhesion of the coating [1]. Especially an “anchor tooth” profile which enables the coating to “fold around” the roughness profile is regarded the optimal situation.

Finally, together with the adhesion value (or rather the maximum force required for failure) it is of prime importance to characterise the failure mode after the test. In practice, two types of failure are discriminated: adhesive failure (the fracture occurs at the interface between the coating and the substrate) and cohesive failure (the interface remains intact but either the coating or the substrate material fractures). Depending on the strength and ductility of the material, one, or a combination of these types will occur. In the case of cohesive failure in the substrate, it can be concluded that the adhesion of the coating will not be the limiting factor.

2.3.1 Pull-Off Tests [13]

Probably the most popular adhesion test for industrial use is the pull-off test. This method is based on loading the coating using a tensile force perpendicular to the plane of the coating/substrate interface and to gradually increase this force until failure occurs. When the failure mode is adhesive failure, the force at time of failure is used as a measure of the adhesion of the coating.

To apply a tensile force to the coating, it is necessary to make a connection to the coating. Normally, this is achieved by gluing a fixture (dolly) to the coating surface (Figure 1). This, of course, is a weak point of the technique, since the adhesion of the dolly needs to be at least as strong as the adhesion between the coating and the substrate. This requirement limits the measurement technique to stresses of 90 MN/m² (epoxy glue). Successful attempts have been published where the liquid adhesive was replaced by soldering which could increase the maximum adhesion value of the technique. [12].

![Figure 1: Schematic diagram of the pull-off test arrangement.](image)

A further disadvantage of this technique, specifically for porous (thermally sprayed) coatings is the penetration of the liquid adhesive into the coating. This can significantly affect the fracture behaviour of the coating and may even reach the surface of the substrate. This is the reason
why standards limit the use of the pull-off technique to coatings with a thickness of over 200 μm. It would be more realistic to limit the amount of porosity in the coating since the level of penetration into a dense HVOF coating will be much less than into a standard flame sprayed coating.

As was shown in the introduction of this section, an important variable in the execution of a pull-off test is the direction of load. To apply a simple tensile stress to the coating, the direction of load needs to be perpendicular to the plane of the coating and the interface. This proves to be very difficult in practice. The surface roughness and irregularities will result in localised complex stress conditions that severely affect the interpretation of the results.

A modification of the tensile pull-off test that avoids this concern is the lap-shear test. This method has the further advantage of the minimisation of deformation of the coating. Also a larger area of the coating can be tested since the method is not restricted by the size of a dolly. [8] The test arrangement (Figure 2) consists of a coated strip of which the coated side is glued to another metal strip with a well-defined overlap. The tensile force is applied parallel to the coating substrate interface, which results in a shear stress over the coating interface. In this arrangement, the stress at fracture will be a direct measure of the maximum tangential component of the adhesion of the coating.

![Figure 2: Schematic diagram of the lap shear test arrangement.](image)

2.3.2 Bending Tests

The problem of the alignment of the direction of load in the tensile test can also be avoided by using bending tests. The simplest form of a bending test is a standard three-point test using staff shaped material. As shown in Figure 3, the staff is divided into two sections of which one is coated with the coating of which the adhesion needs to be measured. The two sections are glued back together, leaving the coating in-between the two sections of the staff. Inserting a well-defined notch at the interface induces failure at the interface of the coating with the first section of the staff. The notch causes a stress concentration at the interface during the bending test that will lead to failure at this point.
Figure 3: Schematic diagram of the notched three point bending test arrangement.

Good definition of the notch will enable calculation of the tensile stresses that occurred at the interface at the moment of fracture. Naturally, the drawbacks of this technique are the notch and the requirement of a liquid adhesive.

A more elegant variation that does not use adhesives is described by Howard [11]. This technique uses a coated sheet substrate that is scratched to the substrate (Figure 4). Bending of the substrate and subsequent registration of the load as a function of the displacement (bending angle) enables measurement of the adhesion of the coating. When the coating is less elastic than the substrate (which is generally the case for thermally sprayed coatings on a metallic substrate) it will disbond at a certain bending angle. This will cause momentary relaxation and subsequent build up when the disbonding has stopped. The relation between the disbonded area and the applied load enables calculation of the amount of energy needed for disbondment.

Figure 4: Schematic diagram of the bending test arrangement for scratched samples.
2.4 Porosity

Probably the most well known property of thermally sprayed coatings is their porosity. Porosity is a very important issue for corrosion applications since, (as discussed in section 1.3) corrosion protection is at least partly based on the shielding of the substrate from an aggressive corrosive environment. [26] The effect of coating porosity on the corrosion protection properties will be extensively discussed in the following chapters.

In literature seven different types of pores are recognised:

Type 1: inter-lamellar pore, caused by stacking of separate particles. The number and size of these pores directly depends on the particle size and distribution of the spray material.

Type 2: trapped gas pockets caused by turbulence of the gas flow.

Type 3: gas bubbles, caused by dissolution of the gas into the molten metal and subsequent evaporation at solidification of the metal.

Type 4: pores caused by disintegration of the spray particle at impact.

Type 5: pores caused by condensation of partially evaporated particles. This type of pores often contains powdery residue.

Type 6: pores caused by the formation of dendrites at solidification of the particles, the highly textured morphology causes a disruption of the coating structure.

Type 7: micro cracks, regardless of origin (solidification, cooling, external load etc.)

![Diagram of different pore types](image_url)

*Figure 5: Schematic of the various pore types that can be encountered in thermal spraying materials.*

The total amount of porosity in a thermally sprayed coating can be defined as:

\[ p = 100\% - 100\% \cdot \left( \frac{\rho_f}{\rho_c} \right) \]  

(3)

with:

- \( p \) = general porosity (%)
- \( \rho_f \) = specific density feedstock (kg/m³)
- \( \rho_c \) = specific density coating (kg/m³)
Besides the seven types listed above, porosity in a thermally sprayed coating can also be divided into three separate types relevant for corrosion protection. These are open porosity, half-open porosity and closed porosity.

Open pores constitute an open connection between the substrate and the outside environment. In principle, this is the worst kind of porosity since the coating loses its barrier function between the substrate and the corrosive environment.

Closed porosity, however, cannot be accessed from the outside. Closed pores are completely sealed free space inside the coating layer that cannot contribute to reactions with the environment.

Half-open porosity is a variation of open porosity that results from a layered build-up of a porous coating. When a singular layer is applied, all porosity will connect the outside environment to the substrate material (all pores are open pores). A subsequent layer will close some of the pores, placing them in the second category. Some pores in the new layer will connect to the pores in the previous layer, these consist of the new open porosity. The remainder of the pores in the new layer will have a connection to the outside, but will end at the previous layer. These are called half-open pores, pores that start at the surface and end somewhere inside the coating without reaching the substrate material. These pores do contribute to the surface area of the coating and could be regarded as an extreme form of roughness.

2.4.1 Image Analysis

Micrographs from either optical or electron microscopy on cross sections of thermally sprayed coatings are often used as a first impression of the quality of the coating. Degree of melting and oxidation as well as an indication of the porosity can be obtained from the photo.

These photographs usually show porosity as black regions within the coating structure. Calculation of the relative surface area of “black” as compared to the total area is easily done using computer image analysis. This method is theoretically correct and, combined with vacuum impregnation methods, can also be used to distinguish open, half-open and closed pores.

The major weak point of this method is the question weather the porosity that is measured is equal to the porosity actually present in the coating. In other words, has the preparation to obtain the photo affected the porosity in any way? Especially breakout of brittle, tough particles in the coating (high temperature oxides) during cutting, grinding and polishing of the sample increases apparent porosity. But also the smearing of soft compounds during preparation can close pores, which can distort the picture in the other direction.

Suggested methods to prevent these phenomena use a viscous impregnation and fixation resin. This, of course, is only possible in the case of (half) open pores.

Unfortunately, literature indicates that the technique of interpretation of the micrographs is subject to a relatively large error due to subjective judgement of the data. [28-32].

2.4.2 Mercury Porosimetry [22]

This technique determines the amount of accessible pores in a material. Applied to a porous coating on a substrate, this would be all but the closed porosity. The technique is based on the filling-up of the pores in a material by submersion in a mercury bath and gradually increasing the pressure. This does not only determine the total amount of pores but can also reveal a distribution of pore size. The smallest detectable diameter is about 0.003 μm.

The technique is based on the Young and Laplace equation for capillary suction:
\[ p = \frac{-4\gamma \cdot \cos \theta}{D} \]  \hspace{1cm} (4)

with:
\begin{align*}
p &= \text{pressure (N/m}^2) \\
\gamma &= \text{surface tension (N/m)} \\
\theta &= \text{contact angle} \\
D &= \text{pore diameter (m)}
\end{align*}

A precondition for this method is that an external pressure is required for the ingress of mercury into the porous structure. This means that the term \( \cos \theta \) in equation (4) should be less than zero, which means that the contact angle must be within 90° and 180°. This is the reason why mercury is used since it meets this requirement for most materials. Unfortunately this method is less suited for use on metallic thermally sprayed coatings because of the tendency of mercury to interact with the metal.

The most important drawback of this method is the fact that the pore size distribution can only detect the smallest part of a pore. Relatively large pores that have a small entrance will be marked as "small". Naturally, this does not affect the total open porosity value.

2.4.3 Pycnometry

This technique is used to determine the porosity by subtracting the volume that is displaced by the porous coating from the outside volume of the coating. This yields the total volume of accessible free space i.e. the (half) open pores.

A carefully calibrated container is used (the "pycnometre") in which the sample is inserted. The container is filled with a liquid that spontaneously should fill all accessible free space. The difference between the volume of the container and the volume of the added liquid yields the volume of solid material of the sample.

Since the intrusion should be spontaneously, the wetting of the sample should be very good. As opposed to the mercury porosimetry, the contact angle of the liquid and the sample should be smaller than 90°.

Using gases increases the degree of penetration of the sample. A commercial helium pycnometre has a detection limit of about 0.0001 μm.

One disadvantage of this technique is that the closed pores are considered "solid material" and are not included into the resulting porosity. But a more important drawback is the fact that the measurement requires an accurate value for the outside volume of the coating. This is considerably complicated by the generally rough outer surface of thermally sprayed coatings.
2.5 Microstructure and Composition

This section provides a brief description of a selection of techniques that can be used to determine the microstructure and composition of thermally sprayed coatings. Since the number of techniques that are available for this purpose is very large, only the techniques that were used for the analysis of the results in this thesis are discussed.

Since the porosity of the coatings was already discussed in section 2.4 it is excluded from the discussion of microstructure in this section. Microstructure in this section should be understood as: size and distribution of splat lamellae, oxide inclusions, unmelted particles, i.e. the physical composition of the coating besides porosity.

A well-controlled physical and chemical composition of the sprayed coating is especially for corrosion purposes of the utmost importance. The generally extremely reactive conditions during the spray application can be expected to lead to significant differences of composition between the sprayed coating and the original material. The formation of oxides and nitrides but also the formation of meta-stable phases or the segregation of alloying elements can cause unexpected corrosion behaviour. [33-35].

2.5.1 Optical Microscopy

The relative ease of use and the low demands for preparation makes optical microscopy a very popular research tool to obtain information on the morphology of the coating. Normal light microscopy on polished cross sections of the coating at magnifications from 100 to 1000 times provides quantitative information on the general microstructure of the coating. As discussed in sub section 2.4.1 also information on the porosity and the degree of melting of the particles can be obtained. Naturally, no information on the composition of the coating can be achieved other than a rough estimate of the amount of oxidation.

2.5.2 Electron Microscopy

Scanning electron microscopy (SEM) uses an electron beam for image formation, which enables the detection of images with a resolution beyond the possibilities of visual light. Depending on the type of microscope and the sample, magnifications up to 100,000 times are possible with a lateral resolution around 100 nm.

The SEM offers two types of imaging, using backscattered primary electrons or secondary electrons activated by the primary electron beam.

The secondary electron image has a better depth of field which makes it better suited for topological information. The backscatter image has a much poorer depth of field but the intensity of the image is dependent on the element in the sample. This enables the visualisation of local differences in composition as shades of grey in an intensity plot.

Irradiation of the sample with an electron beam also triggers the emission of x-rays of which the intensity and wavelength are characteristic for the elements in the sample. The main power of SEM is reached when it is used in conjunction with x-ray analysis equipment. This facilitates the combination of topological information with quantitative element analysis on a micro-scale.
2.5.3 X-Ray Analysis

Analysis of a chemical composition can be obtained from the spectrum of x-rays that are emitted by activation of the elements in the material by an electron beam. The resolution of this technique is relatively small (approx. 1 μm) The analysis of the x-rays can either be done for wavelength (wave dispersive analysis of x-rays: WDX) or energy (energy dispersive analysis of x-rays: EDX). Depending on the acceleration voltage and the material of the sample, the information depth can be varied from 1 to 20 μm. The technique can be used for point analysis, line scan or two-dimensional element mapping. Since the measurement signal is specific for elements irrespective of their valency, it is not possible to identify chemical compounds.

2.5.4 X-Ray Diffraction

This technique is based on the diffraction of electromagnetic radiation by the periodic morphology of crystalline solids. The x-ray diffraction techniques for chemical analysis have a relatively large penetration depth (approx. 10 μm) because of the low dispersion of x-rays, and can be used for bulk analysis.

The technique is based on the fact that crystal planes in the crystalline structure cause an intensity peak of the reflected radiation when they meet the Bragg reflection criterion:

$$2d \sin \theta = \lambda$$

with:

\begin{align*}
    d &= \text{distance between planes (m)} \\
    \theta &= \text{angle of diffraction} \\
    \lambda &= \text{wavelength (m)}
\end{align*}

A complete spectrum of diffraction angles and the intensity of the reflected x-rays can be considered a fingerprint of the material. This fingerprint can be identified using a computer database of previously tested model samples. Depending on the material, also information on the texture, stresses and strain can be obtained. Measurements on thermally sprayed coatings can also reveal information on the particle size in the coating. The lateral resolution of this technique would be in the order of centimetres. The depth resolution is about 10 μm.

The disadvantage for thermally sprayed coatings is that these often contain amorphous phases that do not cause an unambiguous diffraction pattern. Also meta-stable phases can form of which the diffraction pattern is unique and therefore cannot be identified using the database information.
2.6 Electrochemical Behaviour

The electrochemical behaviour of a thermally sprayed coating is defined here as the effect of the anodic and cathodic reactions that take place at the surface of the thermally sprayed coating. These effects include the corrosion and passivation of the coating as well as any galvanic interaction between the coating and its substrate.

The electrochemical behaviour of materials can be measured using electrochemical measurement techniques. These techniques determine either a current or potential associated with one, or a number of the electrochemical reactions as explained in section 1.2. These measurements can provide general information on the corrosion behaviour of the material in its surrounding environment, for example by using corrosion potential monitoring techniques. Also the rate of electrode reactions expressed as a current density can be measured, by for instance polarisation methods.

The following sub sections provide a brief description of the most important electrochemical measurement methods for the assessment of the electrochemical behaviour of thermally sprayed coatings as used in this thesis.

2.6.1 Potential Monitoring

This method determines the general corrosion behaviour of a material in its environment. It consists of the registration of the open circuit potential (corrosion potential) measured on an exposed sample as a function of the exposure time in the corrosive environment. Changes of the surface properties of the sample, as oxidation (passivation) or changes in the localised environment will affect the type or kinetics of the present anodic and cathodic reactions. And since the corrosion potential is coupled to the anodic and cathodic current densities, these effects can be detected using this technique.

Comparing the potential of the substrate to the potential of the coating material provides information on possible galvanic interaction, as explained in section 1.3.

Qualitative information on the degree of shielding of the substrate by the coating (the porosity of the coating) can also be obtained from the corrosion potential of coated samples when compared to the potential of an uncoated sample (Figure 7).
An important advantage of this method of porosity detection is that only the electrochemical effect of the pores is detected. This means that just the pores that significantly affect the corrosion behaviour will be detected. Closed or half open pores, or pores that, for a different reason do not contribute to the corrosion process will not be detected.

![Potential Behaviour Graph](image)

*Figure 7: Schematic impression of the behaviour of the corrosion potential of a coating as a function of its porosity.*

A condition for the effectiveness of this method is a sufficiently large difference in corrosion potential between the coating material and the material of the substrate. For this reason the detection of an active stainless steel coating on a carbon steel substrate will be very difficult since both materials will generally exhibit a similar corrosion potential. Metal combination of titanium or Monel and carbon steel will be much more effective, as demonstrated in chapter 3.

### 2.6.2 Dynamic Polarisation

A very powerful research technique for the study of electrochemical properties is the determination of the polarisation curve [37]. As explained in section 1.2 the polarisation curve describes the relation between the potential and current for the electrochemical reactions on an electrode.

During a measurement of the polarisation curve, current is fed through the sample (the working electrode) and an inert (usually platinum) counter electrode. The resulting potential in the electrolyte is measured using a reference electrode (Figure 8). Usually the potential is scanned over a range of values.

![Dynamic Polarisation Diagram](image)

*Figure 8: Schematic impression of the polarisation measurement cell arrangement, showing the anti-crevise corrosion assembly as a detail in section A.*

The schematic polarisation curve in Figure 9 illustrates the behaviour of the corrosion current as a result of an applied potential.
The scan is usually started from the cathodic direction. It starts at a potential more negative to the corrosion potential. At these values the cathodic reaction is prevalent and the anodic (corrosion) reaction of the sample is suppressed. Moving towards the corrosion potential, the anodic reaction rate will increase and the cathodic reaction will gradually decrease.

![Schematic of a polarisation curve measurement](image)

*Figure 9: Schematic of a polarisation curve measurement. (Compare to figure 5 of section 1.2.3).*

An important consideration when using this type of technique concerns the analysis of the current values. Normally, current values are changed into current densities (current per surface area) to compare the results from various sample sizes. Unfortunately, the determination of the current density for thermally sprayed coatings can be problematic. Since the coating surface is generally extremely rough it can be very difficult to determine the exact active surface area. The high roughness and the half-open porosity will increase the surface area significantly beyond the flat projection of the surface. This means that current density values that are determined at a surface of nominally 1 cm² may in practice be significantly lower.

On the other hand, since the coating can also be very inhomogeneous in composition, specific areas in the coating may be more active than others. Some locations of the coating may be passive whereas others may be freely corroding. This means that the origin of a measured current value may also be much smaller than the flat projection of the surface area, resulting in a higher true current density value.

Another important issue when using these experiments is to minimise the effect of the measurement on the electrochemical behaviour of the sample. Especially notorious is the introduction of crevice corrosion phenomena resulting from the contact point of the specimen and the material of the cell. The embedding of small samples or the clamping of a measurement cell on a larger sample introduces a crevice region on the working electrode that may well affect the electrochemical measurement.

Fortunately this problem is solved in a commercially available electrochemical measurement cell. These anti-crevice cells or "flushed-port cells" eliminate the crevice corrosion problem by continuously pumping a small volume of purified water into the contact area of the cell port. A schematic of the port mounting is shown as a detail in Figure 8.
The specimen is separated from the cell port by a filter paper ring, creating a diffusion barrier between the purified water, the specimen and the test solution. The purified water displaces any electrolyte that would otherwise be in this crevice region. Especially the presence of chloride ions in this region must be prevented. The flow rate of the purified water is typically in the range of 4 to 5 ml/h for a 1 cm² port opening. The cell must be sufficiently large to ensure a minimal dilution effect from the purified water within the time frame of the test.

The exposed sample area is not isolated from the test solution by the purified water because the difference in density makes the purified water flow upward just on the port sides. Furthermore, the stirring mixes the purified water with the test solution as soon as it enters the cell chamber.

2.6.3 Polarisation Resistance Method

The polarisation resistance method is a method to determine the corrosion rate with the aid of a specially designed polarisation measurement. The method is based on the fact that within about 10-20 mV of the corrosion potential the measured current varies linearly with the applied potential.

![Polarisation curve close-up](image)

Figure 10: Close up of a polarisation curve showing the linear current potential relationship around the equilibrium potential.

Stern and Geary derived the following relationship required to calculate the corrosion rate from a polarisation curve:

\[
i_{\text{corr}} = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)} \cdot \frac{\Delta i}{\Delta E}
\]  

(6)

with:

\[
\beta_a = \text{anodic Tafel slope (V/decade)}
\]

\[
\beta_c = \text{cathodic Tafel slope (V/decade)}
\]

\[
\frac{\Delta i}{\Delta E} = \text{slope at } i = 0 \text{ (Ohm m²)}
\]

The term \(\frac{\Delta i}{\Delta E}\) is known as the polarisation resistance. Equation 6 shows that the corrosion rate is inversely proportional to the polarisation resistance. Therefore, by determining the polarisation
resistance from a polarisation curve, a measure of the corrosion rate can be obtained which can be used for qualitative analysis.

2.6.4 Galvanic Coupling

The technique of coupling two dissimilar metals over a zero resistance ammeter is a powerful method to assess their galvanic interaction.

Since the ZRA is present in the circuit, the measured current directly reflects the corrosion rate as a result of the galvanic coupling. Since the amount of current resulting from the galvanic interaction is proportional to the size of the two electrodes, the ratio of the two electrodes should be carefully selected.

This technique is very well suited for the analysis of the effect of defects in a thermally sprayed coating. Two techniques can be used for this purpose. The defect can be introduced as a separate electrode of the same material as the coating substrate and coupled to a thermally sprayed coating. Or the defect is introduced on a thermally sprayed panel that is coupled to an identical panel without a defect. The first situation has the advantage of yielding a direct measure of the galvanic corrosion (or protection) current. The second method incorporates a more realistic configuration, but requires further analysis of the signal.

Since both panels are identical and the defect is very small compared to the area of the coating, about half of the current required by the defect will be obtained from the second panel. Therefore the amount of current flowing through the ZRA is a measure of the corrosion reaction rate caused by the introduction of the defect.

A condition for this technique is that the distance between the defect and the second panel without defect should be kept relatively small. This will minimise differences in current distribution caused by the electrolyte resistance between the two panels.

![Diagram of galvanic coupling setup](image)

*Figure 11: Schematic impression of the cell arrangement for galvanic coupling measurements.*

Figure 11 shows a specially designed cell for galvanic coupling experiments. The two working electrodes are clamped to the top and bottom of the cylinder, ensuring a completely symmetrical configuration. The reference electrode is introduced from the side of the cylinder and fed into the centre of the cell. Since the small volume of the cell would inevitably lead to depletion of reactants or saturation with reaction products, the electrolyte is constantly refreshed by means of the in- and outlets in the figure. The position of the in- and outlet also are symmetrical, to prevent any influence of the electrolyte flow on the current registration between the two panels.
2.7 Discussion and Conclusion

This chapter discussed a number of available techniques for the evaluation of five qualification parameters: coating thickness, adhesion, porosity, composition and electrochemical behaviour.

The order of these properties is not completely random, but was based on the most logical qualification procedure for thermally sprayed coatings. Generally the first parameter that will be measured when a coating is applied is its layer thickness. Especially using the convenient “probe type” methods, this test takes little time or effort. The coating adhesion is generally also checked directly after application. Many commercial applicators use a dolly pull-off test as a standard part of their coating quality assessment procedure. Ignoring the difficulties in the interpretation of the measurement values, as discussed in this section, the test does not require extensive sample preparation.

When more information is required, sample preparation becomes necessary. The preparation of a cross section and determination of the microstructure using visual examination will be the next step. Simultaneously the porosity can be determined using image analysis.

Finally, electrochemical evaluation of the samples can be carried out. These techniques also require the preparation of a sample, and more importantly, also the execution and interpretation of the experiments requires considerable specialised effort.

With exception of the coating thickness determination, each of the described techniques poses problems when applied to thermally sprayed coatings. Primarily the interpretation of the results towards assessment of the corrosion protection quality of the coating proves difficult. A summary of the encountered problems is as follows:

The measurement of adhesion of thermally sprayed coatings is theoretically unreliable since it is impossible to apply a pure tensile force to the interface. Irregularities and different orientations in the coating cause localised stress concentrations, making an accurate measurement impossible. Also the penetration of liquid adhesives into the porous structure may affect the adhesion values. Finally, the coating adhesion often exceeds the fracture strength of the adhesive.

The result of a porosity measurement of a coating is heavily dependent on the preparation of the sample. Also the interpretation of the visual data is subjective. Using visual examination it is not possible to distinguish open and closed porosity, although it is only the open porosity that needs to be controlled for corrosion purposes.

Analysis of composition and microstructure are also dependent on the preparation of the sample. Also this evaluation is hindered by the size of the particles in the sprayed coating. The combination of very small particles and an inhomogeneous structure makes it impossible to determine local composition differences using SEM-EDX. Moreover, the presence of meta-stable phases formed by rapid solidification cannot be accurately identified.

The most important problem when using electrochemical techniques is the uncertainty regarding the surface area of the substrate. The high roughness and the presence of (half) open pores make the interpretation of the results very difficult. The inhomogeneous structure and the local differences in composition also affect the reliability of the measurements.

Nevertheless, the major advantage of electrochemical techniques is that the result of the measurement will inherently incorporate all factors that affect the corrosion behaviour of the sample. The effects of porosity, composition variations, and inhomogeneous structure will directly influence the electrochemical properties as corrosion potential, passive current density, polarisation resistance etc. Based on this fact, semi-quantitative criteria can be formulated that
can be used in a qualification test for a specific coating system to be used in a specific environment.

Generally the demands for a practical qualification method to be used ex-situ by specialised personnel (for instance in a development laboratory) are:

- Accuracy and reproducibility
- Quantitative results, for ease of comparison of different systems

Should the test be available by industrial users for their own quality testing purposes the following demands can be added:

- User friendliness, demands for instruments and personnel need to be relatively low
- Flexibility, testing of complex shapes should be possible, technique should also be possible for renowned problem areas as edges, internal corners etc.
- Easy interpretation, clear criteria should be available that immediately provide relevant information on the quality of the coating.

And finally if the test should also be available for in-situ assessment of coated structures the additional demand will be:

- Non-destructiveness, no adverse effects on the coating can be allowed.

Testing of the described electrochemical methods versus these criteria clearly shows sufficient opportunity for improvement of the techniques.

The demand for reproducibility and quantitative results is reasonably well met by the currently available electrochemical techniques, making them suitable for use in specialised laboratories. However, the execution of the tests and the interpretation of the results do not meet the demand for user friendliness. Also the required flexibility, although theoretically not impossible, cannot be fulfilled by the available methods. Finally, the demand for "non-destructiveness" will disqualify many electrochemical techniques. Anodic current requires anodic dissolution, which is accelerated corrosion of the structure. Perhaps this can be avoided by using simultaneously sprayed test coupons during a coating application. This is common practice for the samples for adhesion tests. For true in-situ measurements, only the non-destructive electrochemical methods are available as monitoring of corrosion potentials and perhaps electrochemical noise measurements.

It can be concluded that the available electrochemical techniques cannot be used as such as standard qualification tests for thermally sprayed coatings, outside of specialised laboratories. However, it remains the only reliable way to obtain relevant information in a short period of time on the expected corrosion behaviour of a thermally sprayed coating. Electrochemical measurement techniques are potentially very useful and therefore the modification and adaptation towards quality assessment of thermally sprayed coatings should deserve extensive attention. This effort should be directed towards the gathering of data on the behaviour of thermally sprayed coatings, together with the development of simplified test procedures and appropriate qualification criteria.
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3 Coatings Cathodic to Their Steel Substrate

3.1 Introduction

This introduction consists of two main topics. First the most important considerations from the introduction of corrosion protection using metallic thermally sprayed coatings are summarised. Then the materials that are used for the experiments described in this chapter are introduced. A more detailed description of the materials can be found in the next sub section.

As was discussed in section 1.1, metallic thermally sprayed coatings, or rather, any metallic coating, can be classified as either anodic or cathodic with respect to their substrate. Naturally, this classification depends entirely on the environmental conditions. Electrolyte composition, temperature, pressure etc. may all affect the cathodic and anodic reaction rates on the surface of the metal and thus determine the corrosion potential of both the coating and its substrate.

The reason why the relative difference in corrosion potential is of interest for coatings that are cathodic to their substrate is because a difference in corrosion potential satisfies the prerequisite for galvanic corrosion. Although this is equally true for the opposite situation described in chapter 4 (coatings that are less noble than their substrate) in the present case it implies a significant driving force for the corrosion of the substrate. Naturally, the substrate can only corrode when it is in direct contact with the corrosive electrolyte, which ideally would not be the case, since the substrate is covered by the coating. Unfortunately, thermally sprayed coatings are renowned for incorporating an, almost inevitable, significant amount of pores.

Still, the presence of pores does not necessarily lead to exposure of the substrate. The pores will have to form a continuous pathway leading from the surface, through the coating, onto the substrate. In the remainder of this chapter, this type of pores will be called “open” pores.

The presence of open pores will result in a situation where an anodic current originating from a relatively very small anode area will be balanced by a cathode, potentially covering the entire outside surface of the coating. As described in section 1.3, this situation may lead to rapid localised corrosion of the substrate, eventually either causing disbonding of the coating, or, worse still, perforation of the coated structure.

![Diagram](image)

Figure 1: Schematic of the two combinations of materials used in this chapter:

A = coating for corrosion protection of the substrate,
B = coating for repair of clad layer (and corrosion protection of the substrate)

The previous discussion considered a system consisting of a metallic substrate covered by a thermally sprayed coating (situation A in Figure 1). Besides this standard system another
configuration will be discussed in this chapter. In this case the thermally sprayed coating is used to repair a damaged clad layer on steel.

A practical example is the repair of the corrosion resistant roll-cladding, present in a carbon steel reactor vessel. When additional appendages need to be fitted to the vessel, the cladding needs to be partially removed. Presence of the cladding during welding would cause contamination of the weld, leading to localised poor structural and corrosion properties. The section of which the cladding was removed needs to be protected before the vessel can be used again. A possible means of protection would be the local application of a thermally sprayed coating.

This situation leads to the presence of a thermally sprayed coating on top of and directly adjacent to the original cladding material (situation B in Figure 1). Additional to any galvanic interaction between the coating and the substrate (through open pores), also the interaction between the coating and the original cladding material needs to be considered.

Note: the combination of a clad layer and the thermally sprayed coating does not meet the criterion of a coating that is cathodic to its substrate, and therefore, technically does not belong in this chapter. However, in order to keep related results together, they will be discussed in this chapter anyway.

The coating compositions chosen for the electrochemical evaluation in this chapter are all based on the composition of materials that are used extensively (as bulk or cladding) in process industry. The nominal coating compositions are (composition of the actual applied coating may differ considerably as discussed in section 1.1):

**Titanium ASTM grade 1**

This material (99.9% pure titanium) is mainly used in situations where other materials suffer from severe localised corrosion. The main area of importance would be the use in marine or seawater supported cooling installations.

**Stainless Steel AISI316L** (17% Cr, 12% Ni, 2.5% Mo, max. 0.03 % C)

This material is extensively used in chemical process industry. An example of a corrosive environment would be organic acids.

**Monel400** (67% Ni, 30% Cu, 2.5% Fe)

Vessels cladded with this material are mainly used in desalination plants. A typical working environment would be a saturated NaCl solution at temperatures up to 80°C.

For this research all thermally sprayed coatings (unless specifically stated otherwise) were applied onto carbon steel. All coatings were also evaluated in combination with clad layers of the same composition as the nominal composition of the spray coatings.

The coatings are tested in sodium chloride solutions to establish a base for comparison of the data. Since most of the materials depend on the formation of a protective oxide layer, a sulphuric acid environment is also included to evaluate the coatings without the presence of an abundance of the chloride ions and thus minimise pitting phenomena.

After a description of the details of the used coating materials in section 3.2, the results on the three selected nominal coating compositions are subsequently discussed in section 3.3. Section 3.4 describes the results of the study of the possibilities for the development of a qualification test for thermally sprayed coatings, based on electrochemical interactions. Finally, the conclusions of the results from this chapter are presented in section 3.5.
3.2 Materials

This section consists of three parts. First the thermal spraying applications that were used are discussed. The next sub section lists the results of the chemical and physical coating characterisation regarding coating composition, oxidation and porosity. The final sub section provides micrographs of the coatings.

The compositions of the used spray materials according to the suppliers are listed in Table 1. The composition of the spray materials was checked using EDX and XRF. No significant deviation from the supplier’s data was discovered.

<table>
<thead>
<tr>
<th>Material/Code</th>
<th>Elements (Weight percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
</tbody>
</table>
| Titanium wire       |     |    |    |    |    |    |    |    | 99.8
| TAFA 14T            |     |    |    |    |    |    |    |    |    |
| RVS wire            | (1) | 67.3 | 5 | 18 |    |    | 8.5 |    | 1 |
| Metcoloy            | (2) | 67-73 | 4-6 | 21-22 |    | 0.7-0.9 |    |    |    |
|                     | (3) | 65.5 | 5.8 | 18.0 |    | 0.16 | 9.3 | 0.32 |    |
| AISI 316L wire      | (1) | 69-62 | 10-14 | 16-18 |    | 2.3 | 2 |    | 1.0 |
| OSU 300/2           | (2) | 62-67 | 11-12 | 20 |    | 1.8-3.9 | 1.8-2.2 |    |
|                     | (3) | 62.6 | 12.3 | 18.2 |    | 3.2 | 1.8 | 0.82 |    |
| AISI 316 powder,    |     |    |    |    |    |    |    |    |    |
| size -106+45μ       |     |    |    |    |    |    |    |    |    |
| Metco 41C           |     |    |    |    |    |    |    |    |    |
| Monel wire          | (1) |    |    |    |    |    |    |    |    |
| OSU 300/2           |     |    |    |    |    |    |    |    |    |
| Monel powder,       | (1) |    |    |    |    |    |    |    |    |
| size -106+10μ       |     |    |    |    |    |    |    |    |    |
| OSU-SJA 846/56      |     |    |    |    |    |    |    |    |    |

3.2.1 Thermal Spraying Procedure

All coatings (unless stated otherwise) were applied on carbon steel (St 37) substrates of approx. 150 x 50 x 5 mm.

Prior to the application, the substrates were first cleaned using acetone. To increase the surface roughness and thus the adhesion of the thermally sprayed coatings, the substrates were grit blasted using clean corundum blasting material of 1.4 to 2.0 mm. The resulting surface roughness of the substrate was 10 to 13 microns (R_a) and 50 to 80 microns (R_max)
Electric Arc Spray

The titanium, AISI 316 and Monel400 coatings were initially applied using electric arc spray. The electric arc spray technique was selected for its combination of flexibility and the quality of the resulting coatings. Flexibility was an important requirement since the thermally sprayed coatings were also evaluated for repair of clad layers, which requires in-situ spraying.

The coatings were applied using an OSU G30/2 SF arc spray installation with a LD/U2 spray gun. The gun was mounted on a robot (ABB type IRB 2000) which transported the gun 10 mm after each lap. To reach an optimal coating thickness distribution, the sample was alternately horizontally and vertically sprayed. The substrate was cooled using an air jet pressure of 5 bar.

The spray conditions are listed in Table 2. The Metcoloy 5 coatings were applied in a commercial spray shop using a similar installation.

Table 2: Spray conditions during coating application using the OSU electric arc installation.

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Voltage (V)</th>
<th>Amperage (A)</th>
<th>Pressure (bar)</th>
<th>Thickness (µm)</th>
<th>General Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium (TAFA 14T), distance 125 mm, gun lateral speed 1000 m/s</td>
<td>air</td>
<td>26</td>
<td>150</td>
<td>3.5</td>
<td>2200</td>
</tr>
<tr>
<td>Metcoloy 5, distance 150 mm, gun lateral speed 500 m/s</td>
<td>air</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4000</td>
</tr>
<tr>
<td>AISI 316L/ER 316LSI/1.4430, distance 150 mm, gun lateral speed 500 m/s</td>
<td>air</td>
<td>28.5</td>
<td>150</td>
<td>3.5</td>
<td>1200-2400</td>
</tr>
<tr>
<td>Monel (OSU-SJA 846/56), distance 150 mm, gun lateral speed 500 m/s</td>
<td>argon</td>
<td>25-27</td>
<td>150</td>
<td>3.0</td>
<td>1400</td>
</tr>
</tbody>
</table>

Atmospheric Plasma Spray (APS)

For the study of the effect of coating thickness and porosity on the electrochemical behaviour as reported in section 3.4 additional coatings were needed with a wide variety of properties. For this reason coatings of AISI 316 and Monel400 were sprayed with a relatively wide range of spray conditions.

The APS coatings were applied using a Metco APS installation and a Metco 7MB gun supported by an ABB type IRB 2000 robot. The robot arm travelled the whole length of the substrate and the gun was transported 7 mm at the end of each lap. The samples were sprayed both horizontally and vertically. The sample was cooled using air jets fitted to the spray gun. The spray conditions are listed in Table 3.

High Velocity Oxygen Fuel Spray (HVOF)

To evaluate the effect of a drastic reduction in coating porosity a HVOF coating of AISI 316L feedstock material was included in the research program. The HVOF coating was applied in a commercial spray shop. The nominal thickness of the coating was 500 µm. No information on the spray conditions of this material are available.
Table 3: Spray conditions during coating application using the Metco atmospheric plasma installation. The numbers will be used during the discussion of the experimental results.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Material</th>
<th>Argon (l/min)</th>
<th>Hydrogen (l/min)</th>
<th>Powder (g/min)</th>
<th>Distance (mm)</th>
<th>Thickness (micron)</th>
<th>General Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AISI 316L</td>
<td>100</td>
<td>15</td>
<td>50</td>
<td>120</td>
<td>550</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>(Metco 41C),</td>
<td>100</td>
<td>15</td>
<td>50</td>
<td>150</td>
<td>600</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>amperage 500 A,</td>
<td>100</td>
<td>15</td>
<td>50</td>
<td>200</td>
<td>650</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>gun lateral speed 1000 /s</td>
<td>100</td>
<td>5</td>
<td>50</td>
<td>120</td>
<td>650</td>
<td>5.2</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>100</td>
<td>10</td>
<td>50</td>
<td>120</td>
<td>550</td>
<td>4.5</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>100</td>
<td>10</td>
<td>50</td>
<td>120</td>
<td>550</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>100</td>
<td>20</td>
<td>50</td>
<td>120</td>
<td>550</td>
<td>4.3</td>
</tr>
<tr>
<td>1</td>
<td>Monel</td>
<td>150</td>
<td>5</td>
<td>46</td>
<td>300</td>
<td>160-180</td>
<td>10.3</td>
</tr>
<tr>
<td>2</td>
<td>(OSU-SJA 846/56),</td>
<td>150</td>
<td>5</td>
<td>34</td>
<td>200</td>
<td>330</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>amperage 500 A</td>
<td>150</td>
<td>5</td>
<td>47</td>
<td>100</td>
<td>350-400</td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>gun lateral speed 1000 m/s</td>
<td>150</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>450-500</td>
<td>5.6</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>150</td>
<td>15</td>
<td>60</td>
<td>100</td>
<td>500-550</td>
<td>5.6</td>
</tr>
</tbody>
</table>

3.2.2 Coating Porosity and Composition

Generally the used coatings were characterised with respect to three parameters: the general porosity, the chemical composition (with respect to alloying elements) and the amount of oxidation.

All porosity values were determined from cross sections of the coatings by a Leitz Quantimet Image Processor. On a microscope picture of a representative cross section of the coating, the percentage of empty space, based on visual characteristics (colour and shape) is determined. The general porosity follows from the determined pore area and the total evaluated area of the coating. An average porosity is calculated, based on the result of 20 separate measurements. The variation of the porosity around the average is for all measurements approximately 30% of the measured value. The porosity values are listed in Table 2 and Table 3.

The compositions of the thermally sprayed coatings were determined using EDX, X-ray analysis (XRF) and gas analysis for the bulk determination of oxygen and nitrogen.

The EDX technique provides relatively localised information on the elements present. It is not the most suitable technique to obtain an overall impression of the oxidation resulting from the application procedure. For this reason the gas analysis technique was used which detects the amount of oxidation in a relatively large sample (mg). The results of the coating composition measurements are discussed together with the electrochemical results in the following sections. Table 4 and Table 5 present an overview of the EDX and gas analysis results.

3.2.3 Micrographs of the Thermally Sprayed Coatings

The next three sub sections give an impression of the microstructure of the used coatings by means of their cross section. Most photographs show the entire thickness of the coating. The coating material can easily be recognised by its typical structure. For example in Figure 9: the black top region is the resin used for embedding of the sample and the uniformly grey area at the bottom is the metal substrate. The area in between these two regions is the thermally sprayed coating.
### Table 4: Overview of coating composition according to EDX (SEM).

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (weight percentage)</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBS Titanium, air</td>
<td></td>
<td>6</td>
<td>16*</td>
<td>77</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EBS Titanium, argon</td>
<td></td>
<td>---</td>
<td>8.3</td>
<td>83.9</td>
<td>7.8</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EBS RVS Metcoloy 5, air</td>
<td>light area</td>
<td>74</td>
<td>6</td>
<td>19-20</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>dark area</td>
<td>54-59</td>
<td>0,3-4</td>
<td>15-16</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>24-27</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>EBS AISI 316L OSU</td>
<td>58-61,2</td>
<td>11-11,6</td>
<td>18-19,2</td>
<td>2,9</td>
<td>&lt;0.9</td>
<td>2.8</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>APS AISI 316L Metco 41C</td>
<td>62.3-60.7</td>
<td>12,6-12,2</td>
<td>18.5-18,2</td>
<td>2.7-2.9</td>
<td>2.1-1,4</td>
<td>1.9-4.6</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>HVOF AISI 316 (commercial)</td>
<td>66,2</td>
<td>11.5</td>
<td>18.3</td>
<td>2.4</td>
<td>1.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EBS Monel</td>
<td></td>
<td>1.5</td>
<td>64</td>
<td>31</td>
<td>---</td>
<td>---</td>
<td>3.4</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>APS Monel</td>
<td>not determined</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 5: Overview of Oxygen and nitrogen content determined using gas analysis.

<table>
<thead>
<tr>
<th>Coating</th>
<th>O (wt %)</th>
<th>N (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBS Titanium</td>
<td>air 9,5</td>
<td>7,7</td>
</tr>
<tr>
<td></td>
<td>argon 5,8</td>
<td>4,6</td>
</tr>
<tr>
<td>EBS Metcoloy 5</td>
<td>3-4</td>
<td>---</td>
</tr>
<tr>
<td>EBS AISI 316L</td>
<td>air 7</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>argon 1.4</td>
<td>0.04</td>
</tr>
<tr>
<td>HVOF AISI 316</td>
<td>2</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The magnification of the photographs is not always indicated by a marker in the photograph since the photos originate from various sources. For this reason the magnification is also listed in the caption of the photos.

**Titanium Feedstock**

Electric arc spraying of titanium spray material using compressed air as propellant gas resulted in extremely porous coatings. The use of argon as propellant resulted in a drastic decrease of the porosity. This difference is most probably caused by the prevention of excessive formation of oxides and nitrides during the argon spraying. The formation of oxides and nitrides will reduce the ductility of the sprayed particles and reduce the amount of flattening at impact with the substrate, causing the observed porosity.

The pores are visible throughout the coating in Figure 2 and Figure 3 as the black areas with the white highlighted edges. The oxides and nitrides cannot be distinguished from these figures but they are expected to be uniformly present in the coating.
AISI 316 Stainless Steel Feedstock

The micrographs of the coatings based on stainless steel feedstock material generally display three roughly distinguishable regions, as in Figure 5. The clear area is the molten metal, the light to dark grey areas represent oxidised metal and the black spots and narrow lines are porosity.

The coatings prove to be sensitive to the type of propellant used. Exchanging the common air propellant by an inert gas (argon) directly leads to a decrease of oxidation in the coating. This difference can be observed from Figure 6 and Figure 7. The coating in Figure 6 shows considerably more oxidation (the light grey areas). The porosity (the black areas) of the two coatings remains roughly the same.

The various atmospheric plasma spray applications that were made to yield different porosity levels for the validation of the qualification methods are represented in Figure 9 to Figure 12. Although some difference in coating porosity is achieved, more significant differences are visible in the cohesion of the coating (the bonding between the various lamellae). The coatings sprayed using the relatively cold plasma (low heat, low H_{2} content) display a more defined lamellar structure with poor cohesion among the lamellae (Figure 9). This indicates a possible insufficient melting of the spray particles during application. Increasing the heat content (Figure 10) results in improved cohesion of the coatings.
The HVOF coating that was used in this research can only be classed as very dense with homogeneously distributed micro pores and little oxidation (Figure 11 and Figure 12). Measurement of the total porosity by image analysis on a cross section for this coating resulted in an extremely low value of 0.4%.
Monel400 Feedstock
This coating material was used for electric arc spraying and atmospheric plasma spraying.

Electric arc spray of Monel400 spray material yields dense, well adherent coatings that are relatively free of oxides (Figure 13 and Figure 14).

Similar to the plasma sprayed AISI 316 coatings, also Monel400 coatings were applied using a wide range of instrument settings. This was expected to result in a range of coating porosity values, that could be used to validate the electrochemical test methods.

Figure 15 to Figure 17 show that increasing the heat content of the plasma directly leads to a decrease of the porosity in the coating. No apparent further effect on the coating morphology can be seen (in contrast to the behaviour of the stainless steels).
Figure 15: Atmospheric plasma spray Monel400 coating, Ar/H₂ : 100/5, distance 100 mm (cold flame, normal distance) (magnification 136x).

Figure 16: Atmospheric plasma spray Monel400 coating, Ar/H₂ : 100/10, distance 100 mm (normal flame, normal distance) (magnification 80x).

Figure 17: Atmospheric plasma spray Monel400 coating, Ar/H₂ : 100/15, distance 100 mm (hot flame, normal distance) (magnification 80x).
3.3 Characterisation Results

3.3.1 Titanium

Summary

The results in this section describe the corrosion behaviour of electric arc sprayed coatings based on titanium feedstock material on steel. The titanium particles proved to react very rapidly with the arc spray atmosphere. This led to extreme levels of porosity (over 50%) and the formation of large amounts of titanium oxides and nitrides in the coating. These effects can largely be reduced by using argon as propellant during the thermal spray application. However, the resulting improvement proved to be insufficient to lead to acceptable corrosion behaviour in sodium chloride solutions or sulphuric acid.

Results

This section describes the electrochemical behaviour of thermally sprayed coatings on steel based on titanium feedstock material. The electrochemical behaviour of these coatings was evaluated to determine their corrosion resistance and to decide whether this type of thermally sprayed material could be used to repair titanium clad layers on steel.

The first coating was applied using a conventional arc spray procedure to an average thickness of approx. 2 mm. Specifics of the coating application were described in section 3.2.

A microscopy evaluation of the cross section, as shown in Figure 18, revealed the high amount of porosity that resulted using standard arc spray parameters. The black region at the top and right side of the photo is epoxy resin used for embedding of the sample. The light coloured region at the bottom of the photo is the carbon steel substrate.

Measurement of the general porosity using image analysis on a cross section of the coating yielded values as high as 50 to 66%.

![Figure 18: Electric arc sprayed Titanium coating using air propellant (magnification 52x).](image)

![Figure 19: Potential monitoring in 0.5 M H₂SO₄ of arc sprayed titanium coating on carbon steel and the titanium clad material.](image)
It was therefore no surprise when the electrochemical behaviour of the spray coating in either 3 \% NaCl or 0.5 M H₂SO₄ did not prove to be in any way similar to the behaviour of the titanium clad material. This is illustrated in Figure 19. This figure shows the spray coating on carbon steel to display a rest potential in 0.5 M H₂SO₄ that is 500 mV more negative than the clad material.

The corrosion potentials in this figure were measured using the technique described in section 2.6.1. The potential values were registered by a HP 3852A data acquisition system. The surface area of the samples was approx. 1 cm².

The polarisation curves of this coating in 3 \% NaCl and sulphuric acid are represented in Figure 20 and Figure 21.

These, and the other polarisation curves in this section were measured using the technique described in section 2.6.2 using a Solartron 1286 electrochemical interface and self developed software. The area of the working electrode was 1 cm² and the potential scanning rate was 10 mV/s. The scan range was −1 V to +1 V in both NaCl and H₂SO₄.

Both these figures show an increased current density over the entire potential range for the sprayed coatings as compared to the clad material. The spray coating performed extremely poorly in the NaCl solution. The corrosion potential of the coating sample could hardly be distinguished from the behaviour of uncoated carbon steel in the same environment.

Based on the polarisation curves and the very high porosity that was found from the analysis of the cross sections, the coating could be expected to contain a high amount of open porosity. Open porosity enables the electrolyte to reach the carbon steel substrate thus leading to substrate corrosion, despite the presence of the titanium based sprayed coating.

The influence of the substrate material on the polarisation behaviour of the coated sample in 3 \% NaCl is illustrated in Figure 24. The coating was not applied on carbon steel as in Figure 20, but directly onto titanium clad material. Resulting from this change of substrate material, the entire polarisation curve appears to have moved about 200 mV in the positive direction compared to the situation in Figure 20. Since neither the coating morphology, nor the chemical composition
was changed, these differences in electrochemical behaviour can directly be attributed to the activity of the substrate at open pores in the coating.

Figure 22: Sketch of the effect on the polarisation curve of a porous Ti-based coating on a steel substrate in 3% NaCl.

Figure 23: Sketch of the effect on the polarisation curve of a porous Ti-based coating on a Titanium cladding in 3% NaCl.

Figure 22 and Figure 23 illustrate the effect of the two substrates on the resulting polarisation. The apparent effect of the steel substrate is a minor increase of the corrosion current at a more or less constant corrosion potential. The titanium substrate causes a further shift of the corrosion potential, but has little effect on the corrosion current as compared to the coating on the steel substrate.

Figure 24: Polarisation curve in 3% NaCl of arc sprayed titanium on titanium clad (surface 1 cm², thickness 2.2 mm; scan rate 10 mV/s) as compared to titanium clad material (black curve) and uncoated carbon steel (grey curve).

Figure 25: Polarisation curve of detached arc sprayed titanium coating in 0.5 M H₂SO₄ (surface 1 cm², thickness 2.2 mm; scan rate 10 mV/s) as compared to titanium clad material (black curve) and uncoated carbon steel (grey curve).
The influence of the substrate material is much less pronounced in sulphuric acid. The difference in anodic current for a detached coating (Figure 25) and the coating on a carbon steel substrate (Figure 21) is minimal.

The reason for this can be found from the relative differences between the corrosion potential of the coating and the substrate material in the two environments. In 3 % NaCl the corrosion potential of the coating on carbon steel is comparable with the corrosion potential of unprotected carbon steel (see Figure 20 and Figure 22). In 0.5 M sulphuric acid however, the coating behaves significantly less noble than carbon steel (Figure 21). This means that, as opposed to the situation in 3 % NaCl, the titanium coating cathodically protects the carbon steel that is exposed through the open pores in the coating. As is illustrated in Figure 26, this will result in the observed limited difference between the polarisation curve measured in 5 M H₂SO₄ on the free film or on the coating on carbon steel.

![Figure 26: Sketch of the effect on the polarisation curve of a porous Ti-based coating on a steel substrate in 0.5 M H₂SO₄.](image)

Alternatively, since no cathodic protection of the substrate is possible in the 3 % NaCl solution, any exposed substrate will have a much greater effect on the resulting anodic current density.

The reason for the very high porosity level in the arc sprayed titanium coating stems from the reaction of the molten titanium particles with the surrounding atmosphere during application. Especially the reaction with oxygen and nitrogen can be expected to be very rapid. The resulting particles can be expected to be less ductile, preventing the formation of a homogeneous microstructure after impact and solidification at the substrate.

EDX analysis of the spray coating composition indicated a combined nitrogen and oxygen content of about 16%. This was separated using gas analysis into 9.5% oxygen and 7.7% nitrogen.

The complete XRD spectrum of the arc sprayed titanium coatings is shown in Figure 27.

Comparison of this spectrum to the spectrum that was measured for the clad material and to the standard spectrum of α-titanium revealed a number of additional spikes on the spectrum of the coating.
The number of counts was normalised to 100 relative to the highest peak to facilitate comparison of the XRD data. Comparing the spectrum of the arc sprayed titanium coating to standard spectra of possible compounds, yielded titanium nitride as the most likely component of the spray coating. This is represented in Figure 28. No oxide compounds could be identified using XRD, although gas analysis has proved the presence of 9.5% of oxygen. This is assumed to be caused by the presence of the oxide as an extremely narrow phase along the particle boundaries and therefore does not form the required bulk to be detected by XRD.

The previous results indicated that the reaction of the titanium particles during the application had to be prevented in order to reduce the porosity of the resulting coating. For this reason the normally used compressed air propellant was exchanged with argon gas.

The result of this was that the oxygen content of the coating was reduced to 5.8% and the nitrogen content to 4.6%. Also, the average porosity (determined using image analysis on a cross section) was improved from 50% using compressed air to 15% for the argon application. (See Figure 29).
The XRD spectra in Figure 30 and Figure 31 show that the intensity of the peaks associated with the nitride compounds had decreased but their presence could still be detected.

![Figure 30: XRD spectra of the titanium clad material (A) and the titanium spray coating using argon as propellant gas. The asterisks (*) indicate the α-Ti phase.](image)

![Figure 31: Normalised XRD spectra of the titanium spray coating using argon propellant as compared to TiN and TiN0.3 reference data. The asterisks (*) indicate the α-Ti phase.](image)

The effect of the porosity reduction had a significant effect on the polarisation curve in the 3% NaCl electrolyte. Caused by the decrease in porosity, both the anodic and cathodic current resulting from the steel substrate will decrease. As illustrated in Figure 32 (as compared to Figure 22) this will result in a shift of the polarisation curve of the coating and substrate combination towards lower currents and a more positive corrosion potential.

![Figure 32: Sketch of the effect on the polarisation curve of a decrease of the porosity from the situation in Figure 22.](image)

A similar decrease of the porosity will have far less effect on the coating in the sulphuric acid electrolyte. As can directly be observed from Figure 26, a further decrease of the anodic and
cathodic current densities on the steel substrate will have little effect on the resulting polarisation curve of the coated substrate. This is in fact observed in Figure 34.

Figure 33: Polarisation curve in 3 % NaCl of titanium spray coating using argon as propellant gas on carbon steel (surface 1 cm², thickness 1.4 mm, scan rate 10 mV/s) as compared to titanium clad material (black curve) and uncoated carbon steel (grey curve).

Figure 34: Polarisation curve in 0.5 M H₂SO₄ of titanium spray coating using argon as propellant gas on carbon steel (surface 1 cm², thickness 1.4 mm, scan rate 10 mV/s) as compared to titanium clad material (black curve) and uncoated carbon steel (grey curve).

Consequently, the use of this type of coating for the repair of titanium clad material is not possible. The considerable difference in corrosion potential between the coating and any intact titanium clad material, that will also be present, will cause rapid galvanic corrosion of the sprayed coating.

Figure 35: Close up of titanium spray coating using argon as propellant gas after exposure to sulphuric acid (magnification 240x).

Figure 36: As Figure 35 after prolonged exposure in sulphuric acid, (magnification 240x).

The use of these type of titanium based thermally sprayed coating for corrosion protection of carbon steel could be contemplated for use in media like 3 % NaCl. However, the extent of
protection in this electrolyte remains modest. Use in sulphuric acid will cathodically protect the carbon steel substrate. However, the titanium material is too inhomogeneous to be useful for this purpose. Preferential attack at particle boundaries would cause the coating to delaminate after prolonged exposure. Also the use of this type of material as a sacrificial anode for carbon steel would be too costly.

An example of the extent of attack is shown in Figure 35 and Figure 36. Especially Figure 36 clearly shows the preferential attack of the particle boundaries. This leads to a deepening of the already present pore structure, effectively opening-up the pores. This will eventually result in exposure of the substrate and breakdown of the coating structure.
3.3.2 Stainless Steel

Summary

The results presented in this section describe the corrosion behaviour of thermally sprayed low carbon austenitic stainless steel (AISI 316L). The corrosion behaviour and specifically the passivation of a standard arc sprayed coating is not acceptable for use in either sodium chloride, or sulphuric acid solutions. The passivation can be improved by decreasing the porosity of the coating and by preventing oxidation of the coating during the spraying procedure. Excessive oxidation during application can be minimised by using a protective atmosphere during application. Porosity of the coating can be controlled by optimising the spraying parameters. The coating can only be allowed to exhibit a very low amount of porosity. Especially open pores have to be prevented at all time. By using a higher particle speed during deposition (the HVOF method) porosity can be kept sufficiently low. Additional improvement of the corrosion properties can be achieved by a heat treatment of the coated sample.

Results

This section describes the electrochemical behaviour of five different thermally sprayed coatings based on AISI 316 type (and similar) feedstock material. The electrochemical behaviour of these coatings was evaluated to determine their corrosion resistance and to decide whether this type of thermally sprayed material could be used to repair AISI 316 clad layers on steel.

Details on the spraying applications and an overview of the coating properties were given in section 3.2. The first series of experiments were performed on an arc sprayed coating of low carbon austenitic stainless steel feedstock material (Metcoloy 5). This material was applied on carbon steel. The nominal thickness of the coating was 4 mm. The general porosity as determined using image analysis on a cross section of the coating was about 3 to 4 %.

Figure 37 and Figure 38 display the corrosion potential of the Metcoloy5 coating in 3 % NaCl and 0.5 M H₂SO₄ as compared to the corrosion potential of AISI 316 clad material. The potentials were measured according to the technique described in section 2.6.1 using a HP 3852A data acquisition system for the NaCl exposure and a Solartron 1286 electrochemical interface for the H₂SO₄ exposure. The samples were exposed in the "as sprayed condition". The total surface area of the samples was approx. 1 cm².

![Figure 37: Potential monitoring in 3 % NaCl of arc-sprayed Metcoloy5 coating as compared to the AISI 316 clad material.](image1)

![Figure 38: Potential monitoring in 0.5 M H₂SO₄ of arc-sprayed Metcoloy5 coating as compared to the AISI 316 clad material.](image2)
These figures show that the corrosion potential in both environments stabilised at a level almost 500 mV more negative to the cladding material. This indicates that when these two materials are used together, the carbon steel panel with the sprayed coating will be anodically polarised.

To determine whether this difference in corrosion potential could also be detected when the two materials are coupled, a simple potential scanning technique was used. This technique was based on the standard measurement of the corrosion potential as described in section 2.6.1 but to enable the detection of local differences, the reference electrode was placed very close to the coated sample. Also, a second reference electrode positioned at a larger distance from the sample surface was used to detect the “overall” corrosion potential.

The sample that was used for this experiment consisted of a carbon steel substrate (10 cm length, 5 cm width, 2 cm height) of which half of the top side was covered by the AISI 361 cladding. The remaining half of the carbon steel substrate was coated using the thermally sprayed stainless steel material. After spraying, the entire surface was polished to grit 1200 to result in the sharp interface shown in Figure 39. The back and sides of the sample were protected using insulating tape. After degreasing the sample was immersed in tap water in a shallow basin with the top face (the two coatings) facing upward (see Figure 39).

The potential values registered by the two reference electrodes were monitored continuously after immersion. One was measured at a relatively large distance from the surface (10 cm); the second electrode was positioned very close to the sample (<1 mm). Tap water was selected as electrolyte because of its lower conductivity compared to 3 % NaCl. This increases the resulting potential differences, making them more easy to register.

The reference electrode close to the surface was scanned over the sample (line scan) with a length of about 4 centimetres. Using this electrode, 8 sets of corrosion potential measurements were performed at 5 mm intervals. At each position, the potential was monitored for a duration of 2 minutes. The result of these measurements and the corrosion potential measured using the second reference electrode at greater distance from the surface are shown in Figure 40.

This figure shows a gradual decrease of the measured corrosion potentials using either the electrode close to or far from the sample surface. This was caused by drift of the corrosion potential during the measurement. Since each set of measurements (each position) took about 2 minutes, the total measurement duration was about 16 minutes. During this time the corrosion potential of the sample dropped about 60 mV, effectively masking the potential difference between the two materials (sprayed coating on steel and cladding).
However, some information on the local corrosion potential can be obtained by calculating the difference between the corrosion potentials at a specific time, as measured by the electrode close to the surface and the electrode far from the surface. This method enables a type of "drift compensation" for the measurement close to the surface. The result of this is shown in Figure 41.

![Graph](image1)

**Figure 40:** Potential development over interface of clad material to sprayed coating measured at various locations close to the surface and a fixed position far from the surface. Measured in tap water.

![Graph](image2)

**Figure 41:** As Figure 40 but represented as the potential difference from the measurements close to the surface and the potential measured far from the surface.

As can be observed in this figure the interface between the two surfaces could accurately be detected using this method.

These results and the results of the potential monitoring experiments in Figure 37 indicate that the thermally sprayed carbon steel will be anodically polarised when being coupled to the clad material. Although this is not favourable when this material is used for repair of cladded steel, it does not necessarily have to cause severe corrosion problems. When the coating does not contain any open pores exposing the substrate material and sufficiently passivates, the service life of the system might remain acceptable. The presence of open pores is unlikely bearing in mind the extreme coating thickness (4 mm) and the moderate total porosity (3-5 %).

![Graph](image3)

**Figure 42:** Polarisation curve in 3 % NaCl of Metcoloys5 (surface 1 cm², thickness 4 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

![Graph](image4)

**Figure 43:** Polarisation curve in 0.5 M H₂SO₄ of Metcoloys5 (surface 1 cm², thickness 4 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).
Therefore, the passivating behaviour was analysed using the polarisation curve.

The polarisation curves in this section were measured using the technique described in section 2.6.2 using a Solartron 1286 electrochemical interface and self developed software. The area of the working electrode was 1 cm$^2$ and the potential scanning rate was 10 mV/s. The scan range was from $-1$ V to +850 mV in NaCl and $-750$ mV to +1V in $\text{H}_2\text{SO}_4$.

The polarisation curves for the Metcoloy5 thermally sprayed coating on carbon steel are shown in Figure 42 and Figure 43. For comparison, these figures also show the polarisation behaviour of the AISI 316L clad layer and unprotected carbon steel.

Since the composition of Metcoloy5 is not completely similar to the composition of the clad material, it was decided that before the results would be analysed any further, another application would be made using feedstock material that had the nominal composition of AISI 316L.

This application was done using OSU 300/2 wire and the nominal coating thickness was limited to 2 mm. Although greater coating thicknesses can be realised on flat substrates (as used in the previous experiments) experience showed that cracking and delamination occurred at more realistically shaped substrates. For this reason it was decided that coating thicknesses over approx. 2 mm must be considered unrealistic. The polarisation curves of the resulting coating are shown in Figure 44 en Figure 45.

From Figure 42 to Figure 45 can be concluded that neither the arc sprayed Metcoloy5 nor the AISI316L coatings showed sufficient passive behaviour to be of use as a corrosion resistant coating on carbon steel. The anodic current increased with potential, similar to the behaviour of uncoated carbon steel in these circumstances.

Using these materials to repair a damaged AISI 316 clad layer will lead to rapid galvanic corrosion of the thermally sprayed area. An example of this can be observed on the sample that was used for the potential scanning experiment (Figure 46). This figure shows local attack on the interface between the sprayed coating and the clad material. In practical applications this type of attack can be expected to lead to much more severe corrosion resulting from the presence of better conductive electrolytes and a much more unfavourable surface area ratio. The sprayed coating in this form is therefore absolutely unsuited for the repair of cladded steel constructions.
Possible reasons for the poor corrosion behaviour of these coatings are that either the composition and/or the microstructure of the sprayed material had changed during the arc spraying application. These changes then prevented the formation of a well protective passive layer.

This behaviour is also recognised in literature and the proposed mechanisms can roughly be divided into two areas: [1-5]

- The coating would be too porous to act as an effective barrier between the electrolyte and the carbon steel. The corrosion of the carbon steel substrate would remain relatively unaffected by the presence of the coating.

- The combination of high temperatures and compressed air would cause successive oxidation and evaporation of required alloying elements, primarily chromium. The resulting coating would not contain enough (non-oxidised) chromium for the formation of a passive film. The effect of the amount of chromium on the passivating behaviour is illustrated in Figure 47 [6].

Figure 47: Schematic polarisation diagram for stainless steels containing various amounts of chromium.
To determine the validity of the first hypothesis, the porosity of the coatings must be addressed. The porosity values for the Metcoloy5 samples varied from 3.3 to 5.4 %. The AISI 316L sprayed coating had an average porosity of 1.5 to 2.7 %. An overview of the measured values is listed in section 3.2 Table 2.

The measured value on the Metcoloy5 sprayed coating is well within the range that can be expected for the arc spraying technique and the porosity of the AISI 316L sprayed coating should be classed as low. As stated before, considering the considerable thickness of the coatings (4 and 2 mm) the presence of open pores is not expected. However, based on the porosity values derived from an analysis of the cross section, no definite statement can be made about the presence of open pores. Only these open pores can cause the substrate material to corrode despite the presence of the sprayed coating.

To determine possible influence of the substrate on the corrosion behaviour through open pores, the sprayed coating was mechanically removed from the substrate. This will of course completely preclude any effect resulting from the substrate material. Since it was expected that any effect of open pores would be the clearest on the coating with the highest general porosity, the polarisation curve was measured for a detached Metcoloy5 coating. The resulting curve is shown in Figure 48.

![Polarisation curve in 3 % NaCl of a detached coating of Metcoloy5 (surface 1 cm², thickness 4 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).](image)

Comparing this curve to Figure 42 (identical coating, but with a carbon steel substrate) shows no improvement. This proves that, as expected, the amount of open porosity that is present in this coating of 4 mm thickness and 3-5% general porosity, does not significantly influence the corrosion behaviour of the system.

The second hypothesis proposed the amount of chromium present in the coating to be insufficient for the formation of a passive film. The application conditions are suspected to cause oxidation and evaporation of chromium, leaving the coating material relatively poor on (non oxidised) chromium.

The nominal composition of Metcoloy5 is Fe 18Cr 8.5 Mn 5Ni 1Si 0.15C and AISI 316L is Fe 17Cr 12Ni 2.5 Mo, max. 0.03C.

To investigate the influence of the spraying application on the composition, electron microscopy (SEM) was used in combination with X-ray analysis (EDX), gas analysis and X-ray diffraction (XRD). Figure 49 through Figure 52 show the structure of the Metcoloy5 coating and the distribution of chromium and oxygen.
Both Figure 49 and Figure 51 show light grey and dark grey (black) areas. The average elemental compositions in these areas are summarised in Table 6. This table also shows the composition of the clad material for comparison.

The table indicates that both coatings indeed take up oxygen during application. The Metcoloy5 micrographs also clearly show an oxidised phase in the coating. The chromium image shows a relatively good distribution of chromium. However, by careful study of the chromium image the lamellae of the splat structure can be recognised. The edges of the lamellae can be found to correspond with the slightly darker areas in the chromium image. This would indicate a lowering of the chromium content along the edges of the lamellae. Nonetheless, as listed in Table 6 the average content in these areas remains at 15 to 16%.

This amount is generally considered sufficient for the formation of a passive film. However, it is required that the chromium is present as a metallic phase in the austenitic matrix, and not bound in stable oxides that may be formed during spraying. Studying Figure 49 and Figure 50 reveals that the edges of the lamellae (the dark areas) are also oxygen rich. This suggests that although the average chromium content is sufficient, a significant amount of the chromium will be present as oxides.
Table 6: Composition of the arc sprayed Metcoloy5 and RVS 316L coatings determined using EDX and gas analysis

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Position</th>
<th>O (gas analysis)</th>
<th>Cr (EDX)</th>
<th>Fe (EDX)</th>
<th>Mo (EDX)</th>
<th>Ni (EDX)</th>
<th>O (EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metcoloy 5</td>
<td>light phase</td>
<td>19-20</td>
<td>74-76</td>
<td>-</td>
<td>6-7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>sprayed coating</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metcoloy 5</td>
<td>dark phase</td>
<td>15-16</td>
<td>54-59</td>
<td>-</td>
<td>0.3-4</td>
<td>24-27</td>
<td></td>
</tr>
<tr>
<td>RVS 316L</td>
<td>general</td>
<td>3-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sprayed coating</td>
<td>general</td>
<td>6-7</td>
<td>18-19</td>
<td>58</td>
<td>2.9-2.9</td>
<td>10-11</td>
<td>8-10</td>
</tr>
</tbody>
</table>

To further analyse the different phases present in the sprayed coatings X-ray diffraction was used (XRD). The results of this analysis are listed in Figure 53.

The spectrum of the 316L clad material corresponds with the austenitic γ-Fe structure. The spectra of the AISI 316L and Metcoloy5 sprayed coating are practically identical and indicate other compounds besides the γ-Fe structure.

![Figure 53: XRD spectra of the AISI 316L clad material (A), the AISI 316L sprayed coating (B) and the Metcoloy5 sprayed coating (C). The asterisk (*) indicates the austenitic (γ-Fe) phase.](image)

![Figure 54: Normalised XRD spectra of NiCr2O4 phase (A) in the AISI 316L sprayed coating (B) and the Metcoloy5 sprayed coating (C). The γ-Fe phase is omitted in this figure.](image)

In Figure 54 the number of counts for the spectra of the sprayed coatings was normalised to 100 relative to the highest peak to facilitate comparison with standard spectra. Comparison to the reference spectra of possible present phases, the resulting spectrum showed the best match with the spectrum of NiCr2O4. Since the spectra were taken from samples that had not been exposed to any corrosive medium (other than air), it was concluded that this phase was formed during application.

Table 6 shows a chromium content of 15 to 16 % (by weight) for the dark phase in the metcoloy5 coating. This means that just 3 to 4 % (by weight) of chromium needs to be bound in the NiCr2O4.
spinel for the general content to drop below the rule-of-thumb level of 12 % required for passivation. Using the molecular weight of chromium and oxygen and the ratio of 2 to 4 with which they are present in the spinel, follows that this would require 2 to 3 % (by weight) of oxygen. This amounts to just 8 to 9 % of the total oxygen content of the coating, to be present in the NiCr₂O₄ spinel. Based on the almost complete resolution of the XRD spectrum in Figure 54 a much higher content is suggested, leading to a very low level of available chromium for passivation.

So it can be concluded that it is possible that the presence of the spinel phase prevents the formation of a passive layer. To further analyse this conclusion, the application of the AISI316L sprayed coating was repeated while preventing the excessive formation of oxides during application.

For this reason the spray gun was adapted to use argon instead of compressed air as the propellant gas.

The XRD spectra of the resulting coating is shown in Figure 55 en Figure 56. These figures show that the development of the oxide phase has significantly been reduced.

![Figure 55: XRD spectra of the AISI 316L clad material (A), the standard AISI 316L sprayed coating (B) and the AISI 316L sprayed coating using argon as propellant (C). The asterisk (*) indicates the austenitic phase.](image)

![Figure 56: Normalised XRD spectra of the NiCr₂O₄ phase (A) in the standard AISI 316L sprayed coating (B) and the AISI 316L sprayed coating using argon as propellant (C). The ɣ-Fe phase has been omitted in this figure.](image)

Gas analysis of the argon sprayed 316L coating indicated an oxygen content of about 1.4 % as compared to the 6 to 7 % for the standard coating that used compressed air. Apart from this, the composition of the coating effectively remained identical, see Table 7. The porosity of the coatings slightly increased. The average porosity values, as determined using image analysis on a cross section, resulted in 1.2 to 3.2 % for the argon sprayed coatings, as compared to 1.5 to 2.7 % for the conventionally sprayed coatings.

Whether these lower oxygen values and the lower amount of NiCr₂O₄ are enough for the formation of a effective passive layer was investigated using the electrochemical behaviour of the argon sprayed coating as reflected by the polarisation curve.

The polarisation curve of the argon sprayed coating on carbon steel is shown in Figure 57. Figure 58 shows the results of the measurement of the identical coating but without the influence of the substrate (detached coating).
Figure 57: Polarisation curve in 3 % NaCl of arc sprayed AISI 316L on carbon steel using argon as propellant (surface 1 cm², thickness 0.5 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

Figure 58: Polarisation curve in 3 % NaCl of detached coating of arc sprayed AISI 316L using argon as propellant (surface 1 cm², thickness 0.5 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

Figure 59: Polarisation curve in 0.5 M H₂SO₄ of arc sprayed AISI 316L on carbon steel using argon as propellant (surface 1 cm², thickness 0.5 mm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

These figures primarily indicate a significant improvement of the corrosion behaviour between the detached coating as compared to the coating on carbon steel. This can be explained from the increased porosity of the argon sprayed coating as compared to the conventional arc sprayed material. Further optimisation of the argon spraying process can be expected to minimise this effect.

More important is the behaviour of the free film. It can be observed that the argon sprayed coating (without the deteriorating effect of open porosity) showed a significantly decreased anodic current density of almost one decade. Although the level of the AISI 316L clad material is not approached, a significant improvement of the corrosion behaviour over the conventionally sprayed coatings is reached.

This result proved that the formation of NiCr₂O₄ had an important adverse affect on the corrosion behaviour of the sprayed coating, and therefore needs to be prevented. However, it is also clear
from Figure 58, that apparently this is not yet sufficient to result in a sprayed coating with similar passivating capacity as the AISI 316L clad material.

**Table 7: Composition of sprayed RVS 316L coatings using EDX and gas analysis.**

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Position</th>
<th>O (gas analysis)</th>
<th>Cr (EDX)</th>
<th>Fe (EDX)</th>
<th>Mo (EDX)</th>
<th>Ni (EDX)</th>
<th>O (EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVS 316L arc spray using argon</td>
<td>general</td>
<td>19-20</td>
<td>61-62</td>
<td>2.7-2.9</td>
<td>11-12</td>
<td>1.8-2.0</td>
<td></td>
</tr>
<tr>
<td>RVS 316L arc spray using air</td>
<td>general</td>
<td>6-7</td>
<td>18-19</td>
<td>58</td>
<td>2.9-2.9</td>
<td>10-11</td>
<td>8-10</td>
</tr>
<tr>
<td>HVOF</td>
<td>general</td>
<td>18-19</td>
<td>66-67</td>
<td>2.4-2.5</td>
<td>11-12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This result showed that the hypotheses used in literature are not able to lead to the explanation of the poor behaviour of this sprayed coating. Neither the open porosity, nor de-alloying effects can be expected to account for the remaining gap between the behaviour of the sprayed coating and the cladded 316 material. A new hypothesis is required.

A notorious mechanism causing severe corrosion of AISI316 type steels in chloride containing environment is the crevice corrosion phenomenon (as explained in section 1.2.4). Occluded cell type of corrosion caused by a different aeration level of various regions on the steel surface prevents passivation. A similar mechanism in the current situation can be assumed. The presence of narrow pores may well affect the accessibility to oxygen leading to a micro crevice corrosion mechanism. Especially the relative improvement of the argon sprayed coating in H₂SO₄ in Figure 59 over the original behaviour in Figure 45 supports this. In the low chloride environment, the crevice corrosion mechanism can be expected to be considerably less severe.

![Figure 60: XRD spectra of the AISI 316L clad material (A), the AISI 316L sprayed coating using argon as propellant (B) and the HVOF sprayed AISI 316 coating (C). The asterisk (*) indicates the austenitic phase.](image)

![Figure 61: Normalised XRD spectra of the NiCr₂O₄ phase (A) in the AISI 316L sprayed coating using argon as propellant (B) and the HVOF sprayed AISI 316 coating (C).](image)
To evaluate this mechanism, a new application series was started which should preserve the composition and chemical structure of the current coating, but with a significantly lower porosity.

To achieve this the HVOF technique (high-velocity oxygen fuel) was used. This technique combines a very high particle speed with a relatively low application temperature, which minimises the reaction rate during application. This combination typically results in very dense coatings that are relatively oxide-free.

The microscopy analysis and the XRD spectra of the HVOF sprayed AISI 316L coating as shown in Figure 60 and Figure 61 indicated no significant oxide phases present in the coating. Measurement of the total porosity by image analysis on a cross section for this coating resulted in an extremely low value of 0.4%.

The polarisation curve of the HVOF 316L coating is shown in Figure 62.

**Figure 62:** Polarisation curve in 3 \% NaCl of HVOF sprayed AISI 316L (surface 1 cm², thickness 500 μm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

**Figure 63:** Polarisation curve in 3 \% NaCl of detached coating of HVOF sprayed AISI 316L (surface 1 cm², thickness 500 μm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).

**Figure 64:** Polarisation curve in 0.5 M H₂SO₄ of HVOF sprayed AISI 316L (surface 1 cm², thickness 500 μm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).
The extremely low porosity of these coatings resulted in the fact that no significant difference can be observed between the coating on carbon steel and the detached coating. This was even more remarkable since the thickness of the coating is just 500 μm.

This coating displayed the lowest current over the anodic potential range. The difference between the HVOF coating and the clad material in the sulphuric acid solution has been reduced to less than one decade. Bearing in mind the higher surface area for the sprayed coating, compared to the cladded sample, leads to the conclusion that this coating comes very close to the corrosion properties of the clad material.

To conclude whether the sprayed coating could be used for the repair of cladded steel constructions, also the long-term stability of the corrosion protection was addressed. For this reason the experiment shown in Figure 64 was repeated after 18 and 75 hour of exposure at the open circuit potential 0.5 M H₂SO₄. The result is presented in Figure 67.

This figure shows that indeed the coating was sensitive to deterioration over time. This ageing behaviour resulted in an increased current. Also the corrosion potential gradually moved towards the value corresponding with unprotected carbon steel.

Apparently, the very low corrosion rate that could be concluded from Figure 64 is sufficient to destroy the protective properties of the coating in a relatively short period of time. This could only be possible when the observed current originated from a very localised form of corrosion that attacked the integrity of the coating structure.

A microscopy analysis of the cross sections of the exposed coating in Figure 66 showed the corrosion attack to be primarily active along the edges of the sprayed particles. This resulted in an increase of the corroding area, disruption of the passive surface film, and opening-up of the pores that eventually will lead to activation of the substrate. The combined effect of these mechanisms resulted in the increase of anodic current that can be observed in Figure 67.

This explanation suggests the degree of ageing of the sprayed coatings to be dependent on the aggressiveness of the corrosive environment. This assumption was strengthened by measurements as given in Figure 68 that shows a similar experiment in a 10 times more diluted electrolyte. In 0.05 M sulphuric acid the passive current density remained moderately low even after 75 hours of immersion.
Further optimisation of the passivation of AISI 316 based sprayed coatings will have to focus on the prevention of the localised attack as shown in Figure 66.

Figure 67: Polarisation curve in 0.5 M H$_2$SO$_4$ of HVOF sprayed AISI 316L as a function of exposure time (surface 1 cm$^2$, thickness 500 µm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve). A= 0 hours, B= 18 hours, C= 75 hours exposure at OCP.

Figure 68: Polarisation curve in 0.05 M H$_2$SO$_4$ of HVOF sprayed AISI 316L as a function of exposure time (surface 1 cm$^2$, thickness 500 µm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve). A= 0 hours, B= 18 hours, C= 75 hours exposure at OCP.

One way to accomplish a more homogeneous distribution of the alloying elements at micro level is by heat treatment. The effectiveness of this technique is demonstrated using a plasma sprayed AISI316 coating. These coatings were treated at 1100°C in a sealed 95% Ar, 5% H$_2$ atmosphere for a duration of 15 hours. The coating was characterised using the polarisation curve, both before and after the heat treatment. The result of these measurements is shown in Figure 69.

Figure 69: Polarisation curve in 0.5 M H$_2$SO$_4$ of APS sprayed AISI 316L before (A) and after (B) heat treatment (15h, 1100°C in Ar5%H$_2$) (surface 1 cm$^2$, thickness 500 µm, scan rate 10 mV/s) as compared to AISI316L clad (black curve) and carbon steel (grey curve).
These results indicate that, as expected, a significant improvement of the corrosion properties of the coating was achieved. To disclose the mechanisms behind this behaviour, an extensive metallographic investigation is required which, as explained before, unfortunately had to remain beyond the scope of this research. However, since the heat treatment cannot be used on site, it can be concluded that the AISI 316 sprayed coatings remain unsuited for practical repair of cladded steel constructions.
3.3.3 Monel400

Summary

The results in this section describe the corrosion behaviour of electric arc sprayed Monel400 (ca. 70%Ni, 30%Cu) coatings on steel. This material shows very favourable corrosion characteristics in both sodium chloride solutions and in sulphuric acid. The corrosion behaviour of the thermally sprayed coating on steel is effectively identical to the behaviour of cladded steel sheet. Also the behaviour in a practical environment, (saturated NaCl at 80°C) is acceptable compared to Monel400 cladded steel, even at prolonged exposure.

Results

This section describes the electrochemical behaviour of thermally sprayed coatings based on Monel400 feedstock material. The electrochemical behaviour of these coatings was evaluated to determine their corrosion resistance and to decide whether this type of thermally sprayed material could be used to repair Monel400 clad layers on steel.

Details on the spraying applications and an overview of the coating properties were given in section 3.2. The experiments were performed on an electric arc sprayed coating from OSU 300/2 feedstock material. The composition of this material is effectively identical to Monel400. This material was applied on carbon steel. The thickness of the coating was 1.7 mm. The general porosity as determined using image analysis on a cross section of the coating was about 3 to 4%.

The corrosion potential of the electric arc sprayed Monel400 coating on carbon steel is shown in Figure 70. The potentials were measured according to the technique described in section 2.6.1 using a HP 3852A data acquisition system. The samples were exposed in the “as sprayed condition”. The total surface area of the samples was approx. 1 cm².

The figure also includes the behaviour of the Monel400 clad material for comparison. For the duration of the measurement, the corrosion potential of the sprayed coating closely resembles the behaviour of the clad material.

![Graph](image)

*Figure 70: Potential monitoring in 3% NaCl of arc sprayed Monel400 coating on carbon steel and Monel400 clad material*

The corrosion behaviour of the thermally sprayed coating was further evaluated using the polarisation curves in both 3% NaCl and 0.5 M H₂SO₄.
The polarisation curves in this section were measured using the technique described in section 2.6.2 using a Solartron 1286 electrochemical interface and self developed software. The area of the working electrode was 1 cm² and the potential scanning rate was 10 mV/s. The scan range was from −750 mV to +1 V in both NaCl and H₂SO₄.

The results of the measurements are shown in Figure 71 and Figure 72. These figures also show the behaviour of the Monel400 clad material and the carbon steel substrate for comparison.

Analytical these figures also reveals no significant difference in the electrochemical behaviour of the sprayed coating as compared to the clad material. Based on this information the arc sprayed coating would appear a suitable anti corrosion coating for steel. Also, since the electrochemical behaviour is so close to the behaviour of the clad material, repair of a damaged cladding might also be possible.

But before any practical attempt can be made using these coatings, some information on the stability of the layer during prolonged exposure must be obtained. The polarisation curves in Figure 71 en Figure 72 were measured directly after exposure to the electrolyte. This means that these figures do not contain information on possible ageing effects during exposure.

Although the stability of the corrosion potential in time as shown in Figure 70 indicated no significant ageing during exposure in 3 % NaCl, prolonged exposure in sulphuric acid does have a significant effect on the corrosion behaviour. Figure 73 shows the polarisation curve after 18 hours of exposure in 0.5 M H₂SO₄.

The effect of the additional 18 hours of exposure in the electrolyte can be observed by comparing the initial situation, as shown in Figure 72 to the polarisation curves in Figure 73. The observed changes are schematically shown in Figure 75.

Initially both the thermally sprayed coating and the clad material essentially behave identically. This is indicated in the figure by “iₐ monel clad” and “iₐ 0h exposure”, resulting in “Eₜₐ₁ 0h”.

After 18 hours the anodic part of the polarisation curve has not changed much. The corrosion reactions during the exposure might have caused some change of the roughness of the surface area, but no drastic effects can be observed in Figure 73.
The cathodic part of the polarisation curves however, has changed dramatically. Not only a translation of the curve has occurred, but also the slope of the curve has changed. This indicates that the rate and/or the type of anodic reaction had changed. A possible cause would be the presence of reducible compounds which have accumulated during the 18 hours of exposure. Copper containing alloys are well known to develop a relatively thick adherent scale of corrosion products.

Figure 75: Schematic diagram of the behaviour of the polarisation curve of arc sprayed Monel400 and Monel400 clad material after exposure in 0.5 M H₂SO₄ for 18 hours.
During the 18 hours the material gradually builds-up a scale of corrosion products. This takes place on both the clad material and the spray coating. After 18 hours this scale has sufficiently grown and is present as a layer on top of the sample. This means that during the cathodic polarisation also the corrosion products were being reduced. This would explain the changes of the cathodic part of the curves.

For the thermally sprayed coating, the current in the cathodic region is higher than for the clad material. This is either the result of the larger surface area of the thermally sprayed sample or by the presence of a larger amount of corrosion products. Since also the anodic part of the polarisation curve shows an increase compared to the clad material, the thermally sprayed coating can be expected to have a larger surface area. But also the roughness of the coating might well facilitate the deposition of more corrosion products than are present on the smooth clad material.

Despite these differences between the clad and the sprayed coating, it can be concluded that the electrochemical behaviour of the Monel400 sprayed coating is practically similar to the Monel400 clad material. As stated before, this is one of the major requirements for a successful repair coating.

However, before a field test can be contemplated, the material has to be evaluated in the laboratory in an industrial electrolyte. Monel400 material is used in the process industry at treatment facilities for chlorine containing waters. A typical environment for this industry would be a saturated NaCl solution at 80°C.

Figure 76 shows the corrosion potential as a function of exposure time in this environment. The polarisation curve in this environment is given in Figure 77.

![Figure 76: Potential monitoring in saturated NaCl solution at 80°C of arc sprayed Monel400 on carbon steel and Monel400 clad material](image)

![Figure 77: Polarisation curve in a saturated NaCl solution at 80°C of arc sprayed Monel400 on carbon steel (area 1 cm², thickness 1.7 mm, scan rate 10 mV/s) as compared to Monel400 clad material (black curve).](image)

From Figure 77 is immediately apparent that the current values measured on the thermally sprayed coating remain below the values for the clad material. Apparently, the higher anodic reaction rate in the anodic region on the clad material results in a higher amount of corrosion products on the surface. These cause the higher cathodic current when they are reduced in the cathodic part of the polarisation curve.

For a reason that unfortunately cannot be resolved by this research, the corrosion products that are formed on the thermally sprayed coating are a more successful barrier under these circumstances. Study of the anodic part of the polarisation curve of the thermally sprayed coating...
reveals a region, roughly between the corrosion potential at -500 mV up to -250 mV in which the anodic current remains constant. The stable corrosion potential as shown in Figure 76 has a value of about -400 mV, placing it in the middle of the constant current region. Assuming that the corrosion current of an exposed sample of this material will corrode at a rate similar to the constant current found in this region, would lead to a corrosion current of approx. 1 mA/cm². Although this value is relatively high compared to the passive current density of a truly passive system, it would appear more than adequate considering the exposure conditions.

Whether or not this result remains valid for longer exposure times is illustrated in Figure 78 and Figure 79. These figures show the development of the polarisation curve of the Monel400 sprayed coating on carbon steel as a function of the exposure time. All measurements were consecutively performed on the same sample. Therefore, the ageing in each measurement not only resulted from the prolonged exposure time but also included the effect of the previous measurement. This can be regarded as a significant increase of the severity of the test circumstances.

It can be observed that the anodic current density increases in time. Still, for these test conditions the effect is modest.

**Figure 78:** Polarisation curve as a function of exposure time in a saturated NaCl solution at 80°C of arc sprayed Monel400 (area 1 cm², thickness 1.7 mm, scan rate 10 mV/s).

**Figure 79:** Close-up of Figure 78

So it can be concluded that no significant corrosion problems using this material in a combination with a clad layer of the same composition can be expected. Therefore it can be recommended to be field tested as a repair coating for damaged clad material to be used in saturated NaCl solutions at 80°C.
3.4 Electrochemical Qualification Test

Summary

This section describes the evaluation of the polarisation curve as a qualification test. It is shown that the polarisation curve can be used to differentiate between the effects of oxidation and the formation of pores. It was also shown that the measurement results could be fed back to the application procedure to optimise application parameters. Furthermore, the polarisation curve was shown to reveal information on the relation between porosity and coating thickness. A simple model is suggested, linking the anodic current to the amount of open porosity. Using this relationship, it is possible to design a method that can be used to provide direct information on the corrosion protection quality. Also an indication of the required coating thickness to reach the optimal corrosion protection can be obtained.

Results

The experience from the work described in the previous sections learned that the polarisation curve is a very useful tool to evaluate thermally sprayed coatings. The polarisation curve provides information on the electrochemical behaviour of the thermally sprayed coating in a given environment and the measurement of a curve takes relatively little time. These characteristics make the technique the perfect tool to provide a first indication of the expected behaviour of the sprayed coating in a practical application.

Qualification tests are only effective when they are combined with good pass-or-fail criteria for the analysis of their results. In this particular case, these criteria will consist of specific properties of the curve as corrosion potential, passive current density, etc. These criteria have to be linked to physical properties of the coating, or even better, to the application parameters of the coating application technique. This would provide a direct control of the process to the applicator and would give a user of the coating the information he needs to qualify the product.

Table 8: Application parameters for the plasma spray AISI 316 coatings with the resulting porosity and oxide content. The numbers correspond to the application numbers in Table 3 of section 3.1

<table>
<thead>
<tr>
<th>number</th>
<th>Ar flow</th>
<th>H₂ flow</th>
<th>pH₂</th>
<th>spray distance</th>
<th>porosity (%)</th>
<th>O content (w%)</th>
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<tr>
<td>1</td>
<td>100</td>
<td>15</td>
<td>0.13</td>
<td>120</td>
<td>4.3</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>15</td>
<td>0.13</td>
<td>150</td>
<td>4.8</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>15</td>
<td>0.13</td>
<td>200</td>
<td>5.8</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5</td>
<td>0.05</td>
<td>120</td>
<td>5.2</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>10</td>
<td>0.09</td>
<td>120</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>10</td>
<td>0.09</td>
<td>120</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>20</td>
<td>0.17</td>
<td>120</td>
<td>4.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

To determine whether polarisation techniques can provide this type of information, a series of experiments was carried out to correlate the polarisation curve to application parameters of the sprayed coating. To be certain that the application parameters would lead to coatings of which the differences could also be determined by standard coating characterisation, the atmospheric plasma spray technique (APS) was used. Using this technique it is relatively simple to produce coatings of various porosity levels and amount of oxidation.
The APS application series was carried out using AISI 316 feedstock powder material. The differences between the coatings were caused by variation of the spray distance and the ratio between the amount of hydrogen gas and argon in the plasma gas. The resulting differences in porosity and oxide content are listed in Table 8.

The polarisation curves in this section were measured using the technique described in section 2.6.2 using a Solartron 1286 electrochemical interface and self developed software. The area of the working electrode was 1 cm² and the potential scanning rate was 10 mV/s. The scan range for this experiments was from −750 mV to +500 mV in both NaCl and H₂SO₄.

Examining the data in Table 8 reveals that when the spray distance increased, both the porosity and the oxide content increased. This is explained by the fact that an increase of the spray distance also increases the time of flight of the particles in the surrounding atmosphere. This provided more time during which the oxidation could take place, leading to the higher oxide content. The higher oxide content caused the particles to be less ductile on impact, leading to higher porosity of the coating.

The coatings that were applied using increasing hydrogen to argon ratio displayed the opposite behaviour. Under these circumstances an increasing oxide content is coupled to a decreasing porosity. This is explained by the higher flame temperature caused by the increased H₂ ratio. This increased the oxidation rate, but, because of the increased particle speed, the resulting loss of ductility is (partially) compensated leading to relatively dense coatings.

The first impression of the electrochemical behaviour did not suggest a great deal of variation between the different coatings. The polarisation curves are shown in Figure 80.

![Figure 80: Polarisation curves in 0.5 M H₂SO₄ of plasma sprayed AISI 316 coatings on carbon steel using various argon to hydrogen pressure ratios and spray distances shown in Table 8 (area 1 cm², thickness 550-650 μm, scan rate 10 mV/s).](image)

However, closer analysis of the data revealed significant differences. The analysis was based on the average anodic current at a specific potential value. Since the corrosion properties of AISI 316 mainly depend on passivation behaviour, a potential value in the passive region was used. For this reason the arbitrary value of 400 mV (vs. Ag/AgCl) was selected.

To facilitate comparison of the effect of the various application parameters, the current values were ranked starting at number 1 for the lowest current. The polarisation measurement was carried out three times consecutively to improve the analysis. Data of the second and third measurements were used for the ranking since the first measurements proved too sensitive to
the sample history. Both measurements were ranked individually. The average ranking of the current density in the two measurements on the same sample was used for further analysis (see Table 9).

Table 9: The average ranking of the current density measured at 400 mV (vs. Ag/AgCl) for plasma sprayed AISI 316 coatings in 0.5 M H₂SO₄. The numbers correspond to the application numbers in Table 3 of section 3.1

<table>
<thead>
<tr>
<th>number</th>
<th>2nd measurement</th>
<th>3rd measurement</th>
<th>average ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mA)</td>
<td>(mA)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.0</td>
<td>1.6</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1.9</td>
<td>2.1</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>2.6</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>1.1</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>1.3</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>1.4</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Also the porosity and the oxide content values were ranked. Plotting the ranking of the current density versus that of the porosity yielded the relationships shown in Figure 81. The ranking of the oxide content is used in Figure 82.

![Figure 81: Relation between the ranking of current density at 400 mV (vs. Ag/AgCl) and the ranking of the average porosity for plasma sprayed AISI 316 coatings in 0.5 M H₂SO₄. A= increasing hydrogen pressure, constant spray distance, B= increasing spray distance, constant hydrogen pressure.](image)

Examining just the data points (and not the lines) in Figure 81 showed no direct relation between the current values and the porosity. However, when additional information (spray distance and hydrogen pressure) was included, two separate dependencies were revealed:

A  Increased porosity resulting from a decrease of the hydrogen pressure improved the electrochemical behaviour.

B  Increased porosity resulting from an increase of the spray distance worsened the electrochemical behaviour.
Comparing the ranking of the oxide content to the ranking of the electrochemical behaviour showed a correlation regardless of application circumstances. As can be seen in Figure 82, the electrochemical behaviour deteriorated when the oxide content increased.

![Figure 82: Relation between the ranking of the current density at 400 mV (vs. Ag/AgCl) and the ranking of the oxide content for plasma sprayed AISI 316 coatings in 0.5 M H₂SO₄.](image)

Based on these results can be concluded that when the porosity differences are relatively small, and open porosity does not play a significant role, the passive current (i.e. corrosion protection) of the coating is mainly determined by the oxide content. Therefore, use of the porosity value as a measure of the corrosion protection quality of the coatings may lead to erroneous results.

![A to C: Relation of open porosity and coating thickness at a constant general porosity. Coating thickness increases from A to C and open porosity decreases. Note that the situation at B and C only show one of the many possible pore distributions. For this reason this graph should be treated as qualitative illustration to equation 1 of page 92.](image)

When this result is fed back to the application parameters (spray distance and hydrogen pressure) it is revealed that the best coating results from a minimal spray distance combined with the lowest hydrogen pressure. Naturally, these considerations are only valid for the used parameter range, and even then, they can only be used as indicative values.
A different situation arises when open porosity influences the anodic current density in a polarisation curve. Since cathodic coatings are extremely sensitive for open pores, a direct relation will exist between the amount of open pores and the resulting corrosion protection of the coating.

It can generally be assumed that the amount of open pores will increase when the general porosity of the coating increases. In this case a further dependency can be assumed between the general porosity, the amount of open pores and the thickness of the coating. As shown in Figure 83 the open porosity will decrease on the average when the coating thickness increases.

The resulting effect of this dependency on the polarisation curve is shown in Figure 84 and Figure 85. These figures show the polarisation curve of an arc sprayed titanium coating in 3 % NaCl as a function of the thickness of the coating. In order to reveal the influence of coating thickness, the coating was mechanically polished after each measurement to the next thickness value. The polishing had to be performed very carefully to prevent any excessive breakout of brittle particles or smearing of the pores.

![Figure 84: Polarisation curves in 3 % NaCl of arc sprayed titanium of various thicknesses on carbon steel as compared to uncoated carbon steel (grey curve) (area 1 cm², scan rate 10 mV/s).](image1)

![Figure 85: Polarisation curves in 3 % NaCl of arc sprayed titanium of various thicknesses on titanium clad material as compared to uncoated titanium clad material (black curve) (area 1 cm², scan rate 10 mV/s).](image2)

As the coating thickness decreased, the amount of open pores increased and the influence of the substrate became ever more apparent. The current values in Figure 84 increased significantly when the coating thickness decreased, to eventually reach the same level as was measured on uncoated steel. Also the equilibrium potential in the graphs moved closer towards carbon steel after each consecutive measurement.
The reverse effect is shown in Figure 85. This figure displays the behaviour of the same coating applied on titanium, instead of carbon steel. Because of the very poor quality of the sprayed coating compared to the titanium cladding, the current density values decreased when the coating thickness decreased. In this case, increase of the open porosity led to a larger exposed area of well-passivating titanium substrate material. Eventually the polarisation curve matched the curve of passive uncoated titanium.

It should be noted that the effect shown in Figure 85 could only be observed because of the very poor quality of the thermally sprayed titanium coating. Had the coating been of good quality, the behaviour of a coating without open pores would be identical to the response of the titanium substrate. In that situation, no change of current would result from a thinning of the coating.

To investigate the relationship between thickness and porosity Figure 84 and Figure 85 were adapted. Similar to the analysis in Figure 81 the current density around a specific potential value was analysed. Since the corrosion behaviour of the cladding and the spray material mainly depend on passivity, a potential in the passive range was selected, (+500 mV vs. Ag/AgCl).

When the corresponding anodic current values were plotted as a function of the coating thickness, Figure 86 resulted from Figure 84, and Figure 87 from Figure 85. The dotted lines in these figures indicate the maximum and minimum values between which the currents can vary. These levels were determined by the response of a coating without open pores and the response of the uncoated substrate material. As described before, the level of the substrate (carbon steel) lies far above the coating level in Figure 86, while the opposite is true in Figure 87 (titanium as substrate).

![Figure 86: Anodic current of arc sprayed titanium coating (surface 1 cm²) on carbon steel at 500 mV (vs. Ag/AgCl) as a function of coating thickness, as compared to the corresponding current of a thick coating (A) (>2 mm) and uncoated carbon steel (B)](image1)

![Figure 87: Anodic current of arc sprayed titanium coating (surface 1 cm²) on titanium clad material at 500 mV (vs. Ag/AgCl) as a function of coating thickness, as compared to the corresponding current of a thick coating (A) (>2 mm) and uncoated titanium clad material (B)](image2)

From these figures can be learned that at least about 1 mm of coating thickness was needed to eliminate any significant effect of the substrate. Only for thicknesses above 1 mm the current value is stable at the level corresponding with the coating.

To further explore this relationship, a similar experiment is described using an arc sprayed Monel400 coating on steel. This coating has shown to be of good quality (see section 3.3.3).
This means that no significant difference could be measured between the anodic current level of a coating without open pores and Monel400 clad material. The polarisation curves as a function of coating thickness are shown in Figure 88.

![Polarisation Curve Image](image)

**Figure 88**: Polarisation curve in 3% NaCl of arc sprayed Monel400 coating of various thickness (range 0.1 to 1.1 mm) on carbon steel as compared to Monel400 clad material (black curve) and uncoated carbon steel (grey curve) (area 1 cm², scan rate 10 mV/s).

![Current vs Coating Thickness Image](image)

**Figure 89**: Anodic current of arc sprayed Monel400 coating (surface 1 cm²) on carbon steel at -200 mV (vs. Ag/AgCl) as a function of coating thickness, as compared to the corresponding current of unprotected carbon steel (B) and uncoated Monel400 clad material (A).

![Logarithmic Current vs Coating Thickness Image](image)

**Figure 90**: As Figure 89, corrosion current normalised to logarithmic scale using equation 7.

Analogous to Figure 86 and Figure 87, the average anodic current at a potential in the passive region (-200 mV vs. Ag/AgCl) as a function of the coating thickness is shown in Figure 89.

For this relationship, a simple model is proposed: The lamellar structure of a thermally sprayed coating can be simplified as a series of porous coating layers, much as the situation in Figure 83. The thickness of this theoretical layer would consist of a coating slice that is penetrated by all the

- 91 -
porosity present. In other words, it is the maximum coating thickness for which the all porosity is open porosity.

Assuming that each of these layers has the same amount of pores penetrating the layer, the general porosity of the coating (p) will be independent of the thickness. In this case, the resulting open porosity can be calculated as a function of the number of layers (n). The total thickness (t) follows from the number of layers (n) and their individual thickness (ti).

\[ P_{open} = P^n \] (1)

with:
- \( p_{open} \) = open porosity (%)
- \( P \) = general porosity (%)
- \( n \) = number of layers

And:

\[ t = n \cdot t_i \] (2)

with:
- \( t \) = coating thickness (m)
- \( t_i \) = layer thickness (m)
- \( n \) = number of layers

The porosity as expressed by equation 1 is a surface fraction. The total area of the exposed substrate due to porosity “p” is calculated by:

\[ A_{substrate} = \frac{P_{open}}{100\%} \cdot A \] (3)

with:
- \( A \) = total surface (m²)
- \( p_{open} \) = open porosity (%)
- \( A_{substrate} \) = exposed substrate (m²)

Any influence of the walls of the pores is assumed to be negligible in this simplified model.

The total anodic current (I) is composed of current resulting from the substrate and from the coating itself. Assuming that the contributions of the two currents are linearly dependent on the respective exposed surface area, leads to:

\[ I = i_{coating}A_{coating} + i_{substrate}A_{substrate} \] (4)

with:
- \( I \) = total anodic current (A)
- \( i_{coating} \) = current density on coating (A/m²)
- \( A_{coating} \) = exposed coating surface (m²)
- \( i_{substrate} \) = current density substrate (A/m²)
- \( A_{substrate} \) = exposed substrate surface (m²)
And:

\[ A = A_{\text{coating}} + A_{\text{substrate}} \]  \hspace{1cm} (5)

with:
- A = total surface
- \( A_{\text{coating}} \) = exposed coating surface
- \( A_{\text{substrate}} \) = exposed substrate surface

Under these assumptions, the relation between the coating thickness and the resulting anodic current can be written as:

\[ \frac{I - i_{\text{coating}} \cdot A_{\text{coating}}}{A} = \left( \frac{P}{100\%} \right)^{\frac{t}{t'}} \cdot i_{\text{substrate}} \]  \hspace{1cm} (6)

Or:

\[ \log \frac{I - i_{\text{coating}} \cdot A_{\text{coating}}}{i_{\text{substrate}} \cdot A} = \frac{t}{t'} \log \left( \frac{P}{100\%} \right) = C \cdot t \]  \hspace{1cm} (7)

with: \( C = \log(p/100\%)/t' \)

This relationship is shown in Figure 90. The slope of the dotted line in this figure will be mainly dependent on the porosity of the coating.

To test this hypothesis an additional series of Monel400 coatings were produced with higher porosity levels than the coating used in Figure 88 to Figure 90. These coatings were applied using the APS technique and the resulting (general) porosity was determined using the same technique as was used on the previous coating (image analysis on cross-sections). The application parameters and the resulting porosity are listed in Table 10.
Table 10: Application parameters for the plasma spray Monel400 coatings with the resulting porosity.

<table>
<thead>
<tr>
<th>H₂ spray distance</th>
<th>thickness</th>
<th>porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>psi/scfh</td>
<td>mm</td>
<td>μm</td>
</tr>
<tr>
<td>50/10</td>
<td>100</td>
<td>450-500</td>
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<tr>
<td>50/15</td>
<td>100</td>
<td>500-550</td>
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<tr>
<td>50/5</td>
<td>300</td>
<td>160-180</td>
</tr>
<tr>
<td>50/5</td>
<td>200</td>
<td>330</td>
</tr>
</tbody>
</table>

Figure 91: As Figure 90 including the anodic current densities of plasma sprayed Monel400 coatings at -200 mV (vs. Ag/AgCl) with the corresponding porosity values as a function of the coating thickness.

Measurement of the polarisation curves and analysis of the current value at -200 mV (vs. Ag/AgCl) yielded average anodic current values similar to the values plotted in Figure 89. Combining these values with Figure 90 results in Figure 91. In this figure the previously discussed arc spray Monel400 coating is compared to the two new APS coatings. This figure indeed shows a higher anodic current for a coating with a higher general porosity at a specific coating thickness.

Using the slope of the dotted lines and the general porosity values from Table 10, the layer thickness from equation 7 could be calculated. The result of this calculation is listed in Table 11.

Table 11: Application parameters for the plasma spray Monel400 coatings with the resulting porosity and layer thickness calculated using equation 7.

<table>
<thead>
<tr>
<th>coating type</th>
<th>general porosity (%)</th>
<th>slope in Figure 91 (1/A)</th>
<th>layer thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>arc spray</td>
<td>3-4</td>
<td>-5.33</td>
<td>0.29</td>
</tr>
<tr>
<td>plasma spray</td>
<td>5-6</td>
<td>-1.61</td>
<td>0.78</td>
</tr>
<tr>
<td>plasma spray</td>
<td>9-10</td>
<td>-1.34</td>
<td>0.75</td>
</tr>
</tbody>
</table>
This table shows that the two coating methods can be identified by their respective layer thicknesses. Since the layer thickness was defined as the thickness of a coating slice in which all porosity is open porosity, the value is a measure of the general pore size. Naturally, this value cannot be treated as an accurate measure, but it does indicate a significant difference in morphology between the arc sprayed coating and the plasma sprayed coatings.

Based on the relationship shown in Figure 91 a rough estimate of the corrosion protection of the plasma sprayed coatings could be made. The data points for the arc sprayed coating showed that the minimal required coating thickness to obtain the lowest anodic current is approximately 0.4 mm. A similar extrapolation of the results from the APS coatings in Figure 91 would indicate that the required thickness of the 9 to 10% porosity containing coating will be around 1.5 mm, as to 1.25 mm for the 5 to 6% porosity containing coating to reach the minimum obtainable corrosion current.

Using this type of interpretation, it may well be possible to determine the amount of open pores without having to make unreliable estimates from coating cross-sections. By measuring the anodic current at a specified potential, together with the coating thickness, an indicative value of the corrosion protection quality of the coating can be obtained. Also an indication of the required coating thickness to reach the optimal corrosion protection is determined. Coatings with a too high amount of open pores can be identified and improved before they are being put to practical use. Finally, using this approach, it can also be decided to remove a coating when the coating is too porous to result in an acceptable corrosion protection within a practical thickness range.
3.5 Conclusions

The results confirm that generally both the electrochemical behaviour and the chemical composition of a thermally sprayed coating significantly differ from bulk material with the same composition. This is the direct result of physical and chemical changes, caused by the thermal spraying coating application process.

In order to attain any level of success, this effect needs to be taken into consideration when contemplating the use of thermally sprayed coatings for corrosion protection or the repair of bulk or cladded materials. Generally, precautions need to be taken at two levels. First, minimisation of the changes during application by selection and process control of the application technique is required. But also careful selection is necessary of a coating material composition that facilitates the required electrochemical properties as closely as possible, mimicking those of the material to be repaired.

Furthermore, especially for coatings that are more noble than the substrate on which they are sprayed, the structural integrity of the coating is another crucial factor. The presence of pores in a coating will rapidly lead to potentially dangerous localised corrosion.

The measurement that incorporates these effects and consequently is most suited to be incorporated in a qualification test procedure is the measurement of the electrochemical behaviour of the coating.

The results described in this chapter prove the potential of electrochemical assessment by a relatively simple measurement of the anodic current at a specific potential. Because of the relatively large difference in corrosion potential between a porous thermally sprayed coating and its substrate (for the combinations that were used in this thesis), the emerging anodic current can be attributed to the exposure of the substrate. Since the current can be expected to be proportional to the surface area of the substrate, it can be taken as an indication of the total area of open pores in the coating.

In other words, the method can be used to determine whether a coating is sufficiently free of open pores. When this is not the case, the method can also be used to estimate the extra coating thickness that needs to be applied to achieve the required amount of pore closure.

The results of using electrochemical techniques together with x-ray analysis and visual characterisation of the titanium, stainless steel, and Monel400 thermally sprayed coatings led to the following conclusions:

Titanium: Standard electric arc spraying of titanium can not result in a coating with adequate corrosion protection properties. The formation of titanium oxides and nitrides during the spray application leads to unacceptable porosity levels. Although this can significantly be reduced by using argon gas as propellant, the resulting coating remains too porous for aqueous corrosion protection purposes.

AISI316: Conventional arc spraying of this material composition induces excessive oxidation of chromium, preventing the formation of an adequate passive film on the surface of the resulting coating. The use of argon as propellant reduces the oxidation significantly and consequently improves the electrochemical behaviour of the coating.

Also when using the atmospheric plasma spray technique, the results show that the corrosion protective quality of the coating, is mainly determined by the amount of oxidation in the coating and to less extend by the porosity. The reason for this behaviour stems from the fact that stainless steel is an alloy and depends on the
distribution of alloying elements (especially chromium) for its corrosion properties. The best results are obtained using low hydrogen to argon ration together with a relatively short spraying distance.

Further improvement of the corrosion properties of thermally sprayed coatings based on this material composition can be achieved by using the high velocity oxygen fuel spray technique. However, the only way to achieve a coating with good corrosion protection behaviour comparable to stainless steel bulk material is as yet to use a post spray heat treatment.

Monel400: Electric arc spraying of Monel400 spraying material results in a coating of which the electrochemical properties are comparable to the Monel400 bulk material. The coating remains intact also after extended exposure in a practical industrial environment. Therefore it can be concluded that this coating can be regarded as a feasible alternative for the repair of Monel400 cladded steel material.

As a final conclusion it can be remarked that the wide range of available electrochemical techniques enables the assessment of practically any relevant corrosion protection property of thermally sprayed coatings. Both traditional techniques as potential monitoring or the measurement of polarisation curves as well as the recently developed localised techniques, can provide relevant information on the mechanisms of corrosion protection. This makes electrochemical measuring methods the most important quality assessment tool for thermally sprayed coatings for corrosion protection.
3.6 References


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10. J.H. Gerretsen, J.H.W. de Wit, The passivation of Ni in 0.5 M sulphuric acid, chapter 8, thesis TUDelft 1990 is gepubliceerd in Journal of electrochemistry

4 Coatings Anodic to Their Steel Substrate

4.1 Introduction

In many countries, including The Netherlands, metal sprayed coatings are ever more considered a promising alternative for heavy-duty anti-corrosion paint systems. Nonetheless, the amount of available research data on the performance of these systems for moderate temperature corrosion protection can be classed as modest. Perhaps for this reason the actual use of metal sprayed coatings for corrosion protection is not in accordance with the expected performance of these systems. However, reported case studies [1-13] and electrochemical investigations [14-21] are almost unanimous about the protective ability of sprayed metal coatings.

Invoked by the Dutch Ministry of Transport, Public Works and Water Management, the most important uncertainties regarding the use of metal sprayed coatings have been addressed. This work was directed specifically towards reducing the risks for a large scale application of thermal sprayed coatings for corrosion protection in marine environment. The selected systems consisted of flame and electric arc sprayed aluminium based coating on mild steel.

The research concerned primarily the paradox of the protective mechanism of an aluminium coated steel which depends on the formation of a passive layer for general corrosion protection, but needs to provide cathodic protection at pores and defects that expose the underlying steel.

A second main area of interest was the role of a sealer coating. Most coating suppliers recommend the use of an organic sealer to be applied on top of the metallic sprayed coating. [22-23] The suggested reason is generally to "block pores... and to extend the service life of the metallic coating". This also invokes a paradox since, generally, organic coatings cannot be expected to last longer than, perhaps half the service life of an uncoated metallic sprayed coating [24-28]. The use of a sealant would then effectively halve the "time to first maintenance" which would consist of removing the deteriorated organic coating and re-applying a new layer. And although the steel substrate would undoubtedly be adequately protected, the thermally sprayed coating would be reduced to a very expensive primer.

The third concern of coating sceptics is that metallic thermally sprayed coatings would be too brittle to be applied on large structures that are subjected to a dynamic load and consecutively show elastic strain during service. The thermally sprayed coating is suspected to be unable to support this movement and crack at the stressed areas.

Finally, since aluminium is known to be sensitive for localised changes in pH or dissolved ions, [29-31] the behaviour in combination with biological fouling organisms was investigated. Barnacle growth on aluminium coatings could not only create pH differences underneath the organism, also the animal’s shell could create de-aeration and crevice corrosion phenomena which would cause rapid attack of the coating layer.

This broad range of subjects involves many protective/failure mechanisms, which in turn demands the use of a wide variety of experimental techniques to address the specific problems. The used techniques incorporated mechanical characterisation, electrochemical characterisation and monitoring during exposure experiments, supported with (electron) microscopy studies.

The results of the measurements are described in the next sections. First an overview of the used materials is provided, including the application parameters and a general impression of the microstructure of the used coatings. The presentation of the actual measurement data is divided into three main fields: “basic characterisation”, “intact coatings” and “coatings with a defect".
In the section "basic characterisation" all non-electrochemical results are presented, including mechanical characterisation and the influence of bio-fouling.

Since metallic coating will be competing with organic systems used for corrosion protection, typical "paint" tests have been used in this section to see how the results compare. The selected tests to determine the properties of the aluminium coated steel panels were the following:

- Flexibility, by means of a three-point bending test.
- Adhesion, by means of a dolly pull-off test.
- Relative toughness by means of the pencil hardness test and the pendulum damping test.
- Effect of biological fouling on the integrity of the thermally sprayed coating.

To evaluate the effect of ageing during exposure, the mechanical properties (flexibility, adhesion and toughness) were investigated before and after 3000 hours of immersion in natural seawater.

The description of the electrochemical behaviour of the coatings is divided into two sections. The first section deals with the behaviour of a normally sprayed coating. This section is titled "intact coating" as opposed to the last section which describes the behaviour of aluminium based coatings that incorporate a significant amount of exposed steel substrate. The title of this section is "coatings with defects". For this reason a part of the aluminium coating was removed to evaluate the resulting electrochemical processes. Naturally, this would not happen wilfully during practical use of this system. But, regretfully, damage of the coating, especially during transport and construction of pre-sprayed parts is not uncommon.
4.2 Materials

For the experiments described in this chapter, two types of thermal spraying techniques were used with two types of aluminium based feedstock materials. The thermal spraying techniques were selected on flexibility and cost. Since these types of metallic coatings are generally applied to extremely large structures (bridges, sluices etc.) the choice of coating method is limited to either flame spraying or arc spraying. Aluminium based feedstock material is by far the most used for corrosion protection, especially in marine environments. In practice either “pure” aluminium or aluminium with 5% of magnesium is used.

The reason why the 5% magnesium alloy is used originally stems from the need to lower the corrosion potential of the sprayed coating. Adding a minimum of about 3.5% of magnesium was recognised as a reliable way to prevent the aluminium from complete passivation, thus keeping the throwing power of the cathodic protection intact. The addition was found only to be required in fresh water. The conditions and composition of sea water are generally sufficiently aggressive to prevent also pure aluminium from complete passivation.

The combination of the two application techniques and the two feedstock materials results in the following four coating materials (although not all experiments were performed on all four coatings):

- flame sprayed Al99.7
- arc sprayed Al99.7
- flame sprayed AlMg5
- arc sprayed AlMg5

The coatings were applied at Sulzer Metco.

The flame sprayed coatings were applied using the type 14E-H installation with a propane/oxygen flame at a spraying distance of 150 to 200 mm. The Aluminium wire diameter was 3.2 mm (1/8”). The AlMg5 wire had a diameter of 1.6 mm.

Figure 1: Cross section of Flame Sprayed Aluminium 99.7 coating. The average thickness of the coating in this figure is approx. 350 μm (magnification approx. 50x).

Figure 2: Cross section of Flame Sprayed Aluminium Magnesium 5 coating. The average thickness of the coating in this figure is approx. 250 μm (magnification approx. 50x).
The cross sections in Figure 1 to Figure 4 show the typical structure of the resulting coatings. These figures show the thermally sprayed coating in the middle of the picture, between the resin used for preparation of the sample (black region) and the steel substrate (grey region). To provide a clear impression of the coating structure they were applied to a much larger thickness than the coatings that are actually used in the experiments. The coatings used for the experiments have an average thickness of about 150 µm.

Since the coatings are deposited by partial melting, the microstructure of the coatings consists of solidified particles and a relatively large number of pores. The close up of the coating cross sections in Figure 5 and Figure 6 gives an impression of the particles in the coating.

The arc sprayed coatings were applied using the SmartArc installation fitted with a fine air cap. The primary air pressure was set at 60 psi at a spraying distance of 150 to 200 mm. Electric arc supply was set at 250 ampere at 26 to 28 volts. The diameter of both the Aluminium 99.7 and AlMg5 wire was 1.6 mm.
A concentration of microscopic pores, either caused by poor control of the spraying gun or contamination of the sample, can easily lead to macroscopic defects or large pores in the coating. An example of this type of defect is shown in Figure 7.

A similar defect in a cathodic coating will undoubtedly lead to corrosion problems, but (as the results in section 4.3.2 show) for aluminium coatings a limited number of this type of defects can be tolerated. The galvanic corrosion of the coating material will prevent corrosion of the substrate material and the resulting aluminium oxides are known to block the defect and limit the corrosion to acceptable levels.

The irregularities of the coating structure will also affect the surface of the material. Thermally sprayed aluminium coatings, as all other thermally sprayed coatings exhibit a relatively rough outer surface. Depending on the application technique, the average roughness values (Ra) can range from 10 up to 30 μm. Figure 8 to Figure 11 give an impression of the outward appearance of the coatings. The darker regions (as in the centre of Figure 10) are depressions of the surface typical for these coating types.

Figure 7: Macroscopic defect in flame sprayed aluminium coating (magnification 160 x).

Figure 8: Surface structure of a flame sprayed aluminium thermally sprayed layer (magnification approx. 40 x).

Figure 9: Surface structure of an arc sprayed aluminium thermally sprayed layer (magnification approx. 40 x).
A typical roughness profile of the Al99.7 flame sprayed coating is shown in Figure 12. Table 1 lists the roughness values for all coatings. The roughness was determined using a Mitutoyo Surface Roughness Tester according to DIN 4766.

The surface roughness not only facilitates the adhesion of any subsequent organic coating (or sealer) but also provides a near perfect surface for growing and sustaining biological fouling organisms. Especially mussels and barnacles are known to attach themselves in great numbers onto the thermally sprayed coating [4,26]. Another important drawback of the high surface roughness of the coatings is that it limits the use as a protective coating in immersion to stationary objects. As a coating for a ship hull, the high surface roughness would generally result in a high drag that would lead to unacceptable fuel consumption.

![Surface roughness profile](image)

**Figure 12: Surface roughness profile of a flame sprayed aluminium coating.**

<table>
<thead>
<tr>
<th>Coating</th>
<th>$Ra (\mu m)$</th>
<th>$Rt (\mu m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fs Al99.7</td>
<td>9.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Fs AlMg5</td>
<td>11.7</td>
<td>1.0</td>
</tr>
<tr>
<td>As Al99.7</td>
<td>18.1</td>
<td>0.8</td>
</tr>
<tr>
<td>As AlMg5</td>
<td>15.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 1: Surface roughness results for aluminium based coatings ($n=3$).**

Although the chemical composition of the coatings is not expected to be as critical as for the cathodic coatings, the thermal spraying application may also affect the composition of the aluminium base coatings. Especially the composition of the AlMg5 coating is of interest since the amount of magnesium in the actual coating may be considerably less than the 5 percent (4.5 weight percent) that was originally present in the thermal spraying wire.
The composition of the used coatings was determined using X-ray fluorescence and EDX. The results are listed in Table 2.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc Spray</td>
<td>Al99.7</td>
<td>0.06</td>
<td>99.56</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Flame Spray</td>
<td>Al99.7</td>
<td>0.04</td>
<td>99.69</td>
<td>0.12</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arc Spray</td>
<td>AlMg5</td>
<td>2.1</td>
<td>97.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flame Spray</td>
<td>AlMg5</td>
<td>5.16</td>
<td>94.11</td>
<td>0.17</td>
<td>0.01</td>
<td>0.05</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
<td>0.11</td>
<td>0.11</td>
<td>0.15</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 2 shows that flame spraying AlMg5 results in a coating that still contains magnesium. In the arc sprayed coating however, the magnesium content has decreased significantly.

As stated before, the original reason why the 5 percent magnesium alloy was used, stems from the need to lower the corrosion potential of the sprayed coating. However, it is generally found that arc spraying of AlMg5 results in a coating with a better adhesion to a steel substrate than a pure aluminium coating, applied under identical circumstances. Two possible mechanisms are proposed. A first explanation is that the high temperatures in the arc discharge cause the magnesium to burn exothermally. The energy released by this process increases the temperature of the flame and causes a better solidification of the spraying material. The second explanation found in literature is that also internal stresses may be relaxed in the resulting coating when the magnesium oxides crumble during cooling of the coating. [34]

Consequently the amount of metallic magnesium in arc spraying coatings is generally very low (Table 2). There is generally no direct effect on the electrochemical behaviour of the coating. Nonetheless, since popular opinion still associates high adhesion to better corrosion protection, the arc sprayed AlMg5 coatings are frequently preferred over other aluminium based coatings by industrial users.
4.3 Characterisation Results

4.3.1 Basic Characterisation

Summary

The results of the basic characterisation described in this section show that the mechanical properties of aluminium sprayed coatings are, generally speaking, superior to the properties of common anti-corrosion paints. Flexibility measurements showed the possible development of cracks onto the steel substrate. However, as the results described in section 4.3.3 indicate, the risk of corrosion of the steel substrate will remain minimal. The formation of cracks will only occur at the very limit of the bending load for these systems. The magnitude of this maximum load is comparable to the values normally associated with high build organic coatings. An important fact regarding the mechanical properties of the Al based thermal spray coatings is that no significant changes could be measured after 3000 hours of immersion in natural seawater. The amount of fouling after immersion in seawater on the coated panels was relatively large. An anti-fouling coating for situations where fouling would be undesirable is therefore necessary. On the other hand, the abundance of biological activity also suggests no harmful effect of the coatings on the environment. The corrosion protection properties of the spray coatings did not suffer from damage by fouling organisms after 23 months of exposure.

Results

Flexibility

Flexibility was tested using a three-point bending arrangement, as shown in Figure 4 of section 2.3.2, but without the scratch in the sprayed coating. Since the flexibility of the coating was tested and not the adhesion, the coating should be tested intact.

The flexibility is expressed as the amount of bending (sag) in millimetres until cracking of the coating was observed. After the test, the bending load was removed and specimens were prepared for microscopic evaluation of the amount and nature of the occurred cracks.

Table 3 lists the results of this investigation. The measurements were duplicated four times.

Table 3 Results of flexibility test using the three-point bending arrangement

<table>
<thead>
<tr>
<th></th>
<th>immersion (mm)</th>
<th>meas. 1 (mm)</th>
<th>meas. 2 (mm)</th>
<th>meas. 3 (mm)</th>
<th>meas. 4 (mm)</th>
<th>avg. (mm)</th>
<th>std. dev. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>flame spray Al</td>
<td>99.7 before</td>
<td>20.40</td>
<td>17.40</td>
<td>17.35</td>
<td>19.90</td>
<td>18.80</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>21.25</td>
<td>12.40</td>
<td>10.20</td>
<td>9.70</td>
<td>13.38</td>
<td>5.37</td>
</tr>
<tr>
<td>arc spray AlMg5</td>
<td>before</td>
<td>5.30</td>
<td>8.55</td>
<td>6.90</td>
<td>7.10</td>
<td>7.00</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>8.40</td>
<td>5.40</td>
<td>4.70</td>
<td>4.70</td>
<td>5.80</td>
<td>1.76</td>
</tr>
<tr>
<td>high-build epoxy</td>
<td>nominal value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.9</td>
<td></td>
</tr>
</tbody>
</table>
This test was carried out on the steel panels with a metallic coating only. No organic sealer or paint was applied since this was not expected to influence the flexibility of the system. In fact, the presence of a, perhaps more flexible, organic coating would make the observation of cracks in the thermal spray layer impossible.

The panels that were aged in seawater before the test, generally displayed a lower bending value at cracking of the coating. It should be stated that this is partially explained by the method of evaluation, since the aged coating was considerably darker than the original coating. This increased the contrast between the cracks and the coating and made the observation of small cracks more easy. The decreased flexibility after exposure is still significant. A quantitative value for this decrease however cannot be taken from these results.

Cross-section analysis showed that all cracks at the end of the experiment went through to the steel substrate. The Al99.7 generally showed a large number of narrow, small cracks whereas the AlMg5 coating displayed less, but considerably wider cracks, as illustrated in Figure 13 and Figure 14.

![Figure 13: Al99.7 after bending test. magnification approx. 50x](image)

![Figure 14: AlMg5 after bending test. magnification approx. 50x](image)

Based on these results it can be concluded that the flexibility values of the aluminium based spray coatings are either comparable or higher than standard high build epoxy coatings. It should be noted that much higher values can be obtained by using special flexible polyurethane based paints.

Adhesion
Coating adhesion was determined using the ISO 4624 “dolly pull-off” test as explained in section 2.3.1.

The adhesion strength was determined from the load value at rupture of the dolly. The adhesion strength of the adhesive used to attach the dolly to the coating was about 16 N/mm², limiting this technique to that value. Apart form the value of the adhesion strength also the place of rupture was noted.

Table 4 lists the results of this investigation. The measurements were duplicated four times.

The suppliers data sheet for the Al 99.7 lists a nominal adhesion strength of 9.1 N/mm² which is easily met on our samples. The place of rupture for this coating lies partly on the dolly/adhesive interface, which indicates an even greater adhesion value for the coating than could be measured using this test arrangement.
Table 4: Results of ISO 4624 Dolly pull-off adhesion test: adhesion strength in N/mm and location of rupture (d = dolly, a = adhesive, Al = coating, St = steel)

<table>
<thead>
<tr>
<th>immersion</th>
<th>meas. 1 (mm)</th>
<th>meas. 2 (mm)</th>
<th>meas. 3 (mm)</th>
<th>meas. 4 (mm)</th>
<th>avg. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>flame spray</td>
<td>before 16 d/a 16 d/a 14 d/a/Al 20% 16 d/a/Al 5% &gt;16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al 99.7</td>
<td>after 12 a/Al 80% 13 a/Al 80% 14 a/Al 90% 16 a/Al 90% &gt;16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>arc spray</td>
<td>before 16 St 11 St 10 St 15 St 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlMg5</td>
<td>after 12 Al/St 2% 12 St 13 St 10 Al/St 5% 12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A completely independent adhesion test carried out as a routine check by the thermal spraying company that applied the AlMg5 coating yielded an average adhesion strength of 15.7 N/mm. This value lies within the range of the listed test results.

No significant effect on the coating adhesion could be detected after 3000 hours immersion in natural seawater.

For comparison, typical adhesion strength of typical heavy-duty organic anti corrosion paints range from 6 to 14 N/mm. This leads to the conclusion that the adhesion of Al based thermal spray coatings is either comparable or better than traditional organic coatings.

![Pendulum surface toughness measurement arrangement](image)

Figure 15: Pendulum surface toughness measurement arrangement.
Toughness
The relative surface toughness of the thermal spray coatings was determined using two techniques typically used for surface toughness measurements on organic paints. The selected methods were the pendulum method and the NEN 5350 pencil-hardness test. Both are qualitative tests by definition but even so the results should be treated very carefully since the surface roughness of the sprayed coatings will influence the measured values.

The pencil hardness measurement according to NEN 5350 uses 17 normalised pencils ranging from hardness 6B to 9H. The outcome of the experiment is defined as the toughest pencil that does not leave a permanent mark when pressed at an angle of 45° and with a pressure of 750 grams onto the coating surface.

The pendulum hardness test, as schematically represented in Figure 15 determines the amount of damping of the pendulum motion, i.e. the dissipated energy in the coating due to deformation. Two metal spheres support the frame of the pendulum and press on the coated surface. The time in seconds required to stop the pendulum motion when a specific amplitude has been applied is a measure of the damping toughness. A soft coating will generally damp the motion more which will result in a low surface toughness value.

The results of the surface toughness tests are listed in Table 5. The pendulum tests were duplicated three times.

<table>
<thead>
<tr>
<th></th>
<th>immersion</th>
<th>pencil test</th>
<th>pendulum test (s)</th>
<th>avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>flame spray Al</td>
<td>before</td>
<td>3-4H</td>
<td>5.6</td>
<td>16.8</td>
</tr>
<tr>
<td>99.7</td>
<td>after</td>
<td>5-6H</td>
<td>89.6</td>
<td>88.2</td>
</tr>
<tr>
<td>arc spray AlMg5</td>
<td>before</td>
<td>&gt;9H</td>
<td>147.0</td>
<td>142.8</td>
</tr>
<tr>
<td></td>
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<td>organic heavy-duty anti corrosion coating (nominal value)</td>
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The surface roughness of the thermal spray coatings has a large influence on the results. The arc spray coating is relatively more smooth than the flame spray coating, resulting in a much higher pendulum surface toughness. Also, the results indicate an increase in coating toughness after 3000 hours of immersion. This may well be explained by the relative "flattening" of the surface due to corrosion of roughness peaks during the exposure.

Nonetheless, the comparison with nominal values for organic systems shows clearly that an Al based thermal spray coating will exhibit a significantly tougher outer surface. The measured values however, should not be used in a quantitative analysis.

Bio-Fouling Effects
From the apparent roughness of the metal coating and the non-toxicity of aluminium, the system would appear the ideal surface for growing and sustaining fouling organisms. For this reason
barnacles were grown on the coated metal surface. These species have been reported to
damage conventional coatings.

![Figure 16: Juvenile barnacle of “Balanus amphirite”](image1)

Barnacles reproduce by spawning larvae, as shown in Figure 16, which attach themselves after
an initial exploration phase to a suitable surface. After attachment the larvae metamorphose into
barnacles. In the TNO laboratories in Den Helder, the barnacle *Balanus amphirite* is reared for
anti-fouling experiments.

During the laboratory experiments, the larvae were added to vessels containing the steel panel
with the aluminium sprayed coating. Immediately after adding the larvae, they displayed distorted
behaviour. Most larvae sank to the bottom of the container, making weak movements with legs
and antenna.

![Figure 17: A89.7 coated steel panel after three months in natural seawater in the Den Helder Harbour](image2)

(he area around the fixture was coated with an
organic paint system.)

![Figure 18: Detail of barnacle shell edge cross-section on Al-based spray coating (magnification approx. 100 x)](image3)
It is proposed that this behaviour was induced by the high electrochemical activity of the aluminium panels directly after immersion, caused by galvanic effects between pores and the aluminium metal. It has been reported before that electrochemical activity can limit the development of fouling. [26] However, after this initial period which lasted for several hours, the larvae recovered and displayed their normal settlement behaviour.

After settlement and the metamorphosis, the juvenile barnacles developed normally indicating no detrimental effect resulting from the aluminium spray coating. Two months after the start of the experiment, 80-90% of the panel was covered with healthy barnacles.

Parallel to the laboratories studies a set of coated panels was exposed in the Den Helder harbour at a depth of 1 metre.

Examination of the panels after three months, revealed that the surfaces were covered for 70 to 95% with healthy barnacles as shown in Figure 17.

After 23 months the grown barnacles were removed and the coating was examined. A cross-sections of the coating directly underneath a barnacle is shown in Figure 18. This figure shows the thermally sprayed coating as the silver/grey layer on the steel substrate (black). The light coloured region perpendicular to the plane of the coating is a section of the barnacle’s shell. The figure shows no penetration of the shell into the thermally sprayed coating. Therefore, no significant damage of the aluminium coating or resulting loss of corrosion protection by barnacle fouling is expected.
4.1.2 Intact Coatings

Summary

The results in this section describe the electrochemical behaviour of various aluminium based thermally sprayed coatings in the as-sprayed condition. It is shown that the corrosion rate of the thermally sprayed layer decreases during the initial period of exposure to a corrosive environment. The rate at which the decrease takes place depends on the conditions during exposure. This effect is most probably the result of the blocking of pores in the thermally sprayed coating by insoluble corrosion products of the aluminium coating. The rate and effectiveness of this mechanism depends on the type of exposure. Based on the corrosion potential it takes about 100 hours to block the majority of pores during immersion in seawater. Immersion in fresh water requires about 100 days to reach the same stage. The corrosion resistance was found to increase after this period. The estimated decrease in corrosion rate after 1000 hours of immersion in seawater is about one order of magnitude compared to the initial value. The pore blocking mechanism is sensitive to water flow across the aluminium surface. It was shown that an increased water flow can re-activate pores; removal of the water flow reverses this effect.

Results

The overall behaviour and stability of the aluminium panels in natural waters was determined by immersion experiments. Freshly coated panels were fitted with an electrical connection and immersed in natural seawater and a fresh water formulation, known as “Dutch Standard Water”. The composition of 1 litre DSW is 228 mg CaCl2·2H2O, 180 mg MgSO4·7H2O, 100 mg NaHCO3, 20 mg KHCO3, dissolved in 1 litre of deionised water.

The natural seawater was taken from the Den Helder Harbour. The chloride content of this water is 16 g/l and the total salinity is approx. 27 g/kg. The seawater was continuously refreshed during the experiment at a rate of 0.5 litres per hour. The fresh water was not refreshed, but to minimise depletion effects, the solution was actively aerated. The volume of the immersion basins was approx. 10 litres. The potentials were measured according to the technique described in section 2.6.1 using a HP 3852A data acquisition system. The samples were exposed in the “as sprayed condition”. The total surface area of the samples was approx. 1 cm².

During 100 days of immersion the overall appearance and the electrode potential of the aluminium coatings were determined. The result of the corrosion potential monitoring during exposure is shown in Figure 19 and Figure 20.

![Figure 19: Corrosion potential during immersion in natural seawater for aluminium based thermally sprayed coatings on steel (coating thickness approx. 150 μm).](image)

![Figure 20: Corrosion potential during immersion in fresh water (Dutch Standard Water) for aluminium based thermally sprayed coatings on steel (coating thickness approx. 150 μm).](image)
The figures show that for the sample immersed in seawater, after an initial period of about 4 to 10 days, the potential stabilises at values around $-950$ to $-1050$ V vs Ag/AgCl. The samples in fresh water apparently need up to 100 days to reach a similar stable value of $-900$ to $-1000$ mV vs Ag/AgCl. Significant differences in corrosion potential exist only in the initial period. These are most probably due to activation by exposure of the steel substrate. The subsequent stabilisation is expected to be the result of blocking of the pores by insoluble corrosion products. The effect of blocking of pores and the result on the electrochemical behaviour will be further discussed.

Figure 21 to Figure 24 give an impression of the change in appearance over the immersion period. As can be seen in these figures no ferrous corrosion products are visible after 6 months of exposure. The thermally sprayed coatings show a change of colour and localised formation of insoluble oxide deposits. These deposits are expected to cause the blocking of the pores as predicted from the potential behaviour.

![Flame sprayed AlMg5 after 2 days of exposure in natural seawater.](image1)

![Flame sprayed AlMg5 after 6 months of exposure in natural seawater.](image2)

Although the results of the corrosion potential monitoring experiment suggest similar corrosion behaviour in the fresh water electrolyte, the polarisation curves reveal significant differences.

The quasi-static polarisation technique is often regarded as perhaps the most valuable tool available for the characterisation of electrochemical processes. For thermally sprayed coatings, this technique has proved useful for the porosity estimation, general corrosion rate etc., but especially for the investigation of passivating properties. [35-40].

The polarisation curves in this section were measured using the technique described in section 2.6.2 using a Solartron 1286 electrochemical interface and self developed software. The area of the working electrode was 1 cm$^2$ and the potential scanning rate (unless stated otherwise) was 10 mV/s. The scan range was from $-1.4$ V to $-250$ mV (vs. Ag/AgCl) in natural seawater and $-1.2$ V to 0 V (vs. Ag/AgCl) in the fresh water solution.
Since the scan rate is relatively high, the curves should not be regarded as representations of real stationary states, but can be used as quantitative indications of the general electrochemical behaviour.

Considering the differences observed in Figure 25 and Figure 26 between the various spray coatings and application techniques, one should be aware that the surface roughness of the various coatings differs considerably. Since the measurement values have not been normalised for the true surface area of the coating (since this is virtually impossible as argued in section 2.6)
the observed differences in current magnitude are expected to be mainly the result of roughness differences.

The difference in behaviour between the two electrolytes does represent a true difference in corrosion behaviour. Although the corrosion potentials of the coatings are similar in seawater and fresh water, the corresponding dissolution rates differ considerably. From these graphs can be estimated that the corrosion rate of the aluminium based thermally sprayed coatings in seawater exceeds the rate in fresh water by almost one order of magnitude.

However, it should be noted that these graphs only represent the behaviour of relatively "new" coatings. As was seen in the "corrosion potential versus exposure time" graphs in Figure 19 and Figure 20, the corrosion behaviour of the thermally sprayed coating can be divided into an initial period in which the activity of the coating rapidly decreases and a stationary region with more or less constant corrosion potential. The polarisation curves in Figure 25 and Figure 26 were measured in the initial period and are therefore expected to display relatively high current density values.

The influence of an extended exposure on the electrochemical behaviour of the aluminium based thermally sprayed coatings is illustrated in Figure 27. This figure shows the change after 1000 hours of exposure in constantly refreshed natural seawater of flame sprayed Al99.7 coating on steel.

![Figure 27: Polarisation curves of thermally sprayed aluminium on steel from different exposures (area 1 cm², thickness approx. 150 μm, scan rate 1 mV/s).](image)

The graph shows a decrease of almost 100 times compared to the current density of a freshly applied coating. As stated before, this behaviour is attributed to the blocking of pores in the thermally sprayed coating, effectively sealing the steel substrate from the electrolyte. Initially, the freshly applied thermally sprayed coating is expected to contain a large number of open pores, connecting the steel substrate to the electrolyte. The resulting galvanic effect will cause the adjacent aluminium coating to corrode more rapidly, resulting in the localised development of aluminium oxides. Since these aluminium oxides are poorly soluble in ambient water, they will settle in the pores, subsequently blocking the connection of the steel to the electrolyte. Ultimately, this will prevent the flow of ions to the steel substrate, eliminating the driving force for the galvanic corrosion.

Further evidence of this behaviour can be obtained by a surface scan of the corrosion potential using the Kelvin probe. The Kelvin probe technique enables the detection of corrosion potentials...
under atmospheric conditions without immersion in an electrolyte. This means that a sample, after being exposed or "aged" in a specific aqueous environment, can be leisurely investigated without the risk of changing the surface properties during the measurement. For this measurement a commercially available Kelvin probe from UBM was used.

Figure 28: Corrosion potential map using Kelvin probe of freshly applied thermally sprayed Al 99.7 coating on steel (thickness approx. 150 μm).

Figure 29: Surface roughness map using Kelvin probe of freshly applied thermally sprayed Al99.7 coating on steel (thickness approx. 150 μm).

Figure 28 shows the potential distribution over 4 mm by 4 mm of a newly applied Al 99.7 coating. Figure 29 shows the surface roughness profile of the same area of coating.

This coating has not been exposed to anything other than air at a relative humidity of 50% at room temperature. It is expected that any present pores are still open to expose the underlying steel substrate.

During the Kelvin probe experiment, the sample is placed in an atmosphere with an increased relative humidity (approx. 90%). Therefore, a water film is expected to be present on the sample to enable the detection of corrosion potentials. It should be noted that, although the measured potential is directly related to the corrosion potential, the values of the potentials listed in the figures differ considerably from the real corrosion potential values measured in immersion. Therefore the results of Kelvin probe measurements presented at this stage can only be used for relative qualitative analysis.

Figure 28 shows that the measured potential distribution varies over a range of almost 350 mV, corresponding with the corrosion potential difference between aluminium and steel. Also, the regions showing high potential values correspond with local low layer thickness as shown in Figure 29, i.e. the places where through porosity to the steel can be expected.
An identical sample that has been immersed in stationary seawater for over 4000 hours was also investigated using the Kelvin probe. Figure 30 shows the resulting potential distribution. Localised potential differences have decreased to no more than 150 mV. This indicates a significant decrease in electrochemical activity and a complete absence of open pores to the steel substrate.

A clearer illustration of the time scale, in which the blocking of pores occurs in natural waters, can in principle be obtained by a series of polarisation experiments during an extended immersion period of the sample. However, since standard polarisation measurements (as in Figure 25) considerably affect the ongoing corrosion processes, even at high scan rates, this technique was considered less suitable. Therefore the following experiment was used: To minimise the effect of the measurement on the corrosion behaviour, a region of 10 mV around the corrosion potential was scanned using a scan rate of 5 mV per second. This method minimises the duration of the polarisation and thus the amount of transferred charge.

These measurements were performed using the technique described in section 2.6.3 using a Solartron electrochemical interface and self developed software. The area of the working electrode was 1 cm. The samples were measured in the “as sprayed” condition.

The resulting current versus potential relationship was analysed using a linear least squares fit, based on which the slope of the relationship was calculated. Since this slope reflects the current increase per unit of polarisation at the corrosion potential, it can be used as a measure of the polarisation resistance of the coated sample.

For these experiments, both the flame and arc spraying techniques were used with Al99.7 and AlMg5 as coating material. It should be noted that all measurements (within one coating system) were made on the same sample. This means that, although the measurement was designed to minimise the effect on the data, values at longer exposures may be affected. For this reason the measurements were terminated after 800 hours.

Figure 31 illustrates the expected behaviour of the thermally sprayed coatings. The initial phase in which the corrosion rate is relatively high and the defects and pores in the thermally sprayed coating are being blocked, is followed by a second phase in which the substrate is effectively sealed from the electrolyte.

Figure 19 reveals that after about 100 to 300 hours after immersion the corrosion potential remains constant. The polarisation resistance in Figure 31 however, still increases at this point. In fact, closer inspection of the potential and polarisation resistance curves in Figure 33 reveals that the polarisation resistance starts to increase after the corrosion potential has reached the stable value around –1000 mV vs Ag/AgCl. A possible explanation for this behaviour is the
continued development of a (passivating) oxide film during exposure, which further limits the rate of the electrode reactions on the surface of the coating.

**Figure 31:** Polarisation resistance as a function of immersion time in natural seawater for various aluminium based thermally sprayed coatings on steel (thickness approx. 150 µm).

**Figure 32:** Polarisation resistance as a function of immersion time in fresh water for various aluminium based thermally sprayed coatings on steel (thickness approx. 150 µm).

**Figure 33:** Polarisation resistance and corrosion potential of flame sprayed AlMg5 on steel as a function of immersion time in natural seawater (thickness approx. 150 µm).
The behaviour of the samples that were immersed in fresh water does not show a clear distinction between an initial and a stable phase. Considering the slow decrease of the corrosion potential in Figure 20, this is no surprise. The low corrosion rates in the fresh water system not only cause a beneficial delay of uniform attack of the aluminium coating, but consequently also delays the blocking of pores in the coating. Fortunately, because the uniform corrosion rate remains at such low values, the presence of pores in the coating is no cause for alarm.

Judging from the results in the potential monitoring graphs (Figure 20) eventually also in fresh water systems a blocking of pores in the coating will occur. The immersion time after which this can be expected will not be around 100 hours as seen in seawater immersion, but rather around 100 days.

Since thermally sprayed aluminium based coatings are not only used in immersion, but also for atmospheric protection, it was decided to also investigate the behaviour in these circumstances. Although an aluminium spray coating exposed in the atmosphere will probably not be wet 100% of the time, the cyclic weathering conditions may well have an increased detrimental effect on the protection mechanism.

The following figures show the results of polarisation measurements on samples that had been exposed for 3 and 6 months to a severe marine atmospheric environment at the Harssens peninsula in Den Helder (The Netherlands).

![Figure 34: Polarisation curve of arc sprayed Al99.7 as a function of atmospheric exposure time (area 1 cm², thickness approx. 150 µm, scan rate 10 mV/s).](image1)

![Figure 35: Polarisation curve of flame sprayed Al99.7 as a function of atmospheric exposure time (area 1 cm², thickness approx. 150 µm, scan rate 10 mV/s).](image2)

Both Figure 34 and Figure 35 do not show a significant decrease of the anodic current density in the passive region after 3 months of exposure. This would indicate that no further improvement of the corrosion protection properties was achieved after the second period of three months. Following the mechanisms described before, this would mean that all through pores are blocked within the first three months of atmospheric exposure at this site.

The shift of the corrosion potential in positive direction as observed in Figure 34 cannot be explained. But it should be noted that the used experiment is not well suited for the accurate determination of the value of the corrosion potential.
In general it can be concluded that the initial stage in which the micro pores in the thermally sprayed coating are blocked is completed after three months of exposure. However, this time period should be used carefully since it can be expected that the relative atmospheric (weather) conditions during this period also play an important role.

The effect of external conditions on the sealing of the micro pores in a thermally sprayed aluminium coating can be illustrated by the following experiment. In this experiment a variable laminar water flow was applied to the aluminium surface. Although the reported aluminium oxides are poorly soluble in water, a sufficiently high flow rate may influence the settlement of the oxides.

Figure 36 shows the behaviour of the corrosion potential of a steel panel coated with a 200 μm Al 99.7 flame spray coating. The grey line in this graph indicates the behaviour of the panel in stationary (but constantly refreshed) natural seawater, showing a stable potential around −1000 mV versus Ag/AgCl. The black line shows the effect of the water flow rate.

![Figure 36: Corrosion potential of thermally sprayed Al 99.7 coating (thickness approx. 150 μm) during exposure to stationary and rapid laminar flow of seawater.](image)

The graph indicates that around the time that the stationary exposed sample reaches the stable potential (around 100 hours), the sample exposed to the high flow rate (0.5 m/s) starts to show signs of activation. The potential rises to values around the corrosion potential of carbon steel in seawater but occasionally drops to levels corresponding to aluminium. The jumps to higher potential become gradually more resilient and after 150 hours the potential is almost stable at the high level.

Decreasing the flow to a relatively low rate (0.1 m/s) results in the reverse behaviour. The potential starts to drop and after some rapid fluctuations, settles at the same value as the sample exposed in stationary seawater.

This behaviour is completely in accordance with the mechanism of pore plugging by corrosion products and indicates the risk of using thermally sprayed aluminium coatings at high water flow rates.
4.1.3 Coatings With a Defect

Summary

The results in this section describe the behaviour of various aluminium based thermally sprayed coatings in seawater when a relatively large part of the steel substrate is exposed (steel to aluminium ratio about 1 to 100). It is shown that after an initial period of which the length depends on the coating age and type, the steel surface becomes blocked by calcareous deposits. These deposits effectively shield the steel surface from the electrolyte, thus limiting the galvanic current to less than half the original magnitude. The resulting service life of damaged thermally sprayed aluminium is consequently significantly increased. The results also indicate that this mechanism will not be effective when the aluminium is over-coated with an organic paint.

Results

Perhaps the most important property of corrosion protection by thermally sprayed aluminium is its power to galvanically protect the steel substrate at defects in the coating. The coating acts as sacrificial anode and a scratch or pinhole that exposes the steel substrate is the localised cathode.

To investigate this property, defects were introduced in an aluminium coated steel panel by drilling a shallow hole, using a flat-headed cutter. The hole was drilled through the aluminium coating onto the steel substrate surface. The diameter of the circular defects was 6 mm, resulting in a surface area of about 0.28 cm². The size of the panels is 50 x 75 mm resulting in a 1 to about 131 steel to aluminium surface ratio. This calculation is on the conservative side since no correction for the surface roughness of the aluminium coating was used.

![Figure 37: Appearance of FS Al 99.7 coated steel panel with a defect onto the steel surface after 2 months of immersion in natural seawater.](image1)

![Figure 38: As Figure 37 but for FS AlMg5 coating.](image2)

![Figure 39: As Figure 37 but for AS Al99.7 coating.](image3)

The aluminium panels used in this experiment had already been immersed in natural seawater for over 3000 hours. This is an important fact since it was shown in the previous section that the aluminium coatings go through at least two stages during immersion. The initial stage of high
electrochemical activity would be ideal from a cathodic protection point of view. The latter, more passive stage, far less so.

Figure 37 to Figure 39 show the surface of three types of aluminium sprayed panels with a defect onto the steel substrate after 2 months of immersion in natural seawater.

Despite the fact that these panels had already been exposed in seawater before the defect was introduced, very little evidence of attack of the exposed steel surface areas was found. Apart from some superficial rusting, the defect areas remain effectively protected by the adjacent aluminium coating material.

During the immersion of the panels also the corrosion potential was monitored using an Ag/AgCl reference electrode and a HP 3852A automatic data acquisition system.

The typical behaviour of the corrosion potential of the aluminium panel with defect is shown in Figure 40.

![Figure 40: Corrosion potential of aluminium thermally sprayed coating with a defect onto the steel substrate in natural seawater (coating thickness approx. 150 μm, aluminium to steel ratio is 131 to 1)](image)

Comparing Figure 40 to the corrosion potential behaviour of the intact coatings as previously discussed in section 4.2.2 (recollected in Figure 41) shows remarkably few differences. Apart from a shift of the corrosion potential of about 100 mV in the positive direction, the stable values could be mistaken for the corrosion potential of an intact aluminium coated panel. Even the behaviour in the first 10 to 20 hours is, apart from the duration of the period, similar to the initial stage of behaviour for a freshly exposed intact coating. Starting at a high potential, caused by the mixed potential of a steel and aluminium surface, the potential drops to a low value corresponding to the corrosion potential of passive aluminium.

For an intact coating, this behaviour was explained by the blocking of the micro pores in the coating by insoluble corrosion products.

A similar blocking of the steel surface in the artificial defect by corrosion products however, appears highly unlikely. The most probable anodic reaction at the exposed steel surface would be the dissolution of iron. And the amount of ferrous oxide compounds visible on the panels in Figure 37 to Figure 39 would not appear to be of the required quantity and nature to have a significant effect on the resulting corrosion potential.
Closer analysis of the defect area in the exposed panels shows a deposit of a different kind. A SEM study showed the presence of calcareous deposits, mainly consisting of calcium and magnesium (Figure 42). The morphology of the substances showed many variations, among which a very dense and tightly adherent scale as shown in Figure 43.

![Figure 42: Typical morphology of the calcareous deposits formed at the surface of the exposed steel (magnification approx. 650 x).](image1)

![Figure 43: Detail of Figure 42 (magnification approx. 6500 x).](image2)

These deposits show great similarity to the calcareous deposits found on cathodically protected surfaces using impressed current in waters with a high carbonate content (as seawater). It has been reported that the local pH increase, caused by the reduction of oxygen at cathode areas, induces the precipitation of calcium and magnesium carbonates onto the cathode surface [41].

Provided that the current density would not be too high, these precipitates are sufficiently dense and resilient to effectively block the cathode and drastically slow down the corrosion reaction that consumes the anode.

Since the aluminium coating takes the place of the anode material in case of a defect on a thermally sprayed panel, this mechanism will significantly increase the service life of the coating in marine environment.

The effectiveness of this highly important self-repair mechanism was further investigated using an amperometric arrangement. To enable a measurement of the galvanic protection current between the exposed steel area and the aluminium coating, the two had to be separated. This was performed by using the technique as described in section 2.6.4, in which both the bare steel and the aluminium coating surface are immersed in seawater in a specially designed cell (section 2.6.4 Figure 9). The galvanic current that emerges when the two metals are connected is measured using a zero resistance ammeter.

For these experiments, the steel surface area remains 0.28 cm² and the aluminium area is about 100 times larger. This ratio is rather arbitrarily selected, however in practical application it can be expected that the damaged coating area remains a small fraction of the intact coating area.

During the experiment the seawater is continuously refreshed to prevent any effects originating from concentration variations. Especially oxygen depletion by the corrosion reactions in the relatively small cell (about 25 cm²) must be prevented since this will severely affect the resulting currents.

The result of this experiment is shown in Figure 44. This figure shows both the galvanic current flowing from the aluminium to the steel and the resulting corrosion potential in the cell.
Figure 44: Corrosion potential and galvanic current between thermally sprayed Al99.7 and uncoated steel in seawater (coating thickness approx. 150 mm).

Figure 44 shows that until about 80 hours the aluminium panel remains active and the steel panel is protected with a current that reaches up to 9 μA. Then the current drops to a stationary level of less than 4 μA which can be converted using Faraday's law to a general corrosion rate of the aluminium surface of less than 6 μm per year.

Figure 45: Corrosion potential and galvanic current between sealed thermally sprayed Al99.7 and uncoated steel in seawater (coating thickness approx. 150 mm).

Figure 46: Appearance of the steel surface after 400 hours of exposure in seawater when coupled to thermally sprayed Al99.7.

Figure 47: same as Figure 46, after removal of deposits and adhesive film.
The steel area at the end of the 400 hours of immersion is shown in Figure 46. This figure shows the calcareous deposits formed at the cathode surface. It is also evident that no ferrous corrosion products can be seen. Further evidence of the fact that the steel surface has remained completely intact during the experiment is shown in Figure 45 where the deposits were removed.

For many applications the use of an additional organic sealer is recommended by the manufacturers of thermally sprayed coatings. It is claimed that the use of a sealer will not only give a more pleasing outward appearance of the corrosion protection system, but will also considerably improve the corrosion resistance. [28].

The effect of an organic coating on the galvanic protection properties is clearly visible in Figure 45. For this figure the previous experiment was repeated by using a fresh sample which was coated with an organic coating, recommended for use on thermally sprayed substrates, on top of the thermally sprayed aluminium coating. It can be expected that since the top coating will obstruct the flow of electrical current (ions) from the anode through the electrolyte to the cathode, adequate galvanic protection will not be possible. Only when the organic coating has deteriorated enough to permit the permeation of water through the organic coating the galvanic protection mechanism can become active.

A visual impression of the effect of an organic coating on the thermally sprayed aluminium is provided in Figure 48. Figure 49 shows the amount of attack on the steel surface, after just 400 hours of immersion in seawater.

![Figure 48: Appearance of the steel surface after 400 hours of exposure in seawater when coupled to thermally sprayed Al 99.7 covered with an organic coating.](image1)

![Figure 49: same as Figure 48, after removal of deposits and adhesive film.](image2)

It should be noted that in a practical situation both the defect and the aluminium spray coating would be on the same substrate. This means that, directly adjacent to the defect, some small area of unsealed spray coating may be present. It can be expected that this area of aluminium will provide a limited amount of protection (and will rapidly corrode), but even so, the use of an
organic coating on top of a thermally sprayed layer can be expected to significantly hinder the galvanic protection mechanism.
4.4 Conclusions

The results of the basic characterisation described in this chapter shows that the mechanical properties of aluminium sprayed coatings are, generally speaking, superior to the properties of common anti-corrosion paints.

Flexibility measurements showed the development of cracks onto the steel substrate. However, as the results described in section 4.3.3 indicate, the risk of corrosion of the steel substrate will remain minimal. The formation of cracks will only occur at the very limit of the bending load for these systems. The magnitude of this maximum load is comparable to the values normally associated with high build organic coatings. An important fact regarding the mechanical properties of the Al based thermally sprayed coatings is that no significant changes could be measured after 3000 hours of immersion in natural seawater.

The amount of fouling after outdoor immersion exposure in seawater on the coated panels was relatively large. An anti-fouling coating for situations where fouling would be undesirable is therefore necessary. On the other hand, the abundance of biological activity also suggests no harmful effect of the coatings on the environment. The corrosion protection properties of the spray coatings did not suffer from damage by fouling organisms after 23 months of exposure.

The electrochemical characterisation of the coatings in the as-sprayed condition ("intact coatings") show that the corrosion rate of the thermally sprayed layer decreases during the initial period of exposure to a corrosive environment. The rate at which the decrease takes place depends on the type of exposure. This effect is most probably the result of the blocking of pores in the thermally sprayed coating by insoluble corrosion products of the aluminium coating. The rate and effectiveness of this mechanism depends on the type of exposure. Based on the corrosion potential it takes about 100 hours to block the majority of pores during immersion in seawater. Immersion in fresh water requires about 100 days to reach the same stage. The corrosion resistance was found to increase after this period. The estimated decrease in corrosion rate after 1000 hours of immersion in seawater is about one order of magnitude compared to the initial value. The pore blocking mechanism is sensitive to water flow across the aluminium surface. It was shown that an increased water flow can re-activate pores; removal of the water flow reverses this effect.

With respect to the behaviour of the aluminium based thermally sprayed coatings with a relatively large defect onto the steel substrate the following can be concluded. It is shown that after an initial period of which the length depends on the coating age and type, the defect surface becomes blocked by calcareous deposits. These deposits effectively shield the steel surface from the electrolyte, thus limiting the galvanic current to less than half the original magnitude. The resulting service life of a damaged thermally sprayed aluminium coating is consequently significantly increased. The results also indicate that this mechanism will not be effective when the aluminium is over-coated with an organic paint.

Finally, the investigation described in this chapter shows that the wide range of available electrochemical techniques enables the assessment of practically any relevant corrosion protection property of thermally sprayed coatings. Both traditional techniques as potential monitoring or the measurement of polarisation curves as well as the recently developed localised techniques as Kelvin probe measurements can provide direct information on the mechanisms of corrosion protection processes. These qualities makes an electrochemical investigation the most important quality assessment of any corrosion protection system.
4.3 References

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5 Conclusions and Future Research

The purpose of this section is twofold: first to provide a brief overview of the most important conclusions from this thesis and second to summarise the opportunities for future work as they were recognised during the research described in this thesis.

The purpose of this thesis, as stated in the preface, was to demonstrate the usefulness of electrochemical measurements for the characterisation of the corrosion properties of thermally sprayed coatings. And although not all encountered phenomena could be addressed adequately, the usefulness of electrochemical methods was clearly demonstrated. Based on the experience obtained from the research for this thesis, it can be stated that electrochemical measurement techniques are essential not only for the characterisation and development of thermally sprayed corrosion resistant coatings, but also for the qualification of these coatings. The development of dedicated electrochemical methods and techniques, specifically for thermally sprayed coatings would therefore be a logical development.

The results described in section 3.4 showed a possible way to simplify the interpretation of the results of an electrochemical measurement, and also illustrated the way the results of the measurement can be fed back to the application parameters of the thermal spraying operation.

Novel dedicated techniques should be developed according to the general requirements for qualification tests as listed in section 2.7. From this list possibly the demand for non-destructive testing may well prove the most difficult obstacle for the development of a reliable, easy to use qualification tool for thermally sprayed coatings to be used in-situ.

Apart from these considerations regarding the usefulness of electrochemical measurements, also a number of other important aspects have emerged with respect to the behaviour of the various thermally sprayed materials used in this thesis.

The thermally sprayed coating based on titanium feedstock material, as described in section 3.3.1 proved far too porous when applied using the conventional method of arc spraying. The reason for this was that the semi-molten titanium particles reacted rapidly with the surrounding atmosphere during the spraying application.

However, a relatively simple modification of the spray process (the exchange of the compressed air propellant by argon) resulted in a decrease of the general porosity of the coating of more than 70%. Unfortunately, this did not prove to be sufficient yet to achieve acceptable electrochemical behaviour. But it does suggest that optimisation of the application procedure, especially regarding the use of inert gas propellants and shrouding of the particle stream during application, may well lead to further improvement of the corrosion properties of the resulting coating.

A similar conclusion may be drawn from the behaviour of the stainless steel material described in section 3.3.2. Also this feedstock material resulted in thermally sprayed coatings with significantly improved corrosion properties when argon was used instead of compressed air propellant. The reason why the argon sprayed coating did not show an acceptable corrosion behaviour yet was caused by their level of porosity. The spraying of stainless steel material using argon was not yet sufficiently developed to keep the resulting porosity within acceptable limits. More experience with this specific application, and perhaps modifications to the spray gun to facilitate better shrouding, are expected to result in much improved coatings.

The HVOF coatings that were applied using AISI 316 feedstock material presented a different problem. Although the total amount of oxidation and their porosity was relatively low, they proved susceptible to preferential attack along the splat boundaries. Further research into the
mechanism that causes this attack may lead to possible ways to prevent this from happening. Perhaps the addition of alloying elements or modification of the application parameters could lead to improvement. Better knowledge of the failure mechanism should also indicate in which electrolytes this mechanism is active. It was shown that the rate of the attack depended on the concentration of the H\textsubscript{2}SO\textsubscript{4} electrolyte. Therefore, the coating may show completely acceptable corrosion behaviour in a different electrolyte.

One successful way to drastically improve the corrosion behaviour of the AISI 316 based thermally sprayed coating was to apply a heat treatment to the as-sprayed coating as demonstrated in section 3.3.2. The resulting electrochemical behaviour was almost identical to the behaviour of the clad layer that was used as reference. However, the use of heat treatment for large thermally sprayed structures will be difficult to realise. Perhaps the use of laser heating methods or localised induction heating would be possible. Nonetheless, it should be stated that the development of a reliable heat treatment method to be used in-situ on large coated structures would drastically increase the opportunities of the thermal spraying application technique.

The Monel400 thermally sprayed coatings proved to perform very successfully, even in simulated industrial conditions. In saturated NaCl at 80\degree C the thermally sprayed layer performed equally well as the Monel400 clad material. For this reason, it was concluded that Monel 400 should be considered a feasible alternative for the clad material, and can be used as a repair coating for damaged cladded layers.

Regarding the aluminium based thermally sprayed coatings discussed in chapter 4, it was concluded that these coatings perform extremely well in both seawater and fresh water. Based on the results it is expected that these thermally sprayed coatings will perform very satisfactorily in many practical applications, and should be considered a serious alternative for heavy-duty organic coating systems. It might even be stated that these coatings will provide a longer lasting and more reliable corrosion protection for many situations than is possible by using organic coatings.

The protection is based on the following four mechanisms: passivation of the aluminium, plugging of pores in the coatings, galvanic protection of any exposed steel and the formation of cathodic deposits. Any further development of this type of galvanically protecting thermally sprayed coatings should be directed to the optimisation of these mechanisms. Also qualification of the corrosion protection quality of such coatings should be aimed at the determination of the effectiveness of these mechanisms. Electrochemical measurement methods will be most suited for this task.

A further interesting observation made in section 4.2.1 concerned the behaviour of fouling organisms in the presence of freshly sprayed aluminium. The organisms refused to settle on the substrate but they did not suffer any physical damage. This would be the behaviour of an ideal anti fouling substance: to repel settlement without toxicity. Unfortunately, the effect lasted not much longer than a few hours. The effect was suspected to be caused by the high electrochemical activity on the freshly sprayed aluminium surface. Better understanding of this effect might be used to extend the period of activity, or it might be possible to periodically reactivate the coating, to remove any present fouling. Since the development of a reliable anti fouling is urgently required after the limitations on the use of tributyltin, this could be a worthwhile research objective.

A second point of interest stems from the demonstrated destructive effect of using an organic top coating on thermally sprayed aluminium coatings. It was demonstrated in section 4.2.3 that this seriously impedes the cathodic protection property of the sprayed coating. However, the possibility of achieving a more aesthetic appearance to the aluminium would seriously increase
its use. For many applications thermally sprayed aluminium will not be considered, mainly because of its outward appearance. Therefore the development of coloured thermally sprayed aluminium coatings deserves further attention. This coloured layer would ideally be applied in a one step process, and the resulting coating should retain (as much as possible) the properties of uncoated aluminium.
General Summary

Chapter 1 provides a broad introduction to the field of corrosion protection using thermally sprayed coatings that may be used as a background to illustrate the relevance of the presented research in this thesis.

The first section concludes that the use of thermally sprayed coatings for corrosion protection is relatively modest, compared to the use of organic coatings despite their potentially superior protection properties. This might result from the more complex protection mechanism. The second section explains this well-defined mechanism by discussing the electrochemical interactions involved.

The third section shows that the combination coating/substrate determines the qualification criteria for corrosion protection in specific cases. Basics of the thermal spraying application techniques used are introduced in section four. The general considerations on the economics of thermal spraying are discussed in section five. It is argued that for many applications a thermal spray coating may well be the most economical solution. However, in general a clear view of the relevant cost considerations is very difficult to obtain, since the cost can only be evaluated reliably for each specific case.

The final section discusses the environmental aspects of thermal spraying. Regarding human safety, these can be compared to the general considerations valid for cutting and welding. Regarding the implications of environmental restrictions, it is argued that organic systems will be subjected to more stringent restriction, which indirectly can be expected to stimulate the use of thermally sprayed coatings for corrosion protection.

Chapter 2 gives an overview of the most used techniques for the assessment of the five most important issues that determine the quality of thermally sprayed coatings for corrosion protection: coating thickness, adhesion, porosity, composition and electrochemical behaviour. The purpose of this section is to show that the assessment of each of these items, (except for coating thickness) poses significant problems when applied to thermally sprayed coatings. Electrochemical measurements are recognised to be able to reveal the most relevant information on corrosion protection quality of the coating. It is concluded that an electrochemical investigation is the only available reliable fast method to obtain an indication of the behaviour in service conditions. Therefore, simplified modification of electrochemical test methods will be the most promising alternative to supplement the existing quality tests (based on coating thickness, adhesion etc.) for corrosion resistant thermally sprayed coatings.

Chapter 3 describes the results of electrochemical characterisation of metallic thermally sprayed coatings that are cathodic to their steel substrates. Three different coating compositions are used: titanium feedstock material, AISI 316 feedstock material and Monel400 feedstock material.

The first section in this chapter describes the corrosion behaviour of electric arc sprayed coatings based on titanium feedstock material on steel. The titanium particles proved to react very rapidly with the arc spray atmosphere. This led to extreme levels of porosity (over 50%) and the formation of large amounts of titanium oxides and nitrides in the coating. These effects can largely be reduced by using argon as propellant during the thermal spray application. However, the resulting improvement proved to be insufficient to lead to acceptable corrosion behaviour in sodium chloride solutions or sulphuric acid.
The second section describes the corrosion behaviour of thermally sprayed low carbon austenitic stainless steel (AISI 316L). The corrosion behaviour and specifically the passivation of a standard arc sprayed coating is not acceptable for use in either sodium chloride, or sulphuric acid solutions. The passivation can be improved by decreasing the porosity of the coating and by preventing oxidation of the coating during the spraying procedure. Excessive oxidation during application can be minimised by using a protective atmosphere during application. Porosity of the coating can be controlled by optimising the spraying parameters. The coating can only be allowed to exhibit a very low amount of porosity. Especially open pores have to be prevented at all time. By using a higher particle speed during deposition (the HVOF method) porosity can be kept sufficiently low. Additional improvement of the corrosion properties can be achieved by a heat treatment of the coated sample.

The third section describes the corrosion behaviour of electric arc sprayed Monel400 (ca. 70%Ni, 30%Cu) coatings on steel. This material shows very favourable corrosion characteristics in both sodium chloride solutions and in sulphuric acid. The corrosion behaviour of the thermally sprayed coating on steel is effectively identical to the behaviour of cladded steel sheet. Also the behaviour in a practical environment, (saturated NaCl at 80°C) is acceptable compared to Monel400 cladded steel, even at prolonged exposure.

The final section of chapter 3 describes the evaluation of the polarisation curve as a qualification test. It is shown that the polarisation curve can be used to differentiate between the effects of oxidation and the formation of pores. It was also shown that the measurement results could be fed back to the application procedure to optimise application parameters. Furthermore, the polarisation curve was shown to reveal information on the relation between porosity and coating thickness. A simple model is suggested, linking the anodic current to the amount of open porosity. Using this relationship, it is possible to design a method that can be used to provide direct information on the corrosion protection quality. Also an indication of the required coating thickness to reach the optimal corrosion protection can be obtained.

Chapter 4 describes the results of electrochemical characterisation of metallic thermally sprayed coatings that are anodic to their steel substrates. Two different coating compositions are used: “pure” aluminium 99.7 and aluminium with 5 percent of magnesium.

The first section describes the results of a series of basic mechanical tests and the effect of fouling organisms on these coating types. The results show that the mechanical properties of aluminium sprayed coatings are, generally speaking, superior to the properties of common anti-corrosion paints. Flexibility measurements showed the possible development of cracks onto the steel substrate. However, as the results described in section 4.3.3 indicate, the risk of corrosion of the steel substrate will remain minimal. The formation of cracks will only occur at the very limit of the bending load for these systems. The magnitude of this maximum load is comparable to the values normally associated with high build organic coatings. An important fact regarding the mechanical properties of the Al based thermal spray coatings is that no significant changes could be measured after 3000 hours of immersion in natural seawater. The amount of fouling after immersion in seawater on the coated panels was relatively large. An anti-fouling coating for situations where fouling would be undesirable is therefore necessary. On the other hand, the abundance of biological activity also suggests no harmful effect of the coatings on the environment. The corrosion protection properties of the spray coatings did not suffer from damage by fouling organisms after 23 months of exposure.

The second section of chapter 4 describes the electrochemical behaviour of various aluminium based thermally sprayed coatings in the as-sprayed condition. It is shown that the corrosion rate of the thermally sprayed layer decreases during the initial period of exposure to a corrosive environment. The rate at which the decrease takes place depends on the conditions during exposure. This effect is most probably the result of the blocking of pores in the thermally sprayed
coating by insoluble corrosion products of the aluminium coating. The rate and effectiveness of this mechanism depends on the type of exposure. Based on the corrosion potential it takes about 100 hours to block the majority of pores during immersion in seawater. Immersion in fresh water requires about 100 days to reach the same stage. The corrosion resistance was found to increase after this period. The estimated decrease in corrosion rate after 1000 hours of immersion in seawater is about one order of magnitude compared to the initial value. The pore blocking mechanism is sensitive to water flow across the aluminium surface. It was shown that an increased water flow can re-activate pores; removal of the water flow reverses this effect.

The third and final section of chapter 4 describes the behaviour of various aluminium based thermally sprayed coatings in seawater when a relatively large part of the steel substrate is exposed (steel to aluminium ratio about 1 to 100). It is shown that after an initial period of which the length depends on the coating age and type, the steel surface becomes blocked by calcareous deposits. These deposits effectively shield the steel surface from the electrolyte, thus limiting the galvanic current to less than half the original magnitude. The resulting service life of damaged aluminium thermally sprayed coatings is consequently significantly increased. The results also indicate that this mechanism will not be effective when the aluminium is over-coated with an organic paint.

Chapter 5 discusses the conclusions and opportunities for further research that emerged from the research described in the previous chapters.

Initially it is concluded that electrochemical techniques are essential for both the development and the qualification of corrosion resistant thermally sprayed coatings. Regarding the used spray materials the following is concluded: The titanium application can be expected to be further improved by optimisation of the argon gas shielding. The AISI 316 material will also benefit from better shrouding of the spray particles during application and better control of the argon spray application to minimise coating porosity. HVOF coatings were shown to greatly benefit from a post spray heat treatment. The development of in situ techniques for heat treating thermally sprayed coatings should therefore deserve attention. Monel400 performed very successfully and can be expected to perform adequately as an alternative or as a repair coating for monel400 clad layers. Regarding the aluminium coatings, it was concluded that these perform extremely well in both seawater and fresh water. Therefore, they should be considered a serious alternative for heavy duty organic coating systems. Both the development and the qualification of this type of coatings should be directed to the corrosion protection mechanisms. Possible areas for further research are the effect of the active aluminium on fouling organisms and the development of aluminium (galvanic protection) thermally sprayed coatings that are aesthetically more attractive.
Samenvatting

Hoofdstuk 1 geeft een algemene introductie van het onderwerp corrosiebescherming met thermisch gespoten deklagen. Deze introductie is bedoeld als achtergrondinformatie voor de gepresenteerde onderzoekresultaten in dit proefschrift.

In de eerste paragraaf wordt gesteld dat corrosiebescherming met thermische gespoten deklagen op slechts zeer bescheiden schaal wordt toegepast in vergelijking met corrosiebeschermende organische coatings. De mate van corrosiebescherming die met deze deklagen bereikt kan worden is echter potentieel superieur. Dit contrast wordt mogelijk veroorzaakt door het meer complexe beschermingsmechanisme van thermisch gespoten deklagen. Dit mechanisme wordt behandeld in de tweede paragraaf.

De derde paragraaf laat zien dat de criteria voor het bepalen van de kwaliteit van een thermisch gespoten deklaag afhangen van de gekozen combinatie van deklaag en substraatmateriaal. De basis van de thermische spuitapplicatiemethoden worden behandeld in paragraaf vier.

Paragraaf vijf beschrijft de algemene overwegingen met betrekking tot de economische aspecten van thermisch gespoten deklagen. Hier wordt gesteld dat thermisch gespoten deklagen voor vele toepassingen de meest economische oplossing zouden kunnen zijn. Deze discussie wordt in de praktijk echter zeer bemoeiijk doordat het bijna onmogelijk is om een duidelijk beeld van de kosten van een thermisch gespoten deklaag te verkrijgen. Deze kosten zijn namelijk zeer sterk afhankelijk van de specifieke omstandigheden bij een praktische applicatie.

De laatste paragraaf van dit hoofdstuk behandelt de milieutechnische aspecten van de thermisch spuittechniek. Met betrekking tot de persoonlijke veiligheid kunnen de overwegingen die bij snijden en lassen van toepassing zijn, worden aangehouden. Wat betreft de vervuiling van het leefmilieu en de restricties op het gebruik van schadelijke stoffen wordt gesteld dat deze zaken in veel sterkere mate van toepassing zijn op organische deklaagssystemen. Hierdoor mag verwacht worden dat het gebruik van thermische spuitlagen in de toekomst indirect gestimuleerd zal worden.

Hoofdstuk 2 beschrijft de meest gebruikte technieken voor de bepaling van de vijf belangrijkste kenmerken van een thermisch gespoten deklaag die samen de kwaliteit van deze deklaag voor corrosiebescherming bepalen. Deze kenmerken zijn: dikte van de coating, hechting, porositeit, samenstelling en electrochemisch gedrag. Het doel van dit hoofdstuk is om aan te geven dat, met uitzondering van de coating dikte, de bepaling van deze kenmerken aan thermisch gespoten deklagen problematisch is. Ondanks de problemen wordt geconcludeerd dat een electrochemische studie toch de enige beschikbare snelle en betrouwbare methode is waarmee een indicatie van het corrosiebeschermingsgedrag in een praktijksituatie verkregen kan worden. De electrochemische meetmethoden zijn echter in de huidig vorm niet geschikt voor gebruik buiten het laboratorium. Verdere ontwikkeling en vereenvoudiging van deze methoden is hierom noodzakelijk.

In Hoofdstuk 3 wordt het corrosiegedrag van metallische thermisch gespoten deklagen die kathodisch zijn ten opzichte van hun substraatmateriaal (staal) behandeld. Drie verschillende spuitmaterialen zijn gebruikt: titanium, AISI 316 en Monel 400.

De eerste paragraaf van dit hoofdstuk beschrijft het corrosiegedrag van elektrische booggespoten coatings, gebaseerd op titanium spuitmateriaal op staal. De titanium deeltjes bleken zeer snel te reageren met de elektrische boog atmosfeer. Dit leidde tot extreme porositeit.
(meer dan 50%) en de vorming van hoge gehaltes aan titaanoxides en nitrides in de coating. Deze effecten konden in belangrijke mate onderdrukt worden door gebruik van een argon atmosfeer tijdens de applicatie. De resulterende verbetering bleek echter onvoldoende om in natriumchloride oplossing of zwavelzuur al van acceptabele corrosiebescherming te kunnen spreken.

De tweede paragraaf beschrijft het corrosiegedrag van thermische gespoten austenitisch roestvast staal (AISI 316L). Het corrosiegedrag en specifiek de passivering van een standaard booggespoten deklaag bleek niet acceptabel voor gebruik in natriumchloride oplossing of zwavelzuur. De passivering kon verbeterd worden door de porositeit van de deklaag te verminderen of door oxidatie tijdens het spuiten te voorkomen. Excessieve oxidatie werd gemenraliseerd door gebruik van een beschermende argon atmosfeer tijdens spuiten. Porositeit van de coating kon beperkt worden door optimalisatie van de spuitparameters. Hierbij moesten met name doorlopende poriën voorkomen worden. Bij gebruik van een hogere deeltjesdenigheid tijdens deklaag depositie (met de HVOF methode) kon de porositeit voldoende laag gehouden worden. Verdere verbetering van het corrosiegedrag werd gerealiseerd door de deklaag een warmtebehandeling te geven.

De derde paragraaf beschrijft het corrosiegedrag van elektrische booggespoten Monel400 (ca. 70%Ni, 30%C) deklagen op staal. Dit materiaal vertoonde zeer acceptabel corrosiegedrag, zowel in natriumchloride oplossing als in zwavelzuur. Het corrosiegedrag van de thermisch gespoten deklaag was vrijwel gelijk aan het gedrag van Monel400 geclad staal. Ook het gedrag in een praktisch gebruiksmilieu (verzadigd NaCl bij 80°C) bleek acceptabel in vergelijking met Monel400 geclad staal, zelfs bij langdurige exposiet.

De laatste paragraaf van hoofdstuk 3 geeft een evaluatie van het gebruik van de polarisatiecurve in een kwalificatieprocedure. Er wordt aangetoond dat de polarisatiecurve gebruikt kan worden om het effect van oxidatie en porositeit te onderscheiden. Tevens bleek dat de informatie teruggekoppeld kan worden naar de applicatieprocedure en zo gebruikt kan worden voor de optimalisatie van applicatieparameters. Verder is aangetoond dat de polarisatiecurve belangrijke informatie over het verband tussen laagdikte en resulterende doorlopende porositeit kan weergeven. Een eenvoudig model wordt gesuggereerd waarin de anodische stroomdichtheid gerelateerd wordt aan het totale oppervlak van de doorlopende poriën. Op basis van deze relatie kan een methode worden ontworpen die gebruikt kan worden om direct de kwaliteit van een coating te bepalen. Uitgaande van een bepaalde porositeit kan hiermee een indicatie van de benodigde deklaagdikte voor het bereiken van een optimale corrosiebescherming worden bepaald.

Hoofdstuk 4 beschrijft het resultaat van de karakterisering van metalen thermisch gespoten deklagen die anodisch zijn ten opzichte van hun stalen substraat. Twee verschillende spuitmaterialen zijn gebruikt: "zuiver" aluminium (99.7%) en aluminium met 5 procent magnesium.

De eerste paragraaf van hoofdstuk vier beschrijft het resultaat van een serie mechanische beproevingsmethoden en van het effect van biologische aangroei op deze coating typen. De resultaten laten zien dat de mechanische eigenschappen in het algemeen superieur zijn aan de eigenschappen van standaard anti-corrosie verf- systemen. De flexibiliteitmetingen lieten zien dat er scheuren in de coating kunnen ontstaan die doorlopen tot op het stalen substraat. Echter, zoals de resultaten in de derde paragraaf van dit hoofdstuk laten zien, zal de corrosie van het stalen substraat minimaal blijven. Een belangrijke factor met betrekking tot het mechanische gedrag van thermisch gespoten aluminium deklagen is dat er geen significant verschil gevonden werd tussen het gedrag van een "verse" coating en een coating die 3000 uur ondergedompeld was in zeeewater. De hoeveelheid biologische aangroei na immersie in zeewater is relatief hoog. Hierom is een aangroeiwerende coating voor gebieden waar aangroei ongewenst is,
noodzakelijk. Anderzijds suggereert de grote mate van aangroei ook dat de coating geen schadelijk effect heeft op het milieu. De corrosieschermende eigenschappen van de deklaag werden niet aangetoond door de biologische aangroei.

De tweede paragraaf van hoofdstuk vier beschrijft het electrochemische gedrag van de verschillende aluminium deklagen. De corrosiesnelheid van de deklagen daalde gedurende de eerste periode van expositie aan een corrosief milieu. De snelheid van deze daling hangt af van de condities tijdens de expositie. Dit effect is waarschijnlijk het resultaat van het verstoppen van poriën in de deklaag door onoplosbare corrosieproducten. De snelheid en de effectiviteit van dit mechanisme hangen af van de expositie omstandigheden. Uitingen van de corrosiepotentiaal duurt het ongeveer 100 uur voordat de meerderheid van de poriën zijn geblokkeerd bij immersie in zeewater. Bij immersie in zoet water heeft dit mechanisme echter ongeveer 100 dagen nodig om hetzelfde effect te bereiken. In beide milieus bleek de polarisatieweerstand na deze periode nog verder te stijgen. De totale geschatte afname van de corrosiesnelheid is ongeveer een factor 10. De verstopping van de poriën is gevoelig voor een waterstroom over het oppervlak van de coating. Het is aangetoond dat boven een bepaalde stroomsnelheid de verstopte poriën weer geactiveerd worden. Na onderbreken van de waterstroom verstoppen de poriën weer.

De derde en laatste paragraaf van hoofdstuk vier beschrijft het gedrag van de verschillende aluminiumgebaseerde thermische sputilagen in zeeewater wanneer een gedeelte van het stalen substraat kaal is gemaakt (oppervlak verhouding staal : aluminium ongeveer 1 : 100). Na een initiële periode waarvan de lengte afhangt van de coating (leeftijd en type) werd het stalen oppervlak spontaan bedekt met kalkachtige afzettingen. Deze afzettingen schermden het staaloppervlak effectief af van de elektrolyt oplossing zodat de corrosiesnelheid sterk daalde. Hierdoor zal de levensduur van een deklaag in praktijkomstandigheden in de buurt van defecten in de deklaag aanmerkelijk toenemen. Overigens bleek dit mechanisme niet effectief wanneer de aluminium deklaag overschilderd is met een organische deklaag.

In hoofdstuk 5 worden de conclusies en mogelijkheden voor verder onderzoek besproken zoals deze naar voren zijn gekomen uit de vorige hoofdstukken.

Allereerst wordt geconcludeerd dat electrochemische technieken essentieel zijn voor de ontwikkeling en de kwalificatie van corrosieschermende thermisch gespoten deklagen. Met betrekking tot de gebruikte sputimaterialen is het volgende geconcludeerd: De applicatie van de titaan deklagen kan verder geoptimaliseerd worden door optimalisatie van de inerte argon atmosfeer. De AlSi316 gebaseerde deklagen zullen ook profiteren van deze ontwikkeling, waarbij voornamelijk de porositeit gereduceerd moet worden. HVOF coatings bleken sterk te verbeteren na een warmtebehandeling van de gespoten deklagen. Hierom verdient een ontwikkeling van in-situ technieken voor het uitvoeren van warmtebehandelingen zeker de aandacht. Monel400 sputcoatings functioneerden zeer goed en van deze coatings mag ook verwacht worden dat zij gebruikt kunnen worden als reparatie voor Monel400 cladlagen. Met betrekking tot de aluminium coatings werd geconcludeerd dat deze deklagen zeer goed functioneren in zowel zeeewater als zoet water. Deze coatings kunnen daarom gezien worden als een serieus alternatief voor traditionele organische “heavy duty” coatingsystemen. De vorming van afzettingen op defecten en poriën in de coating speelt een belangrijke rol in het beschermingsmechanisme van deze deklagen. Deze kennis moet gebruikt worden, zowel bij de verdere ontwikkeling als de kwalificatie van dit type deklagen. Mogelijkheden voor verder onderzoek aan deze deklagen zijn: het effect van actief corrodend aluminium op biologische aangroeionorganismen en de ontwikkeling van (galvanisch beschermende) thermisch gespoten aluminium deklagen met een meer esthetisch uiterlijk.
Curriculum Vitae

Name: Mark Paul Waldemar Vreijling
Date of birth: 5 September 1968
Place of birth: 's-Gravenhage (The Hague), The Netherlands

Education

1986 - 1992: Masters Degree (Ingenieurs examen), Materials Science at the Delft University of Technology, Delft

Employment history

1989 – 1992 Assistant, Materials Science at the Delft University of Technology, Delft
1992 – 1993 Researcher, Shell Research, Arnhem
1993 – 1994 Scientific staff assistant, Royal Military Academy, Breda
From 1994 Researcher, Netherlands Organisation for Applied Scientific Research TNO, Institute of Industrial Technology, Den Helder