Influence of Microstructure on the Corrosion Performance of DP steels

Proefschrift

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CHAPTER 1. INTRODUCTION

1.1 Influence of Corrosion in Automotive Industry

Since the beginning of the automobile history (early 18th century), steel has played a major role as one of the main materials used in the manufacturing process. Even though the first vehicles were characterized by having a wood based frame and wheels, the engine (steam engine in its origins, later developing to the internal combustion engines), has always been fabricated in metals, more specifically iron, copper, tin and their alloys, including steel. Then, with the evolution of the car and components like steering, brakes and transmission, steel became the key material in the automotive industry.

Although in the automotive industry, mechanical properties and performance were the main issues to address, in materials selection, corrosion has always been an important factor affecting the durability and reliability of cars. The presence of steel, as well as other metals, at atmospheric conditions and in the presence of fuels, oils, high temperatures, pressure and friction was a perfect recipe for many kinds of corrosion: uniform corrosion, galvanic coupling, stress and friction-erosion induced corrosion, and crevice were typical features in all automobiles.

The use of paints helped protect the car structures from corrosion effects, but it was not until the beginning of the 20th century that with the high expansion and commercialization of the automotive industry, car manufacturers started taking corrosion effects more seriously. The further understanding of corrosion mechanisms through research studies, as well as the development of stainless steels, started a new era in corrosion protection for automobiles [1-4].

1.2 Automotive Safety

One of the most important, if not the most, transportation media for people all around the world is the automobile. Everywhere people use cars on a daily basis to get to their jobs, to go to schools and universities; to go anywhere. Each day more people are using cars as transport, and because of this, more people are involved in car accidents. Unfortunately, many of these accidents have very serious consequences.

Only in the EU, more than 40000 people die every year and 500000 hospital admissions are registered because of automotive accidents (2005). Although it sounds cruel to label human life with a money value, all this accidents cost the governments around 160 billion Euros. And even though these numbers are getting lower every year (in EU), it is still a very high number. Moreover, the amount of fatalities is larger worldwide, especially in countries with a developing automotive industry like India and China [5].

In order to reduce fatalities or injuries, and reduce the amount of accidents, car manufacturers, governments and private institutes around the world are working together to find possible solutions to this enormous problem.
The ideal condition concerning automotive accidents would be of course to be able to prevent them from happening at all. Car manufacturers have developed many features that help drivers avoid having an accident (Electronic Stability Programs, braking systems, and radar systems among others); at the same time governments have reinforced policies to have a better control of human behavior as a driver (speeding limits, drug and alcohol controls) as well as worked hard to improve all the environment and driving conditions (better roads and its surroundings). Nevertheless, accidents still occur, and there is still going to be quite a long time before Intelligent Automobiles and Roads are capable enough to prevent accidents from happening.

In the meantime, those same entities are working very hard to try to make cars safer, and especially to protect the passengers from any injury or fatality. This is where researchers in the automotive industry and material science come into the picture: lighter, stronger, and more resistant materials (among other characteristics) are needed in order to use them as parts in vehicles. Frames, chassis, panels, engine, drive train are just a few parts that have taken advantage of the material development since the day the first car was built.

Nonetheless this improvement has been especially notorious in the last 30-40 years, when fuel consumption, emissions, weight and safety started to become major issues in the automotive industry; in this same period, the steel industry has focused in the development of High Strength Steels (HSS), which has been a fundamental advance not only for the automotive industry, but also other fields as science and technology [6-9].

That is why development of HSS (Advanced High Strength Steels and/or Ultra High Strength Steels – AHSS & UHSS) and its application on parts like chassis structures, A, B, C pillars and side impact bars have become more important in vehicle design.

But not only the development of new materials is the main focus of researchers around the world: New designs, new processing, joining and forming techniques, as well as new heat and surface treatments have become main research topics in the automotive industry. All these possibilities give designers new choices to make cars lighter and safer.

1.2.1 Corrosion and Safety

The degradation of steel by corrosion can be seen in the form of rust, but actually this is more than just an orange-brownish looking layer on the surface: besides the physical appearance and the modification of the chemical properties, the corrosion of the metal is characterized by the loss of material and the generation of holes and voids on the surface. Depending on the environment and working conditions (as well as the characteristics and corrosion resistance of the steel), this degradation of the material and hole generation can build up to be very significant for the component.

Structurally speaking, there is one very important factor that has an influence on the mechanical performance of a vehicle component: the thickness and consequent
geometry of the element (independent of the material properties). These characteristics are studied and optimized by car designers in order to obtain a good compromise between weight and mechanical performance [10-13].

In terms of thickness of an automotive structural component, it is known that the increase of this parameter is directly proportional to the mechanical resistance of the part, but at the same time also proportional to its weight. Taking into account that the yield and ultimate tensile strength of the material is also directly proportional to the mechanical performance of the part, designers have the chance of playing with these parameters in order to obtain the desired component strength and weight [9, 14-16].

The development of HSS, as well as other structural materials, has allowed designers to reduce the weight of automotive components by decreasing the thickness of the parts [17, 18]. Unfortunately, this decrease in thickness has also brought the necessity of a further development of corrosion protection: lower thickness also means that in case of the component being corroded, the material loss would represent a more significant reduction of thickness, deriving in an increase of the probability of structural failure. Also, the effect of localized corrosion attack in thinner components would represent a more severe generation of weak points (or stress concentrators) which can dramatically decrease the structural integrity of the component [18-20].

Moreover, the new developments in materials by means of heat treatments, alloying elements, and microstructures have also required an evolution of the corrosion studies in order to find an optimum point between mechanical properties and corrosion resistance.

1.3 High Strength Steel HSS

Materials for automotive applications have gone a long way since the first car was built. What used to be a combination of wood and basic carbon steel, has nowadays a range of material possibilities that features from ceramics to highly evolved composites, going through all kinds of polymers and metals. Ironically, the wood that was used on the body structure and frame of the first cars is now used only for decorative purposes in the interior design of luxury cars.

One of the materials that has changed and evolved the most since the beginning of automotive history is steel. Different mixtures of alloying elements and heat treatments have been studied for a long time in order to improve the characteristics of the steel. Plenty of researchers have dedicated their work to find optimum conditions and modify steel for specific applications for over 200 years. But more specifically, in the last 30-40 years, the development of the steel brought the birth of the so called High Strength Steels, HSS.

As its name suggests, HSS are steels that are characterized by having a higher strength than regular carbon steels. But it is not all about strength; increasing the strength of steel comes with a decrease in the ductility. This makes the material brittle and not suitable for all applications. The optimization and compromise between strength and ductility gives a wide range of HSS, which can be seen in Fig. 1.1.
These ones as well as other grades of steel and other metals (like aluminum) are nowadays commonly used in the body structure of a car: from low carbon steel to HSS, depending on the specific body part and requirement (Fig. 1.2).

![Formability chart of steels types based on strength and elongation.](image1)

**Fig 1.1:** Formability chart of steels types based on strength and elongation. [21]

![Different types of steel in a typical frame of a modern automobile.](image2)

**Fig 1.2:** Different types of steel in a typical frame of a modern automobile. [21]

### 1.4 Aim of the Project

As mentioned previously in this chapter, weight reduction of car bodies can be achieved by application of steel components with a lower thickness; however mechanical properties (for constructive and safety reasons) must be maintained, which can be achieved by using HSS. These steels have been designed and optimized for improved mechanical behavior and therefore normally have a poorer or at least not well documented and understood corrosion resistance. Especially since
these HSS components have a lower thickness, attack by corrosion and thereby loss of material resulting in further thickness reduction is even more detrimental to the integrity of car bodies than for normal steels. Therefore, special attention must be paid to the effective corrosion protection of HSS.

One aspect directly influencing the corrosion behavior is the complex phase character of the alloys having more than one phase in its microstructure: phases such as ferrite, bainite, austenite, cementite and martensite, are controlled and combined together to provide an optimum combination of high strength and good ductility.

One of the first developed HSS grades was the Dual Phase steel, or DP steel. The aim of this project is to get detailed insight in the corrosion susceptibility of DP steels, especially the role of the microstructure (as a result of the processing route and heat treatment). The influence of the amount and distribution of these phases on the electrochemical behavior of the steel was studied. This information is the basis for the optimization of the corrosion behavior in relation to mechanical properties

It is important to mention as well that the electrochemical behavior of DP steels has been studied before, but researchers have targeted mainly Dual-Phase Stainless Steel (DSS, which has a microstructure composed of austenite and ferrite) and galvanized DP. Very few studies have been conducted on bare DP, and their results and conclusions are not conclusive or contradictory (Chapter 2).

More specifically in this project, the research is focused on a specific DP steel grade: DP600 in bare condition (no galvanizing layer). It is important to study the bare steel as little is known on the corrosion mechanisms in the phases present on its microstructure. Thus, in order to design the most appropriate solutions for improving the corrosion performance of coated and bare HSS, the corrosion mechanisms need first to be understood. Gaining this knowledge might set the basis for the steel industry to find alternative and more economic ways to protect steel against corrosion, while avoiding the use of chromium (in Stainless) and galvanizing lines.

1.5 Outline of the Thesis

Figure 1.3 shows a schematic overview of the chapters of this thesis. The approach used consists in mainly two parts: Part I covers the general overview of the Dual Phase steels and specifically commercial DP600: In this part, an explanation about what they are and what are their applications is presented, as well as the summary of literature studies covering corrosion behavior of this type of steels (Chapter 2). Furthermore, a detailed explanation of the experimental work performed with the CASIM and the dilatometer for the development of an optimized microstructure for the electrochemical studies (Part II) is presented in Chapter 3.

The second part consists of the experimental approach used throughout this thesis in the attempt to investigate the electrochemical behavior of DP samples. It includes a literature overview of corrosion behavior of steel in carbonate buffered solutions (Chapter 4), as well as the results of the electrochemical testing with different setups
(Chapters 5 to 7). A complementary surface analysis of the samples with AES is studied in Chapter 8.

In Chapter 5, an attempt to study the electrochemical behavior of the samples is performed with standard 3-electrode cells; this proved to be challenging, as crevices were the dominant factor in the tests. After that, in Chapter 6 a modified version of the Avesta cell was used in order to perform the experiments. Even though crevices were allegedly avoided with this setup, noise around the corrosion potential made interpretation of the results a difficult task. In Chapter 7 the electrochemistry is focused on the micro scale, where, with the Micro-Capillary cell setup, electrochemical measurements of the optimized microstructures are presented describing the complete behavior of the system.

Immersion tests and surface analysis are done in Chapter 8 with the help of AES. Together with the electrochemical results of Chapter 7, the results of the AES are used to aid in the description of the model of the electrochemical system suggested in Chapter 9.

Furthermore, the influence of crevice and the reproducibility together with the interpretation of results is discussed in Chapter 9.

Fig 1.3: Schematic structure of the Thesis chapters.
1.6 References

CHAPTER 2. DUAL PHASE STEELS AND DP600

2.1 Dual Phase Steels

Dual Phase (DP) steels are a group of high strength steels characterized by having a microstructure consisting of a matrix of fine ferrite containing small islands of a second harder phase. This second phase is mainly martensite, even though a small percentage of retained austenite or bainite might also be present. Usually, the volume fraction of the martensite in the microstructure is between 10 to 20% (even though ranges from 5 to 30% are also found in literature). The hard martensite islands provide substantial strengthening while the ductile ferrite matrix gives good formability [1-7]. A typical microstructure of a DP steel can be seen in Figure 2.1.

Fig. 2.1: Optical image of typical dual phase microstructure: martensite islands (dark/brown regions) in a ferrite matrix (white regions) [8]

2.1.1 History of DP steels

High Strength Low Alloy (HSLA) Steels were the main material used for automotive applications in the 1950s and 60s. Even though they provided good mechanical properties, their ductility and formability was not as much as necessary to manufacture press-formed car components. This problem was solved with the development of DP steels [4, 9-11].

Although in the 1930s and 40s there were some studies and patents mentioning the use of steels with two phases, it was not until 20 years later when a more fundamental study of DP steels started [4]. In this study, a ferrite-martensite strip was investigated as an alternative to rephosphorized grades for tinplate applications.
Then in the 70s, two significant contributions were made on the development of DPs: a correlation between the strength and the volume fraction of martensite was determined, and the properties of ferrite-martensite steels processed by continuous annealing were discussed. It was at this moment when these kinds of steels were first referred as “dual phase” steels [4, 10, 11].

One of the first commercial dual phase products was marketed in the USA. It was based on a pearlite-reduced vanadium micro alloyed strip steel, commonly encountered in the 1970’s, which was subjected to an additional intercritical annealing process. The steel exhibited a tensile strength of 650MPa, while having yield strength of 350MPa and total elongation of more than 27%. The main application of this DP steel was in bumper reinforcements, but it was also used in other automotive parts including passenger car wheels [4, 10-12].

DP steels are quickly becoming one of the most popular and versatile materials in today's automotive industry. Currently these steels are most commonly used in structural applications where they have replaced more conventional HSLA steels. They offer a great opportunity for part weight reduction. The improved formability, capacity to absorb crash energy, and ability to resist fatigue has driven this substitution. Today's applications include front and rear rails, S-rails, crush cans, rocker reinforcements, B/C pillar reinforcements, back panels, cross members, bumpers, and door intrusion beams. Recently dual phase steels are gaining popularity in automotive closures. DP steels present higher formability than micro-alloyed steels of comparable strength [13-15].

Commercial grades of DP are usually referred accompanied by a number, where this one represents the ultimate tensile strength of the material in MPa; for example, DP600 is a dual phase steel with an ultimate tensile strength of 600MPa. The range of DP available depends on the steel producer, but the most common ones are between DP500 and DP1000 [13].

2.1.2 Characteristics of DP Steels

DP steels have a microstructure of mainly soft ferrite, with islands of hard martensite dispersed throughout. The strength level of these grades is related to the amount of martensite in the microstructure. DP steels have a high work hardening rate, with a typical yield strength-to-tensile strength ratio of about 0.5-0.6. The lower yield strength at a given tensile strength corresponds to higher elongation values and better formability [2, 13, 15-17].

Among the most important characteristics of DP steels we find: a continuous yielding behavior, low yield/tensile strength ratio, high rate of work hardening and high levels of uniform and total elongation. Their high rates of work hardening give them a very high capacity of energy absorption, which leads to very high possibility of weight reduction (Fig. 2.2). This very attractive combination of mechanical properties has made DP steels a key material in the automotive industry for over 20 years [5, 10, 11, 13, 15, 18, 19].
The martensite/ferrite dual phase mixture acts like a particle-reinforced composite. The tensile strength of the composite can be approximated by a simple rule of mixtures:

$$\sigma_{DP} = V_M \sigma_M + V_F \sigma_F \quad [21]$$

Where, $V$ is the volume fraction of the phases and $\sigma$ is tensile strength. The subscripts DP, F and M indicate the composite dual phase structure, the ferrite and martensite phases respectively.

The microstructural characteristic of the dual phase has an influence on the stress-strain curve. The yield strength is determined by the onset of plastic flow in the ferrite phase. At this stage the hard phase is still in the elastic region. With higher applied stress the material exhibits a high work hardening behavior according to a rule for mixtures for two phase microstructures. The strain distribution in the two phases is different, such that in the soft phase the strain and in the hard phase the stress is above the mean value of the composite. This remains even when the hard phase becomes plastic if in a later stage of deformation [16, 22].

As martensite is the stronger phase, increasing the volume fraction increases the strength of the dual phase material [10, 23]. Unfortunately, increasing the martensite content reduces ductility; therefore the volume fraction of martensite is usually restricted in the range of 10 to 20%, where the martensite remains as discrete isolated islands in an interconnected ferrite matrix.

Final microstructure, mechanical properties and phase transformations in DP steels are controlled mainly by its principal alloying element, carbon; it also helps the stability of austenite which leads to the formation of martensite upon cooling [7].

But it is not only carbon that plays an important role in the chemical composition of DP steels. Other elements play important roles in the process: silicon promotes ferrite formation, manganese retards pearlite and bainite development enhancing martensite formation during cooling from the intercritical temperature. Furthermore, phosphorus and/or aluminum (sometimes in combination with chromium) can be used to replace silicon to avoid problems during hot rolling and coating. Also niobium and vanadium are used to limit grain growth resulting in effective strengthening. Molybdenum, titanium, and boron are also present in lower percentage. The mix of
these elements is a key factor in order to have an adequate control of particular annealing conditions and obtaining different strength requirements [4, 7, 11, 24].

Additionally, to maintain high ductility in these steels it is desirable not only to limit the martensite fraction, but also to restrict the carbon content of this phase. At lower carbon contents (<0.4wt %) lath martensite forms, rather than high carbon twinned martensite. Lath martensite is desirable as it will deform to a limited degree and this helps to delay void formation at martensite/ferrite interfaces when the material is strained [4]. Therefore the carbon content of dual phase steels is usually limited to ~0.1wt% maximum. For these typical compositions, with martensite volume fraction of ~15%, DP steels have tensile strengths in the range 550 to 650MPa in the as-rolled condition. This strength is a consequence of carbon concentration and grain refinement [5, 19, 25-27].

2.1.3 Applications of DP Steels

Economic and ecological factors have forced the development of advanced lightweight ground transportation systems, going from automotive vehicles to heavy haul trucks, as well as trains and cargo ships [16, 28]. The reduction of weight brings a reduction of fuel consumption and exhaust gases emission. Weight reduction in car bodies can be achieved by application of steel components with a lower thickness. However, mechanical properties (for structural and safety reasons) must be maintained or improved, which can be achieved by using (Ultra) High Strength Steels ((U) HSS). The development of new grades of (U) HSS, with attractive combinations of strength and manufacturability will help to achieve significant levels of weight reduction, with a minimum impact on structural integrity and cost. One of the most common grades of UHSS is DP steels [29, 30].

<table>
<thead>
<tr>
<th>Producer</th>
<th>Component</th>
<th>Gauge</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Motors</td>
<td>Wheel discs and rims</td>
<td>HR 3.0 and 3.06 mm</td>
<td>For passenger cars and light truck wheels</td>
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<td></td>
<td>Bumper reinforcements, face bars, jok posts</td>
<td>HR 2.00 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water pump pulleys</td>
<td>CR 1.5 mm</td>
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<tr>
<td></td>
<td>Steering couplings reinforcements</td>
<td>CR 1.4 mm</td>
<td></td>
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<tr>
<td></td>
<td>Wheel discs</td>
<td>HR 3.0-4.0 mm</td>
<td></td>
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<tr>
<td>Hoonchi-Estal</td>
<td>Plate brake backing (Girling)</td>
<td>HR 2.5 mm</td>
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<td></td>
<td>Panels for doors, deck (bod) lids, centre</td>
<td>CR 0.5-1.2 mm</td>
<td>Hi-Form 99 showed good formability and</td>
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<tr>
<td></td>
<td>pillars, windshield frames, wheelhouses</td>
<td></td>
<td>behaved rather like Aluminium body sheet</td>
</tr>
<tr>
<td></td>
<td>Bumper face bars, bumper reinforcements,</td>
<td>HR 2.2 mm</td>
<td>2.2 mm DP steels replace 2.0 mm high</td>
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<tr>
<td></td>
<td>rear suspension, wheels, alternator fan blades,</td>
<td>1.9 mm</td>
<td>strength steel</td>
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<td></td>
<td>steering column reinforcements</td>
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<tr>
<td></td>
<td>Styliised wheel discs</td>
<td>HR 2.6-2.9 mm</td>
<td>Parts were made with tooling designed for</td>
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<td></td>
<td></td>
<td>plain carbon steels of thicker gauges</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(3.2-4.0 mm)</td>
</tr>
<tr>
<td>Inland Steel</td>
<td>Door and hood panels and fenders</td>
<td>0.6-2.3 mm</td>
<td>Response to phosphating is just as good</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>as with AK steels 509-700 MPa</td>
</tr>
<tr>
<td>Jones and Laughlin</td>
<td>Bumper stayflacing door impact bars, frames</td>
<td>As rolled</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sections</td>
<td>CR</td>
<td>CAPL treated, 500-700 MPa, 30-35% TE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca-Hillen, low yield ratio type; 350-450,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400-600, and 500-1100 MPa grades</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Box annealed product</td>
</tr>
<tr>
<td></td>
<td>Outer and inner panels, door, beam and</td>
<td>CR 0.7-0.8 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bumper reinforcements</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outer autobody panels</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kawasaki</td>
<td>Styliised wheel discs</td>
<td>HR and CR grades</td>
<td>Used by leading European car makers</td>
</tr>
<tr>
<td></td>
<td>Parts in cars, trucks, busses, farm</td>
<td></td>
<td>USS DP60</td>
</tr>
<tr>
<td></td>
<td>equipment, industrial handling units,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>heavy construction units</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: Range of automotive components build from DP steels (from different manufacturers) [4]
As mentioned previously, the main customer for DP grades is the automotive industry. Depending on the producer - and naturally the customer - DP grades are used to create different components of the car, having a wide range of possibilities: wheel discs, rims, bumper and door reinforcements, A, B, and C pillars, brake components, steering couplings, windshield frames, door and hood outer and inner panels (Table 2.1). Nevertheless, DP’s are also gaining importance in the sector of farm equipment, machine building and heavy construction units.

2.1.4 Applications of DP600

Like other grades of HSS, most of the production of DP600 is used for automotive components. According to major steel producers like Tata Steel, Arcelor Mittal and SSAB, DP600 can be found in (Fig. 2.3):

- Suspension components
- Chassis components for cars and trucks
- Wheel discs
- A and B pillar reinforcements
- Longitudinal members and cross sections
- Safety critical and crash structure parts
- Door beams
- Bumper reinforcements
- Seat tracks
- Fasteners

![Fig. 2.3: Examples of structural components build from DP600. Taken from [31]](image)

Examples of applications of DP600 in sectors different from automotive are:

- Precision tubes
- Train seats
- Liquid Petroleum Gas (LPG) cylinders
- Yellow goods (materials for construction and earth moving equipment, quarrying equipment, and fork lift trucks)
2.2 Corrosion of DP Steels

Since (U) HSS components are designed to have a lower thickness, attack by corrosion and thereby loss of material resulting in further thickness reduction is even more detrimental to the structural integrity of the car bodies than for normal steels. Therefore, special attention must be paid to effective corrosion protection for these steels.

Furthermore, due to the increase of the price of zinc as well as the energy costs involved in hot dip galvanizing, economic and environmental reasons are moving steel industry towards the fundamental study and development of steel without a galvanizing layer. In the specific case of DP, these steels have been designed and optimized for improved mechanical behavior, but their corrosion properties have not yet been studied in detail, or at least not well documented.

In contrast with the non-stainless DP, the corrosion behavior of Duplex Stainless Steel (DSS) is reported extensively in literature. The reason for this that DSS’s are a more commercial grade than DP’s due to the fact that different types of DSS are nowadays extensively used in the petrochemical industry.

DSS grades have a chemical composition characterized by containing more than 20%Cr, 5%Ni and 3 %Mo. Due to this composition (unlike the DP grades), DSS are characterized by having a very stable chromium oxide passive layer, which results in a very good general corrosion resistance. The influence of the microstructure on the corrosion performance of DSS was also reviewed, leading to contradictory information about the effect of the ferrite/martensite/austenite phase ratio. It was suggested that as phase boundaries constitute a zone promoting corrosion due to potential differences between the phases, the increase of phase ratio (and therefore phase boundaries) would deteriorate the corrosion resistance [32]. Additionally, an increase in ferritic microstructure (in heat affected zones) was found to improve the pitting resistance and this effect was attributed to a homogeneous distribution of chromium in the ferrite phase [33, 34]. Nevertheless, a selective dissolution of either of the phases during the electrochemical testing was the general result reported. This behavior was commonly attributed to the difference in the chemical composition between the phases, and even though not discussed in detail, some authors explained this by the depletion of chromium around the martensite precipitates, and concentration of nickel in each of the phases [35]. Moreover, it was also reported that the selective dissolution of both phases is dependent on the electrolyte used, base chemical composition of the steel and geometrical differences of the phases (length and orientation of boundary lines), where either phase can behave as the anode for a specific condition [36-41]. However, it is important to note that most of these studies treat the relation between ferrite and austenite, as this is the characteristic microstructure of commercial DSS (unlike DP grades that are composed of ferrite and martensite).

In literature, few studies can be found in reference to the effect of different phases in the microstructure on corrosion of low carbon heat treated steels [42-45], high strength weathering steels [46, 47] and DP for reinforced bars in concrete structures.
[48-50] with similar base composition as the DP600 that is going to be treated in this study (Chapter 3). In [44], Sarkar et al. performed potentiodynamic polarization scans on dual phase microstructures and reported that an increase of the volume fraction of the martensite phase in the range of 10% together with the refinement of their phase constituents have a negative influence on the corrosion performance of the steel, which was measured by the increase of current density based on Tafel extrapolations. Although ferrite grains were more susceptible to corrosion than the pearlite phase, Osorio et al. [43] measured a deleterious effect on the corrosion resistance of a ferrite/martensite microstructure when compared to the ferrite/pearlite microstructure after heat treating the same base steel. This was attributed to the residual stress from the martensite formation and the generation of extensive micro-galvanic corrosion cells due to the interconnection between the martensite and ferrite phases in very fine needles or lamellas. Electrochemical Impedance Spectroscopy and Tafel extrapolations were used for this analysis, as well as SEM micrographs before and after the polarizations. In contrast with these findings, Zhang et al. [47] reported an opposite behavior: by means of salt spray and exposure tests, it was concluded that the ferrite/martensite microstructure had a better corrosion resistance than the ferrite/pearlite microstructure. Moreover, it is reported that pearlite has a negative effect on the corrosion behavior of steel and that the preferred sites for nucleation of corrosion pits could be associated with the presence of different phases [45]. Also, Townsend [46] conducted long exposure tests on heat treated dual phase microstructures, and reported that the results of testing for 8 years in industrial, rural, and marine environments demonstrated that the corrosion performance of the samples was unaffected by quench-and-temper heat treatments, and that it can be estimated solely on the basis of the initial chemical composition.

In general, researchers have reported differences on the corrosion performance of dual phase microstructures taking into account the phases present. Unfortunately, the conclusions found in these studies are contradictory, and more significantly, clear and detailed experimental procedures and results are not reported in all cases. It is also important to note the absence of remarks concerning the reproducibility and scatter of the results of the tests.
Dual Phase Steels and DP600

2.3 References


CHAPTER 3. DP600: HEAT TREATMENTS AND MICROSTRUCTURAL CHARACTERIZATION

3.1 Introduction

As described in the introduction of this thesis (Chapter 1.4), the main goal of this research is to study the influence of the microstructure on the corrosion performance of DP steels. The first step in the evaluation of the corrosion performance is the selection of the sample that needs to be tested; in this chapter, the procedure to achieve the desired samples for the corrosion and electrochemical testing is described. This process was divided in four main parts:

1. Base material selection
2. Desired modifications of the microstructure
3. Methods to obtain the desired microstructures
4. Characterization of the obtained microstructures

In this chapter, the selection of the base material for the study is discussed: The first step in order to investigate the phenomena was the selection of a specific steel, with a fixed chemical composition. Then, a range of different volume fractions of ferrite/martensite were targeted to define the intended percentage of each of the phases present in the samples. Trial heat treatments were performed by three different experimental approaches (salt bath, Continuous Annealing Simulation (CASIM) and dilatometry) to obtain the desired phase ratio and distribution. After performing the heat treatments, chemical etching and optical microscopy were used together with stereology to analyze the microstructure’s phase ratio and distribution.

3.2 Base Material Selection: DP600

When selecting the base material for this project, the following range of High Strength Steels for automotive applications were considered: multiphase steels like Dual Phase (DP), TRIP, TWIP and Complex Phase (CP) steels. Each of these types of steels has a range of its own, determined by the ultimate tensile strength (UTS) of the variation: for example, TRIP600 and TRIP800 are both TRIP grade steels that have UTS of 600 and 800MPa respectively. The grade and strength of all these steels are controlled mainly by their base chemical composition and their processing route [1, 2].

It was decided then to start with the DP600 for various reasons: first, the fact of being a DP implied having to deal with two phases (ferrite and martensite, Chapter 2) instead of three or more. Second, due to mainly strength level requirements, steels grades like DP800 and DP1000 have more alloying elements in its chemical composition adding more variables to the electrochemical study. And finally
commercial reasons (of the business partner of the project, TATA Steel) as well as availability of the product played an important role in the decision of the starting point.

A mentioned in Chapter 2, DP as well as other high strength steels are used predominantly in the automotive industry. For the DP600, the more common applications are automotive body-in-white structural components like A and B pillar reinforcements, longitudinal members, safety critical and crash structure parts. Besides these automotive applications, DP600 is also used for precision tubes, train seats and Liquid Petroleum Gas (LPG) cylinders[3].

These steels are characterized by having a low ratio of yield strength to tensile strength, high work-hardening capacity, good energy absorption and formability. The basic mechanical properties of these steels are shown in Table 3.1. According to the provider, the amount of martensite present in the microstructure of this steel is approximately 10% (volume).

Table 3.1: Basic mechanical properties DP600 [3]

<table>
<thead>
<tr>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>Elongation</th>
<th>Strain Hardening Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>340-420MPa</td>
<td>600MPa</td>
<td>≥20</td>
<td>≥0.14</td>
</tr>
</tbody>
</table>

The DP600 used in this project was provided by Tata Steel. This is a production material that has been cast, hot rolled and cold rolled until approximately 50 to 60% reduction. The approximate chemical composition in the factory of this DP600 is shown in Table 3.2.

Table 3.2: Chemical composition of DP600 (values in weight percentage)

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
<th>V</th>
<th>Ti</th>
<th>Cu</th>
<th>Sn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻³%</td>
<td>92</td>
<td>1680</td>
<td>241</td>
<td>36</td>
<td>16</td>
<td>4</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>9</td>
<td>3</td>
<td>576</td>
<td>22</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

3.3 Desired modifications to the microstructure

In order to start the study about the influence of the microstructure on the corrosion performance, it was necessary to modify the microstructural features of the steel by means of heat treatments. While keeping the chemical composition, heat treatments provide the option of controlling the amount and distribution of the phases present in the microstructure. This is done by designing and controlling process parameters like heating rate, maximum temperature, intermediate temperature, time and cooling rate.

Even though more phases might be present (such as bainite and retained austenite), DP’s microstructure is characterized by having mainly martensite and ferrite (Chapter 2); the aim of the heat treatments used in this research is to control the amount and distribution of these two phases (disregarding the possible presence of pearlite or retained austenite). In order to do that, three extreme cases concerning the volume percentage of each of the phases were selected as targets to achieve:
1. 0%Martensite + 100%Ferrite
2. 50%Martensite + 50%Ferrite
3. 100%Martensite + 0%Ferrite

It is important to mention that from this point on, the different samples are going to be referred to in terms of the intended amount of martensite present in its microstructure (always volume fraction) as follows: 0%Martensite + 100%Ferrite = 0%M,
50%Martensite + 50%Ferrite = 50%M and 100%Martensite + 0%Ferrite = 100%M.

Besides the volume fraction of the phases present, another microstructural feature that wanted to be controlled was the size of the grains. It was intended to have samples with the same phase ratio but different grain size, e.g., 50%M with “small” grains and 50%M with “big” grains. The idea behind this was to take advantage of localized electrochemical techniques (Micro-Capillary Cell, Chapter 7), in an attempt to measure electrochemical behavior on a single phase or packages (grains) of the same phase; this contrasts with non-localized electrochemical techniques, where the obtained result is actually an average of the behavior of all the microstructural features exposed to the electrolyte while testing, such as grain boundaries, inclusions and/or multiple phases.

### 3.3.1 Obtaining a dual phase microstructure

To produce a dual phase microstructure, the equilibrium pearlite phase needs to be eliminated, with austenite being encouraged to form martensite by rapid cooling. The simplest method for producing dual phase microstructures is to first anneal a ferrite/pearlite steel in the intercritical temperature range, creating a ferrite-austenite mixture [4-6]. This intercritical temperature range is the one between A1 (temperature at which the eutectoid reaction occurs, that is the minimum temperature for austenite) and A3 (the lower temperature boundary of the austenite region at carbon contents below approximately 0.8wt. %C), as seen in Fig 3.1 and Fig. 3.2 [7]. The annealing temperature is controlled within the ferrite-austenite two-phase region, such that much of the ferrite phase available at room temperature remains (Fig. 3.3). The pearlite reverts to carbon rich austenite.

When the steel is then quenched from the annealing temperature, the austenite proportion is sufficiently hardenable to transform to martensite [8]. If the cooling process by quenching is fast enough, all the austenite phase will transform to martensite, avoiding transformations to bainite and pearlite, obtaining a dual phase microstructure; on the other hand, if the cooling process is slower or it has an intermediate stabilization step, part of the austenitic phase will transform to bainite, obtaining this way a microstructure typical for TRIP steels. This can be seen on the TTT diagram and cooling routes in Fig. 3.4. Furthermore, by controlling the steel chemistry and annealing temperature, both the phase fractions and the properties of martensite can be adjusted [9, 10].
The need for a post rolling heat treatment increases the costs significantly, so methods have been developed to produce dual phase microstructures by direct rolling and cooling. This has been achieved through a combination of process control and new alloy design. The new chemistries are low in carbon and rich in hardenability enhancing elements. The low carbon content encourages ferrite to form at temperatures above that necessary for pearlite formation. Other additions delay the pearlite transformation and therefore increase the possibility to form martensite. The post-rolling cooling process is controlled to allow the desired volume fraction of ferrite to form before rapid cooling. The later stage-cooling rate must be sufficient to quench the remaining austenite to martensite.
Fig. 3.2: Portion of Iron-Carbon phase diagram suitable for intercritical annealing low carbon steel [8]

Fig. 3.3: Schematic time-temperature profile for processing DP and TRIP steels; F=ferrite, M=martensite, B=bainite and A=Austenite (retained) [8]
Fig. 3.4: TTT diagram showing temperature profile to obtain DP and TRIP steels, and the influence of alloying elements on the behavior of the curves [12]

First alloy concepts for strip to avoid the intercritical heat treatment were based on Mn, Si, Cr and Mo alloyed steels. Due to the rather high alloy content, these steels were expensive and alternative grades without molybdenum have also been developed. The major application remained to be the automotive wheel and a typical alloy design for such hot strip material with a tensile strength level over 550MPa is: 0.08%C, 0.50%Mn, 0.30%Si, 0.50%Cr and 0.07%P [3].

3.4 Experimental

3.4.1 Methods to obtain desired microstructures: techniques for heat treatments

As mentioned in Chapter 3.3, it is necessary to subject the base material to heat treatments in order to modify and control the microstructural outcome. For this purpose, three different equipment (and processing routes) were chosen to perform the treatments: the first one is the Continuous Annealing Simulator (CASIM), the second one is the Salt Bath and the third one is the Dilatometer.

Continuous Annealing Simulator (CASIM)

The Continuous Annealing Simulator (CASIM) is an equipment used at Tata Steel RD&T to design and study heat cycles for microstructural control. For steel, in the CASIM the samples are annealed at different top temperatures leading to various martensite fractions. The metal sheet of the material is clamped by its edges and is heated to a specific temperature by the application of a controlled current. Depending on the requirements of the heat cycle, for the cooling process, high pressure air is blown to the surface of the sample (for high rate cooling) or the sample is left to cool
down to room temperature (slow rate cooling). The temperature is measured by a thermocouple welded to the center of the plate [13].

**Salt bath**

A salt bath consists of a ceramic or metal container with molten salt, used to provide several kinds of heat treatments. The equipment used for this purpose was the Durferrite GS 660, which was an alkali chloride salt and provides heat treatment with top temperatures in the range of 700°C to 900°C. The maximum sample size for this bath is 300 x 150 x 50 mm³, and the quenching/cooling is done by submerging the sample in a separate bath with oil, water or sand[14].

**Dilatometer**

A dilatometer is a scientific instrument that measures volume changes caused by a physical or chemical process. In this specific case a Bähr 805A/D dilatometer (manufactured by Bähr-Thermoanalyse GmbH) was used to perform the heat treatments on the samples. In this dilatometer, the samples are heated by induction in a vacuum atmosphere and the cooling is done by blowing of high pressure inert gas (Argon or Helium). The temperature is measured by a thermocouple welded to the sample. The time, temperature and deformation are the main parameters recorded during the measurement. According to the manufacturer, the resolution of the equipment is Δl = 0.05µm and Δ°C = 0.05°C[15].

### 3.4.2 Characterization of obtained microstructures: Techniques for revealing microstructural features

The process of characterizing the modification of the microstructure of the DP after the heat treatments was divided in two steps: the first one consisted of chemically etching the surface to reveal the microstructure, and the second one covered the calculation of the volume fractions.

**Chemical Etching techniques**

After the samples were heat treated, polished and cleaned, two main features wanted to be identified from the sample's microstructure:

- Differences between the two phases (ferrite/martensite)
- Austenitic grain boundaries

To recognize the difference between ferritic and martensitic phase, the samples were chemically etched with Nital 2%, for 10s. With this method, the martensitic grains are identified as the dark/brown regions in the micrographs, while the ferrite can be seen as a white area [16].

Revealing the austenitic grain size is an important issue as this way the size of the grains in the fully martensitic microstructure can be determined. In order to do this, a solution of 100 ml of deionized water, 2 gr of picric acid (C₆H₃N₃O₇), 50 ml of sodium...
alkylsulfonate ("Teepol") and 6 to 12 drops of HCl was prepared [17]. For the microstructure to be revealed, the drops of HCl had to be added just before starting the etching of the sample. Moreover, the surface had to be fully immersed in the solution for 9min, and during the whole process the surface had to be whipped with cotton.

After the etching, all the samples were analyzed under the optical microscope at 100, 200, 500 and 1000 times magnification.

**Volume fraction determination: Stereology**

Stereology is the science of the geometrical relationships between a structure that exists in three dimensions and the images of that structure that are fundamentally two-dimensional (2D) [18]. Most commonly, stereological relationships are applied to images (optical microscopy, SEM, among others) to relate the information of the 2D image to important parameters of the actual 3D structure.

![Fig. 3.5: Example of grid point count / volume fraction relationship. Taken from [18]](image)

One of the most straightforward relationships that can be made is the point count to the volume fraction; for this one it is known that the ratio of points from a grid in an image that fall into an alpha phase in a microstructure to the total number of points in the grid, is equal the volume fraction of that alpha phase in the microstructure. An example of this can be seen in Fig. 3.5. In this example it is intended to calculate the volume fraction of the β phase in the microstructure. For this purpose, a 5x5 grid is drawn over a region of the micrograph, and the number of grid points that lay over a β phase grains are counted. As the total number of point in the grid is 25, it is concluded that the volume fraction of the β phase is 5/25, that is 0.25 or 25%
In order to ensure validity of the results, it is normally intended for a stereological experiment to be conducted in samples that isotropic, uniform and random (as much as possible). Although is usually not possible to obtain this, a proper selection of the grid size and a representative number of test samples often help increase the reliability of the results. The point count method is most efficient when the grid spacing is such that adjacent points rarely fall within the same feature, cell or region in the image (they are then said to be independent samples of the structure).

![Figure 3.6: Example of grid used for the point count of the CASIM and Dilatometer samples](image)

In this chapter, stereology is used to estimate the volume fraction of martensite present in the microstructure. For each heat treatment and intended microstructural condition, 3 different samples were prepared for optical microscopy (polished and chemically etched). From each sample, 5 micrographs from different regions of the sample were taken with the optical microscope at 1000 times magnification. A grid was then placed on each micrograph. The grid used consisted of 7 x 5 points. The squares contained in the grid had a 15μm side. An example of the grid used for all the measurements is shown in Fig. 3.6. The point count was based on the fact that after etching the samples with Nital 2%, the ferrite phase can be identified by its white-pale color, while the martensite is characterized by appearing as dark-brown regions. The presence of other phases was disregarded due to the low percentage of them in the microstructures, and the difficulties presented to identify them clearly from one another.

### 3.5 Results and Discussion

#### 3.5.1 CASIM samples

Three sheets (100 x 600 x 1 mm³, Fig. 3.7) of the base material were selected for the CASIM; one for each of the intended 0, 50 and 100%M samples. The sheets are clamped and then a current is applied until it reaches a maximum temperature for each of the intended cases. Then the sheets are cooled by high pressure are at an approximate rate of 80°C/s.
The main difference to obtain the three intended samples is the maximum temperature of the heat cycle: for the 0%M, it was 650˚C; for the 50%M, it was 825˚C; and for the 100%M, it was 870˚C.

According to Tata Steel RD&T, only the middle region from each of the sheets (black sector in Fig. 3.7) is the one that can be expected to have the intended phase composition and a homogeneous distribution of its microstructure. Samples for all the electrochemical testing were cut from this region in each of the sheets.

![Fig. 3.7: Sheet of material for CASIM treatments (all lengths in mm)](image)

After cutting, all the samples were ground with silicon carbide paper FEPA 600, 800, 1200 and 2400, and further polished with diamond paste cloth down to 9, 3, and 1 µm respectively, including intermediate ultrasonic cleaning baths in ethanol.

After the etching with Nital 2%, the samples were studied under the optical microscope at 100, 200, 500 and 1000 times magnification. An example of the microstructures obtained after the CASIM can be seen in Fig. 3.8.

A summary of the results of the volume fraction calculation can be seen in Table 3.3. As indicated in Chapter 3.4.2, 5 different images were taken from each of the samples measured, and 3 samples were selected from each of the 3 heat treatment conditions (0, 50 and 100%M). In the table, Reference indicates the intended percentage of martensite prior to the heat treatment; Ave and STD Sample are the average value and standard deviation of the point count measurement for one sample (results of 5 measurements); and TOT AVE and STD are the average and standard deviation of the 15 measurements (5 measurements x 3 samples) of each heat treatment condition.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Number</th>
<th>Ave Sample</th>
<th>STD Sample</th>
<th>TOT AVE</th>
<th>TOT STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%M</td>
<td>1</td>
<td>7</td>
<td>3</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50%M</td>
<td>1</td>
<td>41</td>
<td>10</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>44</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%M</td>
<td>1</td>
<td>81</td>
<td>7</td>
<td>82</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>85</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>79</td>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.5.2 Salt bath samples

With this technique the temperature control is not very accurate, and procedures as cooling down to an intermediate temperature (necessary for the 50%M intended sample) are not possible. Moreover, even though fully martensitic microstructures were obtained, decarburization will also affect the microstructural control of the samples. For this reason, the attempts of further controlling the microstructure with this technique were not performed.

3.5.3 Dilatometer samples

Dilatometer

The optimal sample geometry for this application is a cylinder 10 mm long and 5 mm diameter. Nevertheless, the samples used were 10 x 5 x 1 mm³, cut from a plate of the base material (Fig. 3.9).

A sheet of base material was cut into samples as shown in Fig. 3.9. Based on the composition of the material, an estimation of the $A_{e1}$, $A_{e3}$ (equilibrium transformation temperatures in steel) and the intercritical temperature to obtain an intended 50% martensite volume fraction (referred to as $A_{50\%M}$) was performed with the help of...
TCW4 Thermo-Calc for Windows (Version 4.1.3.41) [19]. The values obtained were approximately 610, 825 and 780°C for $A_{e1}$, $A_{e3}$ and $A_{50\%M}$ (Fig.3.10).

![Bähr 805A/D dilatometer and sample for dilatometry test](image)

**Fig. 3.9:** Bähr 805A/D dilatometer and sample for dilatometry test

![Volume Fraction of Phases vs Temperature](image)

**Fig. 3.10:** Theoretical values for $A_{e1}$, $A_{e3}$ and intercritical temperature ($A_{50\%M}$) for 50\%M volume fraction calculated with Thermo-Calc [19]

A set of experiments were designed to obtain the desired microstructures. The intended volume fractions were divided in three groups: 0, 50 and 100\%M. For every group, treatments had the same heating rate (5°C/s) and same maximum
temperature. These heat treatments were designed to obtain a fully austenitic microstructure in all the samples; after obtaining the fully austenitic microstructure, different cooling procedures were used to form the 100%M and the 50%M groups. The heat treatment route for each intended volume fraction of martensite are described later in this section.

Furthermore, taking into account that the values obtained for $A_{e1}$, $A_{e3}$ and intercritical temperature are a theoretical approximation, it was decided to run experimental trials on more than one temperature and as well as more than one holding times for each intended volume percentage group. This was done in order to obtain and select the heat treatment that fitted best the desired martensitic volume fraction and the grain size.

Heat treatment to obtain 100%M:

To obtain a 100%M sample, it is necessary to transform the base material to a fully austenitic microstructure and then quench as fast as possible. In order to do that, the sample has to be heated over the $A_{e3}$ temperature (825°C), isothermal holding at maximum temperature for a period of time, and then quench with Argon gas at high pressure to room temperature. The quenching process happened at a rate of approximately 150°C/s.

Three maximum temperatures were selected to obtain 100%M samples: 900, 1000 and 1100°C. These three temperatures were selected in order to control the austenitic grain size, due to the fact that austenitic grain size is directly proportional to the increase in temperature. At each of these temperatures two holding times prior to quenching were tested: 3 and 10 minutes. The aim of these variations was to have enough time for a stable transformation of the austenitic grains. After the holding times at maximum temperature, all the samples were quenched to obtain a fully martensitic microstructure.

Heat treatment to obtain 50%M:

To obtain a 50%M sample, it was decided to first form a fully austenitic microstructure, then promote the transformation to ferrite by cooling until an intercritical temperature ($A_{50}\%M$, Fig. 3.10), followed by a holding period at this temperature, and finally quenching to room temperature.

Like with the 100%M group, to obtain the fully austenitic microstructure, the heating cycle had the same top temperatures (900, 1000 and 1100°C); the holding time at these temperatures was three minutes. At this point a fully austenitic microstructure is obtained. The next step was to have a slow cooling rate (1°C/s) until the calculated intercritical temperature $A_{50}\%M$. At this temperature a one hour holding time was applied to allow the transformation and growth of the ferrite grains. The last step was the quenching to obtain the transformation of the remaining austenite regions to martensite; like the quenching on the 100%M samples, this process was done by blowing Argon gas at high pressure.
After performing the heat treatments, the samples were polished, etched and analyzed with optical microscopy. The percentage of martensite present in the samples obtained with $A_{50\%M} = 780^\circ C$ was greater than 50%, (approximately 70%M). In order to get a martensitic volume fraction closer to 50%, new trials were performed varying the $A_{50\%M}$ to 760 and 740°C; the holding times were also changed in the range from one hour to fifty hours. The whole set of tests are described in Table 3.4.

Heat treatment to obtain 0%M:

Unlike with the CASIM technique, it was decided not to attempt on obtaining a 0%M sample with this technique, as the amount of carbon in the steel will never allow for a fully ferritic microstructure to be formed. This is because base material used for the heat treatments has almost 0.1% C (Table 3.2), and the maximum amount of carbon that can be present in ferrite is approximately 0.025% (Fig. 3.1). Furthermore, after analyzing the results of the attempts to modify the base microstructure with the CASIM to obtain a 0%M (Fig. 3.8), it was seen that the heat treatment had modified the amount of martensite present in the microstructure by just a few percent when compared to the commercial grade (Table 3.3): when comparing the 7% martensite volume obtained in the CASIM with the 10% martensite volume of the commercial grade, it was decided then to use the commercial grade DP600 as the low martensite concentration sample.

Table 3.4: Coding of the samples for the experimental heat treatments. The parameters in the description represent temperatures and their subsequent holding times. All the treatments had the same heating rate until reaching the maximum temperature and included a final quenching step.

<table>
<thead>
<tr>
<th>CODE</th>
<th>Max Temp ºC</th>
<th>Holding time at Max Temp</th>
<th>Intercritical Temp ºC</th>
<th>Holding time at Intercritical Temp</th>
<th>Intended Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>900</td>
<td>3 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>B</td>
<td>900</td>
<td>10 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>C</td>
<td>1000</td>
<td>3 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>D</td>
<td>1000</td>
<td>10 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>E</td>
<td>1100</td>
<td>3 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>F</td>
<td>1100</td>
<td>10 min</td>
<td>-</td>
<td>-</td>
<td>100%M</td>
</tr>
<tr>
<td>G</td>
<td>900</td>
<td>3 min</td>
<td>780</td>
<td>1 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>H</td>
<td>900</td>
<td>3 min</td>
<td>760</td>
<td>1 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>I</td>
<td>900</td>
<td>3 min</td>
<td>740</td>
<td>1 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>J</td>
<td>1000</td>
<td>3 min</td>
<td>740</td>
<td>1 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>K</td>
<td>1100</td>
<td>3 min</td>
<td>740</td>
<td>1 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>L</td>
<td>1000</td>
<td>3 min</td>
<td>740</td>
<td>4 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>M</td>
<td>1100</td>
<td>3 min</td>
<td>740</td>
<td>2.5 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>N</td>
<td>1100</td>
<td>3 min</td>
<td>740</td>
<td>8 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>O</td>
<td>1100</td>
<td>3 min</td>
<td>740</td>
<td>18 hour</td>
<td>50%M</td>
</tr>
<tr>
<td>P</td>
<td>1100</td>
<td>3 min</td>
<td>740</td>
<td>50 hour</td>
<td>50%M</td>
</tr>
</tbody>
</table>

Following the trial heat treatments, all the samples were grind with silicon carbide paper FEPA 600, 800, 1200 and 2400, and further polished with diamond paste cloth.
down to 9, 3, and 1 μm respectively, including intermediate ultrasonic cleaning baths in ethanol.

After polishing, the samples were etched with Nital 2% and studied under the optical microscope at 100, 200, 500 and 1000 times magnification. Considering the volume percentage of martensite, the size of the grains obtained, the homogeneity of the microstructure and the length on the heat treatment, only 3 of the 16 different heat treatments (Table 3.4) were selected: treatment A, which resulted in a fully martensitic microstructure with grains of approximately 20μm in size (100%M with Small grains), treatment E which resulted in a fully martensitic microstructure with a grain size of more than 80μm (100%M with Large grains), and treatment I which had an intended 50%M volume fraction (50%M). The heat treatments that were selected are shown in Fig. 3.11.

![Temperature route for heat treatments](image)

**Fig. 3.11: Temperature route for heat treatments applied for samples A (100%M with Small grains), E (100%M, Large grains) and I (50%M)**

Beside the three selected heat treatment routes, samples from the base material as well as samples of commercial DP600 (with the same base chemical composition) were polished, etched and studied under the same conditions. An example micrograph of these five types of sample microstructures can be seen in Fig. 3.12.

Two important aspects should be mentioned here: the first one concerns the base material sample. This sample is steel with the chemical composition of a commercial DP600, but it is missing the final austenization step in order to transform to a ferritic-martensitic dual phase microstructure. At this stage, this sample composed of a highly deformed ferritic matrix with islands of cementite/pearlite mixture. These islands are the ones that are going to transform to martensite after austenization. When exposed to Nital 2%, the cementite/pearlite mixture is revealed as dark areas,
while the deformed ferrite is white. Details of the cementite/pearlite islands and the deformed ferrite are shown in Fig. 3.13.

The second aspect to mention is that as the etching with Nital 2% helps revealing the differences between ferrite and martensite phases due to amount of carbon present in them, selected heat treatments A and E, which both result in fully martensitic microstructures, are not discernible by this method as seen in Fig. 3.12 c) and d). In order to distinguish the difference in grain size intended, it was necessary to perform a different etching as described in Chapter 3.4.2 [17]. As this etching reveals austenitic grain size, in the fully martensitic microstructures it will reveal the size of martensite grains. The micrographs for samples after treatments A and E after this etching can be seen in Fig. 3.14.

Fig. 3.12: Sample micrographs of the microstructures of the a) base material, b) commercial DP600, c) 100%M with Small grains, d) 100%M with Large grains and e) 50%M
Fig. 3.13: SEM image of BM sample after etched with Nital 2%: The carbides (cementite) are the area that will transform to martensite after austenization.

Fig. 3.14: Sample micrographs with revealed austenitic grain boundaries Treatment A, 100%M with Small grains (left), and Treatment E, 100%M with Large grains (right)

Besides the chemical etching and optical microscopy, it is also necessary to use the data recorded in the dilatometer to support the results obtained in terms of identification of phases present in the microstructure. As mentioned in the description of the equipment, the dilatometer not only controls the time and temperature of the heat treatment, but also records the changes in length of the probe. Fig. 3.15 shows the complete description deformation measured on the samples subjected to the three selected heat treatments (A, E and I) in the dilatometer. It can be seen that the heat rate, time for stabilization at maximum temperature and quench rate were the same for all the treatments.
Fig. 3.15: Measured deformation during heat treatments applied for Treatment A (100% with Small grains), E (100%M with Large grains) and I (50%M).

The microstructural information is complemented by the deformation vs. temperature curve, where the phase changes can be identified by dilatation/contraction of the probe in the dilatometer. The blue arrows indicate the direction of the process. From this graph it can be seen that the 3 treatments have an identical increase in length due to the increase in temperature until approximately 760°C; at this point, all the treatments have a constant decrease in length until 845°C. This decrease is due to the change of the ferritic structure (BCC) to an austenitic structure (FCC): at the lower temperature the transformation begins, and at the higher temperature the contraction stops because the complete microstructure is now austenitic (the 3 treatments have a fully austenitic microstructure). These two temperatures, 760°C and 845°C, are referred as $A_{c1}$ (temperature at which ferrite starts transforming into austenite during heating) and $A_{c3}$ (temperature at which the transformation of ferrite to austenite is complete upon heating) respectively.

From this point, a gradual constant and growth is seen again due to the increase in temperature, and it continues until the maximum temperature of each treatment is reached (900°C for A and I, and 1100°C for E). This growth is due to increase in the size of the austenitic grains, which means that the grains of treatment E are larger in size. After each treatment reaches its maximum temperature, a 3 minute holding time at maximum temperature is applied; during this holding time, there is no significant deformation of the samples for any treatment.

The cooling down of the treatments can be divided in two groups: immediate quench to room temperature (A and E), and cool down until intercritical temperature, holding at intercritical temperature and finally quench to room temperature (I).
For treatments A and E, an immediate quench after the holding time at top temperature is performed. The samples in both treatments show a constant contraction until approximately 450°C, where there is a small plateau with no deformation followed by an increase in length. This behavior is a consequence of a phase transformation, assumed to be martensite. In order to be certain about the composition of the phase transformation, it is necessary to calculate $M_s$, or martensite start temperature. This temperature represents the point at which austenite starts transforming into martensite while in a cooling process. If the cooling process continues after this point, the austenite grains that were present when $M_s$ is reached will transform to martensite.

The determination of $M_s$ is an important parameter to find as it helps designing processes to obtain desired microstructures. This parameter has been studied extensively, and it is well known that the $M_s$ is strongly dependent of the composition of the austenitic phase [20, 21]. One of the most complete studies of the influence of the elements in the austenitic phase on the $M_s$ was performed by Andrews [21]. From this study, a linear formula to calculate $M_s$ in terms of the composition of the steel was developed:

$$M_s = 539 - 423C - 30.4Mn - 12.1Cr - 17.7Ni - 7.5Mo + 10Co - 7.5Si \quad (3.1)$$

The composition of the base material (Table 3.2) was then used to calculate the theoretical value of $M_s$ equal to 440°C. This value would suggest that if there is no phase transformation during the cooling process before reaching 440°C, it can be assumed that a fully austenitic microstructure reaches $M_s$, and that this one will transform to a 100% martensitic microstructure. As there is no increase in the length of the probes exposed to heat treatments A and E before approximately 450°C (Fig 3.15), it can be concluded the all the austenite is transformed to martensite during quenching, therefore obtaining a fully martensitic microstructure.

For treatment I, the process is identical until reaching the maximum temperature and the 3 minute holding time. After this, a controlled cooling at a 1°C/sec is performed until reaching 740°C, showing the same contraction as the one seen for treatments A and E (due to the decrease in the temperature). At 740°C, there is an increase in the length of the sample while at the 60 minute holding. During this time, the fully austenitic microstructure starts transforming into ferrite, this transformation being the reason for the increase in length (change from FCC austenite to BCC ferrite). The combination of this intercritical temperature and holding time are responsible for generating the desired volume fraction of approximately 50% ferrite.

After this holding time is finished, the sample is quenched aiming for the 50% remaining austenite to transform to martensite. As with treatments A and E, a calculation of theoretical $M_s$ (which in this case will be referred to as $M_{s50\%M}$) is necessary to ensure that the austenite reaches $M_{s50\%M}$ without transforming to other phases before. Andrews’ linear formula (3.1) is also valid for this purpose, but the mass fractions of the elements in the austenite had to be calculated because a percentage of them are now present in the ferritic phase. For that purpose, a
calculation was performed with the help of TCW4 Thermo-Calc for Windows in order to estimate the mass fractions of the elements in the austenitic phase at 740°C. The weight percentage values for this intercritical temperature are presented in Table 3.5.

Table 3.5: Chemical composition of austenitic grains at intercritical temperature 740°C (values in weight percentage, calculated with Thermo-Calc)

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-3}%</td>
<td>305</td>
<td>3078</td>
<td>212</td>
<td>759</td>
<td>38</td>
<td>2</td>
</tr>
</tbody>
</table>

After calculating the weight percentage values at 740°C, the results are used in Andrew’s formula (1), obtaining a theoretical $M_{50\%M}$ equal to 305°C, which would suggest that the remaining austenite would transform to martensite if there is no phase transformation (increase in probe length) before reaching approximately 305°C. According to Fig. 3.15, the change in length during the cooling process starts around 350°C, so it is possible that a small fraction of the austenite transform into bainite, but in general terms it can be considered that the main transformation is to martensite.

Table 3.6: Summary of the point count measurement for the Dilatometer samples; BM = Base Material, DP600 = Commercial DP600, I-50%M = 50%M, A-100%M_SG = Fully Martensitic with Small Grains and E-100%M_LG = Fully Martensitic with Large Grains

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Number</th>
<th>Ave Sample</th>
<th>STD Sample</th>
<th>TOT AVE</th>
<th>TOT STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>1</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP600</td>
<td>1</td>
<td>11</td>
<td>2</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-50%M</td>
<td>1</td>
<td>59</td>
<td>5</td>
<td>58</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>58</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>58</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-100%M_SG</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-100%M_LG</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Like with the CASIM samples, after grinding, polishing and etching with Nital 2%, the volume fraction of the martensite was calculated. A summary of these results can be seen in Table 3.6. Five different images were taken from each of the samples measured, and 3 samples were selected from each of the 5 heat treatment conditions (base material, commercial DP600, treatments I, A and E). In the table; Reference indicates the intended percentage of martensite prior to the heat treatment; Ave and STD Sample are the average value and standard deviation of the
point count measurement for one sample (results of 5 measurements); and TOT AVE and STD are the average and standard deviation of the 15 measurements (5 measurements x 3 samples) of each heat treatment condition.

### 3.6 Conclusions

In general terms, the resulting microstructures (with the exception of the salt bath trial), satisfied the requirements of the intended percentage of martensite. It should be noted that from the 3 extremes intended (0, 50 and 100%M), only the 0%M is not actually possible because the amount of carbon present in the steel is too high (more than the amount that ferrite is capable of containing), and requires the presence of another phase different than ferrite. Moreover, phases like retained austenite and bainite may be present in some of the samples, but in a percentage low enough to disregard its effects.

After obtaining the samples with the modified microstructures of DP600 with the CASIM and the dilatometer, some remarks can be made about the equipment used for the heat treatments and the results obtained. Parameters like temperature control (both in heating and cooling), homogeneity, and size/shape of the samples are compared in the following paragraphs.

#### Temperature Control:

Both equipment rely on the use of a thermo-couple welded to the middle of the sample in order to measure the temperature during the experiment. Even though in principle it should be the same for both equipment, the fact of the CASIM working with bigger samples would imply more difficulties on having the same temperature over the whole surface of the sample. Nevertheless that is exactly the reason why only the middle section of the sheet subjected to the CASIM is considered to have the desired microstructure.

Moreover, during the quenching this temperature control becomes more critical as this is the step determining the phase fractions of martensite. While in the dilatometer inert gas is blown at high pressure in a vacuum environment for a 5x10x1 mm³ sample, in the CASIM high pressured air is blown to a 100x600x1 mm³ sheet of steel, no vacuum. This does not only make it more difficult to have temperature control due to the size of the sample and the quenching media, but does not provide a cooling rate fast enough to transform all the austenite to martensite, as it can be seen in Fig. 3.8. The intended 100%M in the CASIM resulted in a microstructure closer to 80%M, unlike the dilatometer samples under treatments A and E, which had a fully martensitic microstructure.

#### Homogeneity:

This parameter is very much related to the temperature control: a better temperature control provides a more well-defined microstructure, as designed by the heat treatment. This fact, together with the size of the samples, the quenching method and the vacuum atmosphere, provided the dilatometer samples with a more homogenous microstructure. This is confirmed by the images taken from the samples (Fig. 3.8 as
compared to Fig. 3.12), as well as the results from the point count (Tables 3.3 as compared to Table 3.6).

When comparing the 100%M samples from the CASIM with the ones of obtained with treatment A and E, it is clear that not only the intended martensite percentage was not reached, but the homogeneity of the samples (measured basically in terms of the standard deviation of the point count: smaller deviation results in a more homogeneous microstructure) is better in the dilatometer samples. This is also seen when comparing the samples intended for 50%M with both equipment (50%M CASIM and treatment I in the dilatometer): even though the martensite fractions obtained are similarly off the goal (40%M in CASIM and 58%M in dilatometer), the total standard deviation indicates that the distribution of the phases of the dilatometer samples is more constant (9 in the CASIM to 4 in the dilatometer). This effect can be seen even more clearly when you analyze the standard deviation for each of the 3 samples of each condition, as one of the samples of the CASIM presented a deviation of more than 10 and another one of just over 6, while the 3 samples of the dilatometer had a deviation of around 4.

Size/shape of the samples:

Concerning this parameter, the CASIM provides a couple of advantages: one heat treatment in the CASIM provides a usable heat treated area of approximately 200x100mm². This allows several samples to be cut from the treated area in basically any size/shape needed, making the CASIM a more economical treatment in terms of time and energy consumption. In the dilatometer only one sample is treated each time, and it is only possible to have the 5x10mm² rectangle; as the samples are intended for electrochemical testing, and standard 3 electrode electrochemical cell uses and exposed area of a circle with 10mm diameter, the small dilatometer samples are not suitable for the standard 3 electrode setup as the one used in Chapters 5 and 6.

Nevertheless, the microstructures obtained with both equipment fulfill a basic requirement: even though it was intended to have extreme cases of 0, 50 100%M, the samples obtained show big enough differences in the amount of martensite present in the microstructure in order to attempt to measure any influence that this feature might have in its electrochemical behavior, if any. Even more, the group of samples obtained with treatment E in the dilatometer brings the possibility of pursuing an electrochemical study in a single grain of a single phase with a localized technique, as the one used in Chapter 7.

3.7 Acknowledgment

The author would like to acknowledge the participation of Dr. Maria Santofimia (TU Delft) for her help and guidance with the experimental technique used throughout this chapter.
3.8 References


CHAPTER 4. ELECTROCHEMICAL BEHAVIOR OF STEEL

4.1. Introduction

In this chapter, an overview of the electrochemical behavior of steel is presented. Firstly, the basics of the corrosion process of steel are discussed. This is done in order to give a general background and comparison point for the electrochemical work performed throughout this work, which is discussed in detail for DP steels in chapters 5, 6 and 7.

Polarization curves are analyzed in detail in order to get a better understanding of the electrochemistry of steel. The information obtained from polarization curves is complemented by the use of other electrochemical or surface analysis methods.

After providing a first insight into basics of corrosion and polarization curves, this chapter covers an extensive literature review covering electrolytes, buffers, cathodic and anodic reactions, oxides and oxide layers, oxidation and reduction potentials, passivity and breakdown analysis obtained by various electrochemical and surface analysis methods.

4.1.1 Basics of Steel Corrosion

When the word “corrosion” is mentioned, one of the first ideas that go into most people’s mind is an old rusting car laying in a junkyard. From this point of view, “corrosion” is referring to the brownish-looking product over the metallic structure and this is related exclusively to steel. But actually, as described in [1], “Corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties”. However, the most common corrosion product encountered is rust which forms on the surface of steel.

For corrosion to happen the major component of steel, iron (Fe), undergoes a number of changes; these changes are of electrochemical nature. The dissolution of Fe can be represented by the following electrochemical reaction equation:

\[ \text{Fe} \leftrightarrow \text{Fe}^{2+} + 2\text{e}^- \]  

(4.1)

where an iron atom at the surface of the steel in contact with an aqueous solution is transformed into a positively charged iron ion (equation 4.1). This ion is dissolving in the aqueous phase, while the negatively charged electron remains in the metal. An electrochemical double layer is formed. Equilibrium is established at the Fe reduction potential (approximately -0.45mV under standard conditions).

In an acid environment, as iron has a reduction potential more active (negative) than hydrogen, the electrons are used to reduce the hydrogen ion to hydrogen gas (equation 4.2). The driving force for these reactions is the difference in reduction
potential of Fe/Fe$^{2+}$ and H$^+$/H$_2$. Equilibrium is disturbed and corrosion takes place according to the overall reaction 4.3:

$$2H^+ + 2e^- \rightarrow H_2 \quad (4.2)$$

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (4.3)$$

Thus a stationary corrosion reaction is established, the rate of which is determined by the driving force ($\Delta E^0$) and the kinetics of both half reactions. Reduction of oxygen present in aqueous solution will take place in parallel in both low and high pH solutions. For an acid solution, according to the following electrochemical equation (4.4)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (4.4)$$

For high pH solutions the oxygen reduction is the main cathodic reaction. Then electrons in the metal can react with oxygen molecules, producing hydroxyl ions; this reaction is also known as Oxygen Reduction Reaction (ORR).

The actual corrosion reaction is more complicated. The first step is the formation of FeOH$^+$ or the direct precipitation of Fe(OH)$_2$ where after further oxidation may take place to form FeOOH or Fe(OH)$_3$.

The solid corrosion products are mostly porous due to the complexity of the transport/diffusion reactions.

The rate of the established stationary corrosion reactions can be calculated from the corrosion reactions current density. The corrosion current density cannot be measured directly, but can be determined from the relationship between current density and potential (polarization curve) by linear extrapolation.

### 4.1.2 Polarization curves

It is well known that corrosion is a major problem that affects every industry, and the costs associated with corrosion ascend to billions of Euros (or dollars) all over the world [1-6]. Because of this, governments and companies have invested great quantities of resources in trying to prevent corrosion of metals by studying its mechanisms to estimate the life expectancy of metallic structures. Measuring the corrosion process becomes the first step in this work.

When attempting to measure and predict the corrosion behavior of a metal in a specified environment, three experimental approaches are commonly used: Exposure (mainly outdoor) tests, accelerated tests and electrochemical evaluation tests.

Exposure are tests in which the metal is directly exposed to the environment under investigation; these tests provide the most reliable answer to questions related to the corrosion behavior of the metal in the specific environment, as it offers a good representation of the actual service. But such tests, if at all possible, are time
consuming usually taking up to a few decades to carry out. Furthermore the variability of the natural exposure conditions, changes the response of the metal in the system over time and therefore the corrosion rate, making it difficult to accurately predict long term effects. [7, 8]

Accelerated tests are tests in which variables of exposure tests as pH, temperature and salt concentration are increased, attempting to increase the speed of the corrosion reaction. Salt spray and cyclic tests are examples, and they provide results in a much shorter range of time than exposure tests (months, weeks, or even days). However, the validity of these tests depends on the assumption that the corrosion mechanism will only be enhanced (therefore reducing testing time) and not modified during the test which normally results in very poor correlation between the results of accelerated and exposure tests as reported in literature [7].

Electrochemical evaluation tests provide fair estimations of instantaneous corrosion rates. Measuring polarization curves takes only a short time (hour or minute range). It does not only provide a numerical, reproducible and accurate estimation of corrosion rate in a short period of time, but through proper analysis of its results it also provides an insight of the actual corrosion mechanism taking place [7].

4.1.2.1 Measuring polarization curves

Polarization curves can be determined with the help of setup as shown schematically in Fig 4.1. The setup pictured is commonly referred to as a 3-electrode setup, where the working electrode (WE) is the investigated material. This complete system is controlled by a potentiostat, which is linked to software that provides an output of the measured data [3-6, 9, 10]. The relationship between the potential of the working electrode and the current density is measured.

![Fig. 4.1: Schematic diagram to determine polarization curves using a potentiostat][10]
The measured relation between the current density and the applied potential gives information on the corrosion rate and on some characteristics of the reaction scheme, like e.g. whether passivation or pitting takes place. In Figure 4.2 a schematic picture of a measured polarization plot for a metal M corroding in an acid aqueous solution is given. By linear extrapolation from the linear part in the potential vs. log i plot, the corrosion current density and the corrosion potential are determined. For the linear polarization method we refer further to literature [3-6, 9, 10].

4.2 Corrosion of Steel

Even though corrosion is a phenomenon that affects nearly all metals, due to the wide usage of steel, corrosion of steel is probably the most investigated. Extensive literature is available on the corrosion of steel. Although the fundamentals of the corrosion behavior of steel (as presented in Section 4.1) are generally understood, due to the extensive amount of sources describing different fields of application it is common to encounter discrepancies in the electrochemical results and their interpretation.

In this chapter, therefore some key aspects of the study of steel found in literature are presented focusing on the electrochemical behavior; polarization curves and "passivation" in different electrochemical systems are compared with a focus on carbonate buffered solutions, which were studied in this thesis.

Fig. 4.2: Schematic anodic and cathodic polarization curves for a metal in acid solution [10]
4.2.1 Corrosion of Steel in carbonate buffered solutions

In order to get a better understanding and control of the mechanisms involved in corrosion of carbon steel (and iron), extensive research has been done making use of variations of the electrochemical system: different inorganic inhibitors, presence/absence of chloride ions, buffer solutions, temperature and oxygen content control are among the many variables that have been modified in order to study the changes in the corrosion process. Similarly, a wide range of experimental techniques have been used in the attempt to understand and explain the details of the corrosion process and the identification of oxide (oxy-hydroxide) layers and thus passivity of the system.

This chapter focuses on the information found in literature concerning the influence of carbonate (bicarbonate) and chlorides on the corrosion behavior of steel.

As a general result, it was found that the majority of the sources reviewed agreed on the fact that the addition of carbonate ions had considerable influence on the passive behavior: lower passive currents and higher pitting potentials were measured during electrochemical testing. Another finding was, as expected, the negative effect of chlorides on the protective properties of the passive layer.

The experimental approach found in literature consisted of the following:

- preparation of the steel (or iron) sample: cutting, embedding, heat treatments
- definition of the electrolyte: type and concentration of anions, deaeration, pH, chlorides, temperature
- electrochemical pre-treatment: open circuit potential, cathodic pre-polarization, immersion in etching solution
- the application of various electrochemical techniques: Potentiodynamic polarization, galvanostatic polarization, cyclic polarization (voltametry), SVET, the use of the rotating disc electrode, OCP measurements during fixed time intervals and (L)EIS.
- the application of various “surface sensitive” techniques: SEM, AES, Raman Spectroscopy, XRD, X-ray Photoelectron Spectroscopy, Photo electrochemical techniques and FTIR.

All polarization diagrams in literature starting at low potentials displayed an oxidation peak current, a passivity region and a transpassive region at high potentials for the potential sweep in the anodic direction. The electrochemical behavior of steel in carbonate containing solution can be summarized as follows and is further put in a schedule in Table 4.1.
## Table 4.1: Summary of previous work found in literature

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>SAMPLE</th>
<th>HISTORY</th>
<th>SOLUTION</th>
<th>pH</th>
<th>TECHNIQUES USED</th>
<th>RESULTS/ FLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>[11]</td>
<td>CS</td>
<td>1 hour OCP</td>
<td>3.5%NaCl, SiO₂+ HCO₃⁻ oxygen free, room temp.</td>
<td>8.5</td>
<td>Adjusted by NaOH or HCl</td>
<td>Pot. Dyn., EIS, XPS</td>
</tr>
<tr>
<td>[12]</td>
<td>Fe</td>
<td>Cathodically reduced surface</td>
<td>0.1M NaCO₃</td>
<td>11</td>
<td></td>
<td>Pot. Dyn. and Pot. Stat.</td>
</tr>
<tr>
<td>[13]</td>
<td>CS 4.5Cr Steel</td>
<td>Prepolarization 10 min</td>
<td>0.5M NaHCO₃ and 0.5M NaHCO₃ + 0.01M KCl aerated</td>
<td>8.6 and 8.5</td>
<td>EIS, Pot. Dyn.</td>
<td>Passive films present n-type semiconductor behavior</td>
</tr>
<tr>
<td>[14]</td>
<td>CS 4.5Cr Steel</td>
<td></td>
<td>0.5M NaHCO₃ and 0.5M NaHCO₃ + 0.01M KCl aerated</td>
<td>8.6 and 8.5</td>
<td>Pot. Dyn.</td>
<td>Formation of γ-Fe₂O₃/Fe₃O₄. Cl diminishes stability of passive layer. Heat treatment modifying micro do not change electro behavior.</td>
</tr>
<tr>
<td>[15]</td>
<td>CS</td>
<td>Precathodization</td>
<td>0.5M NaHCO₃, deaerated</td>
<td>8.72</td>
<td>Voltametric, -1.26V to 1.26V, cyclic</td>
<td>Fe₃O₄/γ-Fe₂O₃ double layer</td>
</tr>
<tr>
<td>[16]</td>
<td>Fe</td>
<td>Precathodization</td>
<td>0.05K₂CO₃, 0.75M KHCO₃</td>
<td>8.8 borat buffer to adjust pH</td>
<td>AES, anodic polarization</td>
<td>First: Fe(OH)₃ or FeO₄ along with FeCO₃, then second layer is Fe₂O₃.</td>
</tr>
<tr>
<td>[17]</td>
<td>CS</td>
<td>Etched in 20% HCl 5 min, then short rinse in 1% HCl, no drying, O₂ free NaHCO₃ solutions</td>
<td>8.2-3.8</td>
<td>Anodic polarization</td>
<td>Passivating film had localized breakdown without polarization</td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>CS</td>
<td>OCP, -835mV</td>
<td>0.05/0.5M NaHCO₃</td>
<td>8.9</td>
<td>Voltamograms, Rot. Disc. Elec.</td>
<td>γ-Fe₂O₃/Fe₃O₄</td>
</tr>
<tr>
<td>[19]</td>
<td>CS</td>
<td>Polished, cleaned. With and without preanodization 45min at -0.4V</td>
<td>0.1M NaHCO₃</td>
<td>9</td>
<td>Raman Spectroscopy, Pot. Dyn.</td>
<td>CI break passivity</td>
</tr>
<tr>
<td>SOURCE</td>
<td>SAMPLE</td>
<td>HISTORY</td>
<td>SOLUTION</td>
<td>pH</td>
<td>TECHNIQUES USED</td>
<td>RESULTS/ PHILM</td>
</tr>
<tr>
<td>--------</td>
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<td>----</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>[20]</td>
<td>CS</td>
<td>Prepolarization at -1.2V for 20min</td>
<td>1M NaHCO₃/0.5M Na₂CO₃</td>
<td>9.21</td>
<td>EIS, Mott-Schottky</td>
<td>n-type Fe₂O₃, FeO, Fe₂O₃ inner with n-type Fe₂O₃, increase Cl defects on passive film</td>
</tr>
<tr>
<td>[21]</td>
<td>CS</td>
<td>Prepolarization at -0.6V</td>
<td>NaHCO₃ (NaCO₃)</td>
<td>6.7-11 (10)</td>
<td>Cyclic, EIS, Mott-Schottky</td>
<td>FeCO₃ formed, which oxidizes to γ-Fe₂O₃/Fe₃O₄ n-type</td>
</tr>
<tr>
<td>[22]</td>
<td>Fe</td>
<td>30 sec negative potential to produce hydrogen evolution</td>
<td>KHCO₃/K₂CO₃</td>
<td>8.4-10.3</td>
<td>Rot. Disc. Elec., XPS</td>
<td>FeOH then passivity Fe(OH)₃, which grows to composite layer Fe₂O₃ and hydrox FeOOH (by Raman, X-ray, Mössbauer ellips.)</td>
</tr>
<tr>
<td>[23]</td>
<td>Fe</td>
<td>Polishing and cleaning</td>
<td>NasCO₃ with NaCl and Na₂S</td>
<td></td>
<td>OCP</td>
<td>Thckening of oxide follows log growth law. Linear with Na₂CO₃ concentration. Lower values of OCP with increasing concentration of NaCl and Na₂S</td>
</tr>
<tr>
<td>[24]</td>
<td>CS</td>
<td>OCP</td>
<td>1M NaHCO₃ + 0.5 Na₂CO₃ + Cl⁻</td>
<td>9.5</td>
<td>Pot. Dyn., Mott-Schottky</td>
<td>Low potentials, decreasing OCPs, double E. Pot. Cl initiate pitting</td>
</tr>
<tr>
<td>[25]</td>
<td>CS</td>
<td>-1.2V for 20 min</td>
<td>1M NaHCO₃ + 0.5M Na₂CO₃</td>
<td></td>
<td>Photo electrochemical, Mott-Schottky</td>
<td>γ-Fe₂O₃/Fe₃O₄ n-type semiconductor</td>
</tr>
<tr>
<td>[26]</td>
<td>Fe</td>
<td>Prepolarization at -1V</td>
<td>0.05M carb. bicar. buffer</td>
<td>9.4</td>
<td>Raman Spectroscopy</td>
<td>Surface oxidation = &gt; formation 'green rust' (a hydrated hydroxy-carbonate), followed by α and β FeOOH with an under layering Fe₂O₃ formed on the cathodic (reduction) cycle α = goethite β = akaganeite</td>
</tr>
<tr>
<td>[27]</td>
<td>Fe</td>
<td>Ground till 4000</td>
<td>Deaerated NaHCO₃ with NaCl</td>
<td>Adj. to 8.5-9.5 with NaOH</td>
<td>EIS/Pot. Dyn. FTIR</td>
<td>FeCO₃, amorp. FeOOH and green rust</td>
</tr>
<tr>
<td>[28]</td>
<td>CS</td>
<td>-1.3V 1h</td>
<td>0.1M NaHCO₃ deaerated</td>
<td></td>
<td>Polarization</td>
<td>Effect of Cl and temp. on pitting pot.</td>
</tr>
</tbody>
</table>
Table 4.1: Summary of previous work found in literature

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>SAMPLE</th>
<th>HISTORY</th>
<th>SOLUTION</th>
<th>pH</th>
<th>TECHNIQUES USED</th>
<th>RESULTS/ FILM</th>
</tr>
</thead>
<tbody>
<tr>
<td>[28]</td>
<td>CS</td>
<td>-950mV 30 min</td>
<td>0.005 to 1M NaHCO₃</td>
<td>8.2-9.5</td>
<td>Pot. Dyn., SEM</td>
<td>First peak: Fe to Fe²⁺; product Fe(OH)₃ and/or FeCO₃. Second anodic peak: Fe²⁺ oxidized to form Fe₂O₃. High concentration of HCO₃⁻; more resistance to pitting. Other films in neutral and alkaline solutions.</td>
</tr>
<tr>
<td>[30]</td>
<td>Fe</td>
<td>Silver deposition on surface: -0.9V for 10 min</td>
<td>0.15M Na₂CO₃ + 0.15M NaHCO₃</td>
<td>10</td>
<td>Raman Spectroscopy, polarization in potential steps</td>
<td>Same for nitrate and carbonate solutions Fe(OH)₃ + Fe₃O₂/y-Fe₃O₄; y-FeOCOH at higher potentials.</td>
</tr>
<tr>
<td>[31]</td>
<td>CS</td>
<td>OCP 1h, then polarized cathodically</td>
<td>NaHCO₃ and NaCl</td>
<td>Electrochemical noise, EIS, Pot. Dyn.</td>
<td>Passivity due to formation of Fe₂O₃/Fe₃O₄.</td>
<td></td>
</tr>
<tr>
<td>[32]</td>
<td>CS</td>
<td>Prepolarization at -1V for 1min</td>
<td>1N NaHCO₃ + 1N Na₂CO₃</td>
<td>Pot. Stat. ex situ crystallography and ex situ Raman Spectroscopy</td>
<td>Potentials more positive than OCP; starts with a FeCo₃ layer that disappears as potential increases, while a maghemite-magnetite layer appears.</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
Pot. Dyn.: Potentiodynamic polarization
Pot. Stat.: Potentiostatic polarization
Cyclic: Cyclic polarization
Rot. Disc. Elec.: Rotating Disc Electrode
The first step when polarizing in anodic direction is the formation of insoluble iron species FeCO$_3$ simultaneously with ferrous hydroxide [18]:

\[
\begin{align*}
\text{Fe} + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \quad (4.5) \\
\text{Fe} + \text{HCO}_3^- & \rightarrow \text{FeCO}_3 + \text{H}^+ + 2\text{e}^- \quad (4.6)
\end{align*}
\]

where the ferrous carbonate and Fe(OH)$_2$ create a first protective film on the surface [11, 12, 16, 17, 19, 21-25, 29, 31]. According to [22], the mechanism is a dissolution/precipitation reaction of the Fe(II) species. The precipitation process is further stimulated at high pH and CO$_3^{2-}$ / HCO$_3^-$ concentration[19].

After the hydroxy-carbonate layer has been formed, passivity based on an oxide layer can result at higher potentials according to the oxidation reactions 4.7 and 4.8[11]:

\[
\begin{align*}
2\text{FeCO}_3 + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 + 2\text{CO}_3^{2-} + 6\text{H}^+ + 2\text{e}^- \quad (4.7) \\
or \\
3\text{Fe(OH)}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \quad (4.8)
\end{align*}
\]

Davies and Videm [16, 17] found a similar result using AES concluding that only magnetite was the oxide layer formed, according to equation 4.x.4. Castro also reported in [22] a single oxide film working as a passive layer, but in this case using the RRDE together with XPS he found that it was formed following equation (4.9):

\[
2\text{FeCO}_3 + 3\text{H}_2\text{O} \rightarrow \gamma\text{-Fe}_2\text{O}_3 + 2\text{CO}_3^{2-} + 6\text{H}^+ + 2\text{e}^- \quad (4.9)
\]

After running galvanostatic and OCP measurements, Simard [18] concluded that the anodic film produced is a mixture of different oxides: \(\gamma\)-Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe(OH)$_2$ or FeCO$_3$, greatly depending on the growth potential and possible anodic pre-treatment. However, a sandwich type of layer he thought improbable based on the fact that the charge that was measured at reduction corresponded to just one monolayer oxide.

Thomas [12] suggested that passivation takes place through 2 different stages: in the first stage, magnetite and ferrous carbonate form on the iron surface. In the second stage, the ferrous carbonate is oxidized to hydrated ferric oxide. However, no further surface analysis of the corrosion products was performed by this author.

Passivation in the form of a double layer was mentioned by several authors: Alves and Li stated in [13, 14, 21] that passivation of the steel occurs when the potential becomes sufficiently positive, attributed to the formation of a double layered \(\gamma\)-Fe$_2$O$_3$/Fe$_3$O$_4$ film by EIS and polarization investigations respectively. Similarly, El-Naggar presents in [15] a schematic representation of the double layer model (Fig 4.3), and derives the reactions to obtain each of the oxides:
Electrochemical Behavior of Steel

\[
\text{Fe} + 2\text{Fe(OH)}_2 + 4\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 4e^- \quad (4.10)
\]

And then

\[
2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \rightarrow 3\gamma\text{-Fe}_2\text{O}_3 + 2\text{H}^+ + 2e^- \quad (4.11)
\]

Similar conclusions were obtained by others in [12, 25, 29, 30]. Likewise, several authors as Flis [33] and Bojinov [34] have also found similar results, even though working with different base electrolytes like KOH and LiOH.

Further characteristics of the oxide film were n-type semiconductor behavior, revealed with Mott-Schottky plots [13, 20, 21, 25]. Others used Raman Spectroscopy and found both an inverse spinel type \(\text{Fe}_3\text{O}_4\) and an amorphous passive layer, under certain conditions[30].

Fig. 4.3: Schematic representation of the double layer model for the passivity of steel. Taken from [15]

An important conclusion reported by several authors was that chlorides did not have any influence on the formation and/or composition of the passive films. Naturally, higher concentration of these ions generated an earlier break down of the passive layer, identified in the polarization diagrams by sudden increase in current density, and localized attack on the surface of the steel sample, as presented by Jelinek in [28]. When no aggressive ions were present in the solution, anodic polarization could continue up to high values corresponding to oxygen evolution potentials.

In [24], Xue identified a double layer consisting of \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_3\text{O}_4\), in which both are a product of the oxidation of \(\text{FeCO}_3\) following

\[
4\text{FeCO}_3 + \text{O}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{HCO}_3^- + 4\text{H}^+ \quad (4.12)
\]

and

\[
6\text{FeCO}_3 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 6\text{HCO}_3^- + 6\text{H}^+ \quad (4.13)
\]

An alternative evolution of the passive film formation on iron was proposed by Larroumet in [26]; in this case the formation of “green rust” (a hydrated hydroxyl-carbonate) is incorporated. The potential dependence of the layer composition is given in Fig 4.4:
Legrand [27] also identified the presence of green rust GR1(CO$_3$) as part of the oxidation product by using FTIR together with SEM.

![Diagram](image)

**Fig. 4.4: Evolution of the passive film formation on iron in a 0.05M carbonate/bicarbonate buffer with respect to the applied potential. Taken from [26]**

To establish the chemical composition of passive layers, Hirnyi [32] used a combination of potentiostatic polarization with *ex situ* crystallographic and Raman methods to analyse the surface and diffraction patterns of the polarized steel. He identified FeCO$_3$ at potentials slightly higher than the corrosion potential, but noticed that increasing the potential changed the composition of the passive layer to different compositions ranging from groups of various iron oxyhydroxides, going through green rust 1 and 2, and finally reaching a dual magnetite-maghemite film.

Rahner [35] concluded that the disagreement surrounding the existence of single or two layer model forming the passive layer of iron can be completely attributed to the experimental conditions presented by different authors.

In [36] Drissi used XRD and Mossbauer Spectroscopy to analyse the reaction products of iron in a carbonate-containing solution; the results of these experiments were used to create a representation of a Pourbaix diagram, where it can be seen that at pH values around 10 and higher, the main oxidation sequence (increasing potential) is identified as Fe to Fe(OH)$_2$ to GR1(CO$_3^{2-}$) (*Green Rust 1*), and finally α-FeOOH.
4.2.2 Conclusions and implications for this work

The review of the work done by several researchers using different experimental approaches and techniques on the development of oxide layers on iron/steel in carbonate buffered solutions is presented in this chapter. Dissimilar types of iron oxy-hydroxides as well as carbonate compounds were identified by several authors as a result of the variety of techniques and approaches.

It is difficult to reach a common and unified conclusion about the development of the passive layer(s) mainly because from a purely thermo dynamical point of view, all the compounds and oxides described are in principal possible to obtain.

However, the behavior, development and rate of growth of the layers are completely determined by the kinetics of the electrochemical system. For this reason, polarization curves have been used for over 70 years to help in the study of corrosion reactions based on mixed-potential theory.

In order to get a better understanding of the corrosion of Dual Phase steels, chapters 5, 6 and 7 of this investigation are dedicated exclusively to the measurement and interpretation of polarization curves of different sample steels with modified microstructures in mainly carbonate buffered solutions.

The extensive experimental approach performed with only this technique was done to ensure not only a high degree of reproducibility of the results, but also in depth study in order to avoid common misinterpretations of the data obtained.

Furthermore, an advanced technique like the Micro Capillary cell was used to investigate the influence of the microstructure on corrosion behavior in more detail.

Later in Chapter 8, AES together optical microscopy are used to complement the polarization work by further identification of the oxide/passive layers formed on the samples.
Chapter 4

4.3 References


CHAPTER 5. MACRO ELECTROCHEMICAL MEASUREMENTS ON DP STEELS: EXPERIMENTS WITH CONVENTIONAL CELL

5.1 Introduction

From the literature survey in Chapter 4 we learned that detailed information on the electrochemical behavior of steel is needed as a function of the microstructure especially for the DP steels where we may expect local differences in surface reactivity. A first step is to evaluate the average behavior of the DP steel surface using polarization experiments.

Open Circuit Potential and potentiodynamic polarization experiments were performed under different conditions and with different setups.

The electrochemical behavior of DP600 as well as of samples whose microstructure had been modified by heat treatments as described in Chapter 3 was studied.

5.2 Experimental details

OCP and potentiodynamic polarization curves were measured with standard 3-electrode electrochemical cell setups. Two different setups were used due to the different size of the samples. Details are described in the following paragraphs.

5.2.1 Samples

As described in Chapter 3, two different types of samples were obtained as a result of different experimental procedures after thermal treatment to control the composition of their microstructure.

Type 1: CASIM samples.

These were the samples obtained from the Continuous Annealing Simulator CASIM, as described in Chapter 3.5.1 (Fig. 3.8). It is important to remember that each of the 3 groups of these samples are going to be referred to in terms of the intended volume fraction of martensite present in their microstructure, being 0, 50 and 100%M.

Type 2: Dilatometer samples.

These were the samples obtained from the dilatometer heat treatments, as described in Chapter 3.5.3 (Fig. 3.12). Four groups of samples as presented in Fig. 3.12 were used for electrochemical testing: type BM (base material, 10% cementite/pearlite), I-50%M (50% martensitic), A-100%M_SG (fully martensitic with small grains) and E-100%M_LG (fully martensitic with large grains). It is important to remember that each of these groups of samples are going to be referred to as BM, I, A and E respectively.
All the samples used for these measurements were previously ground with silicon carbide paper FEPA 1200 and 2400, and further polished with diamond paste cloth down to 9, 6, 3, and 1µm respectively, including intermediate ultrasonic cleaning baths in ethanol. All the tests were done at room temperature.

5.2.2 3-electrode electrochemical cell setups

Due to the different size of the samples, two standard setups were used for the experiment in this chapter. The main difference between the setups is the area of the working electrode (sample to be tested) exposed to the electrolyte: In setup 1 (Fig. 5.1) the area of the working electrode is defined by a circle of 10mm in diameter (0.78cm²), while in setup 2 (Fig 5.2) the circle had a diameter of 3mm (0.07cm²).

![Fig.5.1: Setup 1, exposed area 0.78mm² (d=10mm)](image)

Commercial 3-electrode cell setups are characterized by having a working electrode area defined by a circle with diameters that range from 5 to 20mm; due to the fact that the dilatometer samples (Chapter 3.5.3) have a size of 5 x 10mm, it was necessary to create a custom made electrochemical cell (Fig 5.2). Even though small samples are usually embedded in epoxy resin for testing, it is well known that it is difficult to avoid the formation of crevices at the sample-epoxy interface [1-5].

5.2.3 Electrolytes

Two different electrolytes were used for the experiments:

**Electrolyte 1:**

A 1.5M NaCl solution in a phosphate buffered solution with a pH of 5.6. When using this electrolyte, two types of electrochemical measurements were performed: Open Circuit Potential (OCP) followed immediately by a potentiodynamic polarization scan. The duration of the OCP measurement was 1 hour; the subsequent polarization in
the anodic direction which started at -850mV with respect to the reference electrode at a scan rate of 1mV/s.

**Electrolyte 2:**

The electrolyte chosen for these experiments was a 0.1M NaCl solution in a carbonate buffered solution with a pH of 10.

Like with electrolyte 1, two types of electrochemical measurements were performed: Open Circuit Potential (OCP) followed immediately by a potentiodynamic polarization scan. The duration of the OCP measurement was 3 hours; the subsequent polarization in the anodic direction which started from -100mV with respect to the measured rest potential value (-50mV for in setup 2), and it was performed at a scan rate of 1mV/s.

![Fig.5.2: Setup 2, exposed area 0.07mm² (d=3mm)](image)

### 5.2.4 Experimental parameters

The reference electrode used for setup 1 was an Ag/AlCl -3M KCL-, (+199mV with respect to SHE), while for setup 2 was a standard calomel electrode SCE (+244mV with respect to SHE). In both setups the counter electrode was a platinum mesh of 30mm diameter (with a hole of 10mm diameter in the center of the mesh). The testing setups were connected to a Solartron Electrochemical setup (1250 Frequency response analyzer and SI 1286 Electrochemical Interface) with software CorrWare for Windows Version 2.80.

Each of the OCP/polarization scans were performed a minimum of 3 times for each volume fraction percentage. This was done to check reproducibility of the results. When presented in graphs, a representative curve from the measurements is shown.

The following table shows a summary of the experimental details for each of the cases analyzed.
5.3 Results and discussion

All potentials shown for experiments in Case 1 and 2 are measured with respect to the Ag/AlCl\textsubscript{3}M KCl\textsubscript{-}, (+199mV with respect to SHE), while the experiments for Case 3 are measured with against the SCE (+244mV with respect to SHE).

**Table 5.1: Summary of experimental details per experimental case**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CASE 1</th>
<th>CASE 2</th>
<th>CASE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
<td>Type 1: CASIM: 1. 0%M 2. 50%M 3. 100%M</td>
<td>Type 1: CASIM: 1. 0%M 2. 50%M 3. 100%M</td>
<td>Type 2: Dilatometer: 1. BM-10% Cementite /Pearlite 2. A-100%M Small Grains 3. E-100%M Large Grains 4. l-50%M</td>
</tr>
<tr>
<td>PREPARATION</td>
<td>Ground-polished till 1µm, cleaned and dried</td>
<td>Ground -polished till 1µm, cleaned and dried</td>
<td>Ground -polished till 1µm, cleaned and dried</td>
</tr>
<tr>
<td>3-ELECTRODE SETUP</td>
<td>Setup 1: d=10mm</td>
<td>Setup 1: d=10mm</td>
<td>Setup 2: d=3mm</td>
</tr>
<tr>
<td>ELECTROLYTE</td>
<td>1.5M NaCl with phosphate buffer pH 5.6</td>
<td>0.1M NaCl with carbonate buffer pH10</td>
<td>0.1M NaCl with carbonate buffer pH10</td>
</tr>
<tr>
<td>REFERENCE ELECTRODE</td>
<td>Ag/AlCl\textsubscript{3}M KCl\textsubscript{-}, (+199mV with respect to SHE)</td>
<td>Ag/AlCl\textsubscript{3}M KCl\textsubscript{-}, (+199mV with respect to SHE)</td>
<td>SCE (+244mV with respect to SHE)</td>
</tr>
<tr>
<td>OCP DURATION</td>
<td>1 hour</td>
<td>3 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>STARTING POINT OF POTENTIODYNAMIC SCAN</td>
<td>-850mV vs. Reference electrode</td>
<td>-100mV vs. measured OCP</td>
<td>-50mV vs. measured OCP</td>
</tr>
<tr>
<td>SCAN RATE</td>
<td>1mV/s</td>
<td>1mV/s</td>
<td>1mV/s</td>
</tr>
</tbody>
</table>

5.3.1 Case 1

Fig 5.3 shows one representative curve of the OCP for each type of sample measured. All the experiments showed decreasing potential with time. However, the decrease in potential was only of about 10 to 20mV from the beginning of the
measurement (t=0s) until stabilization of the potential. All the measurements performed had a potential value in the range of -690 to -720mV, independent of the type of sample measured.

These results show that a high degree of reproducibility of the results was achieved while all the measured OCP values after one hour were found inside a range of only 30mV; however, that also implies that the OCP cannot discriminate between different microstructures.

The observed small decrease in the corrosion potential of all the samples can be explained by the dissolution of small amounts of hydr(oxides) which will most probably have been on the polished surface before exposure till a steady state has been obtained.

Similar behavior is reported by several authors in [6-9], where the decrease of the corrosion potential occurs while dissolution and development of corrosion products on the surface was observed during the measurement. It is also suggested that the presence of phosphate ions may induce repassivation of the initial corrosion sites during the anodic dissolution of the sample, but that this effect is normally overruled by the presence of chloride ions which break the repassivation and accelerate the corrosion degradation process [10-14].

![Fig.5.3: OCP of CASIM samples in 1.5M NaCl with phosphate buffer pH 5.6, with d=10mm exposed](image)

Representative potentiodynamic polarization curves (following the OCP measurements presented in Fig. 5.3) are shown in Fig. 5.4. The corrosion potential, $E_{corr}$, was identified around -660mV ($\pm$15mV) for all the experiments performed, independent of the type of sample tested.
This corrosion potential has a slightly higher value than the OCP in figure 5.3, due to the low potential where the potentiodynamic scan started. At this potential the surface of the metal will be activated resulting in a faster hydrogen reduction reaction (an increase of the exchange current density) explaining the small increase in corrosion potential.

![Fig.5.4: Potentiodynamic polarization of CASIM samples in 1.5M NaCl with phosphate buffer pH 5.6, with d=10mm exposed](image)

No clear Tafel region could be identified; therefore it was not possible to do an approximation of the current density, $i_{corr}$. However, it could be clearly seen that the behavior of the all samples was essentially identical throughout the polarization curve. Also, no indication of passivity was seen on the anodic branch of the polarization, an indication of continuous dissolution of the sample, which was in agreement with the uniform corrosion attack as observed after exposure.

### 5.3.2 Case 2

A representative selection of the results of the potentiodynamic polarization curves is presented in Fig 5.5. Two different groups were identified in the experiments performed: one group had $E_{corr}$ values between -400 and -250mV and current densities of over 1µA/cm²: this group will be referred in this paragraph as Group 1. The second group had $E_{corr}$ values of -150mV and much lower current densities throughout the full polarization curve; it will be referred to as Group 2.

From the 15 polarizations performed (5 for each of the 3 different samples), 13 curves were found in Group 1, and the other 2 in Group 2; furthermore, Group 2 was composed of one measurement of sample 100%M (experiment number 3 of this type of sample), and one sample 0%M (experiment number 4 of this type of sample). All of the measurements made on sample 50%M were found in Group 1.
It should also be mentioned that the curves from Group 1 presented a very noisy behavior, especially in the anodic branch, as seen in Fig. 5.5. Also more spread in the results concerning potential and current values was seen, while the two curves from Group 2 showed basically no difference between them.

The open circuit potential measurement performed on the samples of Group 2 (thick lines, potentials approximately -150mV at the final part of the curve) and one random selection of a sample of Group 1 are presented in Fig. 5.6 (thin line, experiment number 2 of the 100%M samples, potential around -400mV at the final part of the curve). These measurements were performed immediately before the potentiodynamic scans. It can be seen that the behavior of the curve for both samples of Group 2 is characterized by a constant increase in the rest potential value during the complete measurement, reaching a value of approximately -150mV after the 3 hour immersion in the electrolyte. Also, the starting potential measurement was found to be in around -275mV for both measurements. On the other hand, all the curves of Group 1 presented a more irregular behavior throughout the complete measurement, having starting potentials in the range from -100 to -400, uneven evolution during the experiment (noise-like behavior) and final potential spread in a range of 200mV.

---

**Fig.5.5: Potentiodynamic polarization of CASIM samples in 0.1M NaCl with carbonate buffer pH 10, with d=10mm exposed**
Macro Electrochemical Measurements on DP Steels: Conventional Cell

Fig.5.6: OCP of CASIM samples in 0.1M NaCl with carbonate buffer pH 10, with d=10mm exposed

Fig.5.7: Localized attack on samples after polarizations in 0.1M NaCl with carbonate buffer pH 10, with d=10mm exposed. Left: Sample 100%M-2, Right: Sample 50%M-1

Photographs were taken from the surface of the samples after the complete polarization experiments. These are presented as Fig 5.7. Severe localized attack can be seen in these pictures in areas were the O-ring of the electrochemical cell touched the surface of the samples. The photographs presented in Fig. 5.7 correspond to experiments from Group 1; no evidence of crevice was seen on the samples from Group 2. As reported in [14-20], the increase in the values of the
current density together with the localized attack seen at the junction between the 
specimen and the holder in the electrochemical cell, are clear indicators of the 
presence of crevice corrosion in the polarization measurements.

The 2 experiments in Group 2 were characterized by having current values almost 2 
orders of magnitude lower than the ones seen on Group 1, an $E_{\text{corr}}$ around -150mV, a 
steady and monotonically increasing OCP curve, as well as a more stable 
potentiodynamic scan.

Even though the potentiodynamic scans do not show a sudden increase in the 
measured current during the polarizations of the samples in Group 1, it is suggested 
that a localized attack was already affecting the surface of the sample during the 
OCP measurement (decreasing and noisy-influenced corrosion potential), generating 
higher general current values throughout the subsequent polarization scan. So we 
will not further discuss the experiments from Group 1.

Visual inspection showed no clear indication of crevice on the surface of the samples 
in Group 2; taking into account the significant difference in the electrochemical 
behavior of both groups, it is fair to state that these samples are crevice-free. And 
even though only 2 curves were part of this group, it is interesting to notice that their 
results were practically identical, especially as one of the curves is a 0%M and the 
other one was a 100%M.

Although there were not enough experiments in Group 2 to make an adequate 
assessment of the influence of the microstructure on the electrochemical behavior, it 
seems justified to suggest that the amount of martensite does not have an effect in 
the response. As this electrochemical system is studied in the same electrolyte as 
Case 3, further discussion on the results of this Case are covered in 5.3.3. In this 
paragraph we will also discuss further work to try to avoid crevice corrosion.

5.3.3 Case 3

The first set of experiments performed on the samples showed that, like in Case 2 of 
this chapter, the measurements performed for all the dilatometer samples in the 
electrochemical cell with exposed 3mm diameter were extensively affected by 
crevice. In order to try to avoid the generation of crevice effects on the surfaces, 
several additional attempts were performed on a single microstructure (sample A, 
fully martensitic sample, small grains) while varying the pressure applied on the 
surface of the sample by the O-ring (Fig.5.8). This was controlled by adjusting the 
torque applied on the screws of the electrochemical cell to ensure tightness while still 
avoiding leakage of electrolyte. The reason behind this was that due to the fact that 
the O-ring is made of donut-shaped butadiene rubber, a highly deformable 
elastomer, when applying a high strength on the O-ring against the surface the high 
deformation of the rubber increases the chances of crevices being formed between 
the O-ring and the surface. Nevertheless, when applying a low amount of strength in 
the attempt of generating hardly any deformation of the O-ring resulted in leakage of 
electrolyte. The attempts were recorded and can be seen in Fig. 5.8.
Fig. 5.8: Crevice on the surfaces of 7 different specimens of samples type A after OCP and potentiodynamic polarization in 0.1M NaCl with carbonate buffer pH 10, with d=3mm exposed.

As it can be seen from Fig. 5.8, the electrochemical tests with butadiene O-ring showed a predominant effect of crevice. It was then decided to change the material and shape of the O-ring to try to avoid crevice corrosion: a new cylindrically shaped Viton O-ring was selected (Fig 5.9).

Fig. 5.9: 3mm diameter O-rings: donut shaped butadiene (black, left) and cylindrical shaped Viton (white, right).

Viton\(^1\) is a brand of synthetic rubber and fluoro-polymer elastomer commonly used in O-rings and other moulded or extruded goods. This material was selected because it does not possess the elastic properties of butadiene, preventing the excess of elastic deformation on the surface of the sample. Moreover, the cylindrical shape helped

\(^1\) The name is a registered trademark of DuPont Performance Elastomers L.L.C.
avoiding the formation of crevices as the flat O-ring is pressed against the flat surface, unlike the donut-shaped one where the curved surface of the O-ring is deformed against the flat surface.

Two complete polarization curves made with the Viton O-ring are compared in Fig. 5.10; both measurements were made on 2 identical specimens of samples type A. It can be seen from Fig 5.10 that both samples, though tested in the same electrochemical system showed a very different behavior.

When analyzing the condition of the surfaces after the polarization, it was clearly seen that the differences measured electrochemically could also be identified on the surface: sample A1 only showed signs of localized attack in the area exposed to the electrolyte, while sample A8 showed, besides signs of localized attack in the form of pits in the exposed area, a very clear and dramatic localized attack in the area covered by the O-ring, which is clearly seen in Fig. 5.10. As discussed for Case 2 (paragraph 5.3.2), this was identified as crevice corrosion.

The type of behavior showed in Fig 5.10, although presented here for only samples type A, was characteristic of the tests performed on the four types of samples for Case 3 listed in table 5.1. A total of 43 experiments were performed with the Viton O-ring on the 4 types of sample; only four polarization tests showed the behavior seen in sample A1, meaning by this a hypothetically crevice-free measurement. Table 5.2
shows a summary of the complete set of experiments performed with the Viton O-ring.

Table 5.2: Summary of polarization tests and hypothetically crevice free experiments of on the dilatometer samples with the Viton O-ring

<table>
<thead>
<tr>
<th>Type of microstructure</th>
<th>Total number of experiments</th>
<th>Number experiments with no evident indication of crevice</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>I-50%M</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>A-100%M_SG</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>E-100%M_LG</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

As the vast majority of the electrochemical measurements performed were influenced by the presence of crevice, it was not possible to determine the electrochemical behavior of the system by this method.

Even though it was possible to obtain what appeared to be a crevice-free measurement by using the Viton O-ring, only less than 10% of the experiments presented this kind of behavior. Furthermore, these O-rings presented other drawbacks that diminished the reproducibility of the tests: the main difference between the characteristics of the butadiene and the Viton O-rings is the elasticity. The elastic deformation range of the first one is much higher than the second, and this characteristic helps in the control of leakage. The Viton O-ring has to be tightened with much greater force in order to ensure that no leakage happened during the test. This force exceeded the elastic range of the material, generating a plastic deformation (permanent deformation) of both the O-ring and the base of the electrochemical cell which is also made of polymer. The permanent deformation of both elements compromised the measurement of the area of the sample exposed to the electrolyte, and the general geometry of the cell: this effect meant dealing with different cell geometries and/or damaged O-rings in subsequent measurements, making the reproducibility of the test a difficult task. This explains why crevice was only avoided in a few of the experiments.

Using only the limited number of crevice-free measurements in combination with surface analysis showed that the OCP regularly increase in value and after 3 hours is around -200mV with respect to the SCE electrode. This value is very similar to the -150mV vs. Ag/AgCl electrode measured for the CASIM samples in Case 2 of this chapter. This will be used in the discussion given in paragraph 5.4. Also the current density values around the corrosion potential are low and around 0.1μA/cm², for the crevice free measurements.

Now, the electrochemistry of Case 3 as well as Case 2 can be described as follows: beside the dissolution of Fe, the high pH of the solution makes the oxygen reduction reaction the main cathodic reaction of the system. As described in Chapter 4, the free electrons in the metal react with the oxygen molecules to produce hydroxyl ions. This induces the direct precipitation of Fe(OH)₂/Fe(OH)₃ on the surface of the sample. This Iron hydroxide, together with possibly FeCO₃ forms a first protective film on the
surface of the sample during the OCP [18, 21-31]. This explains the increase in the value of the OCP shown in Fig. 5.6 and 5.10.

Fig. 5.10 indicates a continuous moderate increase in the current values as a function of increasing potential, until approximately 300mV, where a sudden increase in the current suggests the development of localized attack. This pitting attack is the result of the breaking down of the formed passive layer (probably by then a double oxide layer, γ-Fe₂O₃/Fe₃O₄ as described in Chapter 4) on the surface of the sample resulting from the high concentration of Cl⁻ ions. The pits are clearly observable in Fig. 5.11; this figure is a detail of the sample A1 from Fig. 5.10.

Fig. 5.11: Detail of the surface of sample A1 (Fig. 5.10) after polarizations. The black circle represents the approximate position of the O-ring during the test.

5.4 Conclusions

The selection of the two electrolytes had as a purpose the identification and comparison of the electrochemical behavior for the samples under an aggressive environment (low pH and high concentration of chlorides) and also a mild environment (high pH, low concentration of chlorides). By studying both electrolytes, it was intended to identify differences in the breakdown potential of each of the samples as well as in the possible general dissolution behavior.

In this chapter, 3 different experimental approaches are presented. The intention of studying the electrochemical response of the system as a function of microstructural variations on the samples was only obtained with the experimental work shown in Part 1. The results of the experiments in Case 2 and 3 of this chapter are dominated by the presence of crevice corrosion.

For Case 1, all experiments had a very similar response throughout the complete polarization. It could be said that the behavior of the sample was independent of the amount of martensite present in the microstructure. However the high concentration of chlorides and the active state of the sample due to the low pH in the system, provided a highly aggressive solution for bare steel, leading to a masking effect of any possible differences between the microstructures. A key factor then, in order to identify and quantify a difference (if any), was the selection of the electrolyte used for the polarization.
Unfortunately, the crevice corrosion control of the experiments in Case 2 and 3 prevented a proficient description of the electrochemical system from being made. Nevertheless the results of these two parts together bring important conclusions:

Even though only a limited number of experiments appeared to have a crevice free surface, it was possible to determine that by observing the behavior of the OCP it was possible to determine if crevice was being formed during the experiment: when measuring with the 0.1M NaCl with pH 10 electrolyte, the OCP should have a monotonically increasing behavior, and should have a value of approximately -200mV vs. SCE after 3 hours of exposure. It can be concluded (though statistically inaccurate due to the limited number of experiments), that this behavior was not affected by the martensite concentration in the microstructure; and even more, it also did not seem to be affected by the type of sample or setup, as this behavior (and value) was measured for both the CASIM samples in a setup with exposed diameter of 10mm and the dilatometer samples in the setup with exposed diameter of 3mm.

The crevice-free measurements had current levels around 0.1µA/cm², independent on the heat treatment route used. Although only few measurements support this, this current behavior was also independent of the underlying microstructure of the samples.
5.5 References

CHAPTER 6.  MACRO ELECTROCHEMICAL MEASUREMENTES ON CASIM SAMPLES WITH AVESTA CELL

6.1 Introduction

Chapter 5 describes several approaches that were made in order to perform macro electrochemical measurements on the modified DP microstructures. Unfortunately, the great majority of the results were hindered due to crevice corrosion. This type of corrosion proved to be the dominant factor when analyzing the results of the polarization measurements. Thus it proved impossible to decide on different electrochemical behavior for the various microstructures.

In the attempt of avoiding crevice a slightly modified Avesta cell was used to run OCP and potentiodynamic scans. Due to the size of the cell, the setup is only suitable for the DP samples that were modified in the CASIM equipment (Chapter 3). For these samples, that are characterized by having phase ratios ranging from nearly fully ferritic to fully martensitic, the effect of the individual and combined ferrite and martensite phases on the corrosion performance and electrochemical behavior was investigated. The effect of the chloride concentration and the presence of a carbonate buffer solution in the electrolyte were also taken into account. The electrochemical work was complemented by optical surface analysis.

6.1.1 Avesta cell background

A very frequent but often neglected problem faced, when dealing with electrochemical corrosion tests is the occurrence of crevice corrosion below coated or isolated parts of the working electrode, as also discussed in Chapter 5 inducing an early breakdown of passivity and erroneous interpretations of experimental data as we will discuss in chapter 7.

In the late 1980's at the corrosion laboratory of Avesta Steel in Sweden, a new method of specimen mounting was developed by Rolf Qvarfort [1-5]. The surface of the working electrode is pressed against an opening in the bottom of the electrochemical cell. A ring of filter paper tightens the border line of the specimen, as shown in Fig. 6.2. Distilled water is passed through this filter paper ring into the cell at a very low rate (usually between 0.5 and 5ml/hr) controlled by a peristaltic pump. The idea behind this is to avoid the contact between the corroding electrolyte and the zone between the surface of the sample and the O-ring, preventing accumulation of aggressive electrolytes in the artificial crevice. Considering the fact that only a small volume of distilled water is added to the original electrolyte, it can be assumed that it does not have any significant influence on the test, therefore avoiding disturbance or modification of the electrochemical system during the measurement.
6.2 Experimental

The samples used for these experiments were the modified microstructures obtained with the CASIM, as described in paragraph 3.4.1.

Potentiodynamic curves for the 3 groups of samples were measured. The experimental conditions and settings of the set of tests are presented in Table 6.1. All
the potentiodynamic polarization experiments were done immediately after a 30
minute OCP measurement where the electrochemical system was stabilized.

Table 6.1: Electrochemical conditions and settings for Potentiodynamic scans

<table>
<thead>
<tr>
<th></th>
<th>Macro Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>-75mV to 1V wrt OCP*</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>1mV/s</td>
</tr>
<tr>
<td>Exposed Area</td>
<td>2.69cm²</td>
</tr>
<tr>
<td>Reference Electrode</td>
<td>Standard Calomel Electrode</td>
</tr>
<tr>
<td>Counter Electrode</td>
<td>Platinum</td>
</tr>
</tbody>
</table>

*The range of the scan varied slightly depending on the electrolyte

Seven different sets of experiments were performed (Table 6.2). The difference
between these sets of experiments was the electrolyte used. The electrolytes were
prepared in deionised water, while the carbonate buffer consisted of a mixture of
Na₂CO₃ and NaHCO₃ (10.6 and 8.4 grams respectively) in one litre of deionised
water.

Table 6.2: Electrolyte composition

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02M NaCl</td>
</tr>
<tr>
<td>2</td>
<td>0.1M NaCl</td>
</tr>
<tr>
<td>3</td>
<td>0.5M NaCl</td>
</tr>
<tr>
<td>4</td>
<td>0M NaCl with carbonate buffer pH 10</td>
</tr>
<tr>
<td>5</td>
<td>0.02M NaCl with carbonate buffer pH 10</td>
</tr>
<tr>
<td>6</td>
<td>0.1M NaCl with carbonate buffer pH 10</td>
</tr>
<tr>
<td>7</td>
<td>0.5M NaCl with carbonate buffer pH 10</td>
</tr>
</tbody>
</table>

The selection of these electrolytes was based on the following: First, different sodium
chloride concentrations were used because a very aggressive electrolyte might
dominate and mask the microstructural influence on the corrosion performance, if
any. Also, a high concentration of chlorides can increase/enhance the effect of
crevices present in the setup. Furthermore, a buffer solution with alkaline pH will
generate a passive layer on the steel surface which might lead to an identification of
differences based on the breakdown of that passivity by local microstructural
variations.

All the samples used for these measurements were previously ground with silicon
carbide paper FEPA 1200 and 2400, and further polished with diamond paste cloth
down to 9, 6, 3, and 1µm respectively, including intermediate ultrasonic cleaning
baths in ethanol. All the tests were performed at room temperature. The polarization
curves for each of the 21 different conditions (3 martensite concentrations in 7
electrolyte variations) were measured a minimum of 3 times per condition.

The three electrode electrochemical cell setup used was the Avesta Cell from Bank
Elektronik Intelligent Controls GmbH and the equipment used for all the polarization
measurements was a Solartron Electrochemical Interface with software CorrWare for
Windows Version 2.80. This setup was used in order to prevent and delay as much
as possible the generation of crevices in the surface of the samples. It is important to
mention that even though an Avesta cell setup was used, two main modifications were established in the experimental procedures with respect to [1-5]: to prevent early crevicing, no filter paper was used between the O-ring and the working sample, and the flux used was the same electrolyte instead of deionised water. Furthermore, the flux of the same testing electrolyte to the sample surface by peristaltic pumping was fixed at a rate of 10 ml/hour.

These two modifications were applied because during the first trial experiments with the Avesta cell, the filter paper seemed to be concentrating the chlorides contained in the solution, augmenting the localized effect and generating severe localized corrosion. Several runs were performed until it was discovered that removing the filter paper resulted in an apparently crevice free surface. It is thought that the reason for this is that while the Avesta cell was developed for passivating metals like Al or Stainless Steels, the filter paper served as mechanism to prevent the formation of crevice on the O-ring / sample interface on a naturally passivated surface. As the passive layer on these CASIM samples is obtained thanks to the reaction of the surface with the buffered electrolyte, the use of the filter paper created an unprotected area of the sample due to the restricted contact between surface and electrolyte; the use of the filter paper therefore induced localized attack.

6.3 Results

To study the effect of reproducibility and significance of variations observed, all figures representing OCP evolution and potentiodynamic polarization measurements presented in this chapter include 2 measurements for each experimental condition (fixed microstructure and fixed electrolyte). These measurements represent the upper and lower boundary limits of each experimental condition, and were selected based on the highest and lowest value of potential measured after the 30 minute OCP, respectively. All potential values presented in this chapter are measured vs. the Standard Calomel Electrode.

6.3.1 Electrolytes 1, 2 and 3: No Buffer solution

The results of the OCP and potentiodynamic polarization measurements for a fixed microstructure (50%M) in the solutions without buffer are presented in Fig. 6.3a and b. Fig. 6.3a shows a gradual decrease of OCP as a function of time for 0.02M, 0.1M and 0.5M NaCl electrolytes. This decrease appeared to be more pronounced and towards a more negative potential as a function of increased chloride concentration in the solution. The largest decrease in OCP can be observed for the 0.5M NaCl electrolyte towards approximately -750mV after 30 minutes of exposure. The OCP stabilization period decreased with increasing NaCl concentration. Fig. 6.3b shows a distinct increase in anodic current densities as a function of over-polarization and NaCl concentration. These experiments indicate that the increase in the concentration of chloride induces an increase in the general corrosion of the sample.
Fig. 6.3: Typical OCP (a, left) and potentiodynamic (b, right) curves for 50%M microstructures in 0.02M, 0.1M and 0.5M NaCl

Figure 6.4 shows the surface of a sample of each 0, 50 and 100%M groups after polarization for each of the electrolytes without buffer. For all the experiments the severity of corrosion attack increased with the NaCl concentration in the electrolyte. A general uniform corrosion attack was observed for all samples. Even though some signs of crevice are still noticeable, this effect was considered not to be a dominant factor during the polarizations.

<table>
<thead>
<tr>
<th></th>
<th>0.02M NaCl</th>
<th>0.1M NaCl</th>
<th>0.5M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0%M</strong></td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td><strong>50%M</strong></td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td><strong>100%M</strong></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 6.4: Examples of the surface of the specimens after polarizations in chloride containing unbuffered solutions
Fig. 6.5 through 6.7 show the different martensite phase ratios compared for the 3 electrolytes without buffer.

Fig. 6.5: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.02M NaCl

Fig. 6.6: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.1M NaCl

Fig. 6.7: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.5M NaCl
Table 6.3 shows a summary of the results obtained in the Open Circuit Potential and polarization curves of the samples in unbuffered solutions with different concentration of chlorides, as presented in Fig. 6.5 to 6.7.

Table 6.3: Summary results polarization curves for CASIM sample in Un-Buffered solutions with different chloride concentrations

<table>
<thead>
<tr>
<th>ELECTROLYTE</th>
<th>SAMPLE</th>
<th>OCP (mV)</th>
<th>Ecorr (mV)</th>
<th>Icorr (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No BUFFER</td>
<td>0.02M</td>
<td>0%M</td>
<td>-579 28</td>
<td>-583 29</td>
</tr>
<tr>
<td></td>
<td>50%M</td>
<td>-605 19</td>
<td>-612 19</td>
<td>7.3 4.9</td>
</tr>
<tr>
<td></td>
<td>100%M</td>
<td>-575 57</td>
<td>-582 54</td>
<td>6.8 4.5</td>
</tr>
<tr>
<td></td>
<td>0.1M</td>
<td>0%M</td>
<td>-630 49</td>
<td>-635 50</td>
</tr>
<tr>
<td></td>
<td>50%M</td>
<td>-634 16</td>
<td>-641 15</td>
<td>16.2 6.8</td>
</tr>
<tr>
<td></td>
<td>100%M</td>
<td>-660 38</td>
<td>-666 37</td>
<td>15.5 6.6</td>
</tr>
<tr>
<td></td>
<td>0.5M</td>
<td>0%M</td>
<td>-702 39</td>
<td>-708 44</td>
</tr>
<tr>
<td></td>
<td>50%M</td>
<td>-696 65</td>
<td>-698 64</td>
<td>11.6 5.6</td>
</tr>
<tr>
<td></td>
<td>100%M</td>
<td>-682 53</td>
<td>-686 54</td>
<td>10.4 0.7</td>
</tr>
</tbody>
</table>

In general terms, for all the measurements performed in electrolytes without the carbonate buffer (Fig. 6.5 to 6.7), the OCP decrease with time corresponds to general corrosion of the substrate surface. Within the 30 minutes of exposure the decrease of the OCP is highest and fastest for the highest NaCl concentration of 0.5M NaCl. No passive behavior could be identified, and general corrosion was observed for all samples (Fig. 6.4). This is in agreement with the increasing anodic current density observed in the polarization curves.

While a clear correlation with the NaCl concentration was observed, the polarization curves for all NaCl concentrations showed no significant correlation with the amount of martensite present in the microstructure of the samples.

6.3.2 Electrolytes 4, 5, 6 and 7: Carbonate Buffer solution at pH 10

The results of the OCP measurements and the potentiodynamic scans for the 50%M sample in the carbonate buffer are presented in Fig. 6.8a and b. Unlike for the unbuffered solutions, the different concentrations of NaCl showed different evolution trends of the OCP and the polarization curves. Fig. 6.7a shows that for the highest NaCl concentration (0.5M), the OCP had a different evolution with time as compared to that for the other 3 concentrations: while the OCP values of the buffered 0M, 0.02M and 0.1M NaCl increase throughout the 30 minutes stabilization period, the potential of the samples in the buffered 0.5M NaCl electrolyte decreased throughout the measurement, showing a trend more similar to the ones obtained in the unbuffered solutions.

Fig. 6.8b shows different polarization behavior for each of the electrolytes. The polarization curves in the buffered 0M, 0.02M and 0.1M NaCl showed a passive behavior at potentials higher than the corrosion potential (characteristic plateau showing a near constant current density with increasing potential), while no passivity could be identified for the buffered 0.5M NaCl electrolyte. It can also be observed that the breakdown potential for this passivity varies with the NaCl concentration: when the concentration of NaCl in the electrolyte increases, the value of the breakdown potential decreases. This was not the case for the buffered 0.5M NaCl.
Macro Electrochemical Measurements on CASIM samples with Avesta Cell

electrolyte, as no breakdown potential could be identified after a clearly visible passive range.

Nevertheless, two characteristics suggest that the carbonate buffer does have a passivating effect on the samples: first, the OCP value after 30 min immersion is almost 300 mV higher than obtained with the unbuffered solution. Second, the pitting behavior observed on the samples (Fig 6.9c) suggest the formation (and break) of a protective layer, unlike the general corrosion effect seen on the unbuffered samples. Another important fact to be noticed from Fig. 6.8b is the noisy response of the curve around the corrosion potential. This behavior was especially noticeable in the buffered 0.02 M NaCl solution where it spread for more than 200 mV, while in the buffered 0.1 M NaCl electrolyte the potential range of this noise was around 50 mV and in the buffered 0 M NaCl solution was not detectable. The curves of the samples polarized in the buffered 0.5 M NaCl solution did not show any noise-like behavior. This noise seems to start just before reaching the corrosion potential, and continued on the anodic branch of the curve until the start of the passivity range of the curves.

![Fig. 6.8: Typical OCP (a, left) and potentiodynamic (b, right) curves for 50%M microstructures in 0M, 0.02M, 0.1M and 0.5M NaCl with carbonate buffer pH10](image)

Fig. 6.8 shows the surface of the 50%M sample immediately after the polarization experiment for each of the electrolytes with carbonate buffer. In all the experiments involving the presence of NaCl, a characteristic localized pitting attack was observed (Figure 6.9 a, b and c). The samples polarized in buffered 0 M NaCl electrolyte clearly showed no signs of localized attack (Fig. 6.9d).

![Fig. 6.9: 50%M sample surfaces after polarizations in carbonate buffered a) 0.02M, b) 0.1M, c) 0.5M and d) 0M NaCl](image)
Like in Fig. 6.8 and 6.9, the results of the electrochemical experiments performed on the 0%M and 100%M samples showed similar results for these conditions. Figures 6.10 to 6.13 show the different martensite phase ratios compared for the 4 electrolytes with carbonate buffer.

Fig. 6.10: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0M NaCl with carbonate buffer

Fig. 6.11: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.02M NaCl with carbonate buffer

Fig. 6.12: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.1M NaCl with carbonate buffer
Macro Electrochemical Measurements on CASIM samples with Avesta Cell

Fig. 6.13: Typical OCP (a, left) and potentiodynamic (b, right) curves for 0, 50 and 100%M microstructures in 0.5M NaCl with carbonate buffer

Table 6.4 shows a summary of the results obtained in carbonate buffered solutions with different concentration of chlorides, as presented in Fig. 6.10 to 6.13. The values presented in this table are OCP (as measured after exposure for 30min), Ecorr, Break and “Range Ecorr”. Break represents the breakdown potential (potential at which a sudden and fast increase of current density appeared, related to the appearance of pitting breaking the passive layer on the surface of the sample).

The “Range Ecorr” is a term introduced in this table to account for the oscillatory behavior of the current density values identified in the polarization curves around the corrosion potential, particularly clear in the experiments performed with the buffered electrolytes with 0.02 and 0.1M NaCl. This “Range Ecorr” was calculated as the potential covered from the starting to the end point of the oscillatory behavior of the measurement. This parameter was determined while it was impossible to determine values for Ecorr and Icorr under those experimental conditions.

Table 6.4: Summary results polarization curves for CASIM sample in carbonate buffered solutions with different chloride concentrations

<table>
<thead>
<tr>
<th>ELECTROLYTE</th>
<th>SAMPLE</th>
<th>OCP (mV vs SCE)</th>
<th>Ecorr (mV vs SCE)</th>
<th>&quot;Range Ecorr&quot;</th>
<th>Icorr (µA/cm²)</th>
<th>Break (mV vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH10 0M</td>
<td>0% M</td>
<td>-261 5 -290 4</td>
<td>&quot; &quot; 1,1 0,1</td>
<td>813 18</td>
<td>* * * * *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% M</td>
<td>-265 13 -288 13</td>
<td>&quot; &quot; 2,0 0,4</td>
<td>788 60</td>
<td>* * * * *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% M</td>
<td>-259 2 -283 10</td>
<td>&quot; &quot; 0,8 0,2</td>
<td>810 15</td>
<td>* * * * *</td>
<td></td>
</tr>
<tr>
<td>pH10 0.02M</td>
<td>0% M</td>
<td>-213 55 415 296</td>
<td>&quot; &quot; * 443 38</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% M</td>
<td>-252 30 237 110</td>
<td>&quot; &quot; * 560 92</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% M</td>
<td>-268 77 430 139</td>
<td>&quot; &quot; * 470 10</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH10 0.1M</td>
<td>0% M</td>
<td>-250 46 57 12</td>
<td>&quot; &quot; * 17 29</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% M</td>
<td>-234 11 53 13</td>
<td>&quot; &quot; * -62 14</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% M</td>
<td>-303 39 50 0</td>
<td>&quot; &quot; * -10 15</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH10 0.5M</td>
<td>0% M</td>
<td>-462 22 -472 31</td>
<td>&quot; &quot; 6,2 1,5</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% M</td>
<td>-447 15 -450 10</td>
<td>&quot; &quot; 3,4 0,3</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% M</td>
<td>-470 22 -463 39</td>
<td>&quot; &quot; 5,8 3,5</td>
<td>* * * * * *</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regarding the experiments with the carbonate buffer (Fig. 6.10 through 6.13), two different cases should be analysed. The first one is the case for low concentrations of NaCl (buffered 0M, 0.02M and 0.1M, Fig. 6.10, 6.11 and 6.12 respectively): the OCP values increased to a more anodic value during the 30 minutes of immersion in the electrolyte, suggesting some passivation. The other case is the one with the highest concentration of NaCl (buffered 0.5M, Fig. 6.13a): the OCP decreased in time as for the electrolytes without buffer. In this case, the high concentration of NaCl seemed to
result in a deterioration of the passive film compared to the other buffered solutions with lower NaCl concentrations. The buffered 0.5M NaCl case showed indeed localized attack in the form of pits (like all the samples in the buffered solutions with NaCl, Fig. 6.9).

In the potentiodynamic polarization scans for the buffered 0.02M and 0.1M NaCl electrolytes (Fig. 6.11b and 6.12b), a noise-like zone was measured in the range between the cathodic and anodic branches of the polarization. This effect was especially noticeable in the samples tested in the buffered 0.02M NaCl concentration electrolyte, where the noise extended for over 200 mV for all cases. Likewise, in the electrolyte with buffered 0M NaCl (Fig. 6.10b) the noise-like behavior extended for around 25 mV, but it was still possible to identify a corrosion potential within these polarizations. In the buffered 0.5M NaCl electrolyte, no noise was observed, and a clear corrosion potential could be identified.

Another aspect of the potentiodynamic scans was the identification of a passive behavior (characteristic plateau showing a near constant current density with increasing potential). In the buffered 0M NaCl electrolyte, this plateau did not show a breakdown before reaching 800mV for all the samples, while for the buffered 0.02M and 0.1M NaCl, a breakdown could be identified around 500mV and 0mV respectively. This breakdown was characterized by the occurrence of pitting in the surface of the sample. For the buffered 0.5M NaCl electrolyte the passivity range was not clearly visible. The corrosion current was very high and despite the observation that some pitting events took place, the overall corrosion overwhelmed the behavior immediately. No breakdown was seen in the curves of the electrolyte without NaCl, and no pits appeared on the surface of those samples.

The polarization curves for the 4 different buffered NaCl concentrations showed no distinct correlation with the amount of martensite present in the microstructure of the samples.

6.4 Discussion

This chapter aims to study the influence of microstructure on the electrochemical behavior of DP steels. Three model samples obtained with the CASIM are studied with different amount of ferrite and martensite phases: the martensite phase area percentages ranges varied from approximately 5% martensite (referred to as 0%M), to 80% martensite (referred to as 100%M). The results are discussed taking into account the presence/absence of buffer in the electrolyte.

ELECTROLYTES WITHOUT BUFFER:

The differences in the electrochemical behavior for all samples studied can be attributed and correlated to the concentration of NaCl present in the electrolyte. As reported by other authors, e.g.[6-9], a typical behavior of the OCP measurements was identified: the corrosion potential after 30 minutes of exposure of the 3 different microstructures decreased with the NaCl concentration in the electrolyte. Uniform corrosion was observed on the surface of all samples, and although largely reduced with the use of the modified Avesta Cell setup, some minor indications of crevices
were still noticeable especially for the 0.02M and 0.1M NaCl solutions. No noise-like behavior, no passivity and no breakdown potential could be identified in the polarization curves of these experiments.

No relation or trend could be established between the ferrite/martensite ratio and the electrochemical response in OCP and polarization experiments. Differences observed were within the range of reproducibility.

ELECTROLYTES WITH CARBONATE BUFFER pH 10:

As has been described also by other authors [10-19], a “passive” layer could be identified by the presence of a plateau region (constant current density) in the anodic branch of the polarization curves. For non stainless steel grades a relatively high pH (10 in our case) is needed in order to obtain any layer formation. Furthermore as also reported by Al-Kharafi in [16], the potential range for the passive region is strongly dependent on the chloride concentration. However, it still should be mentioned that this passive layer formed can be considered relatively poor when compared to the natural oxide passive effect seen on Stainless grades: SS have higher OCP values (close to 0mV) and lower passive currents in the range of 0.1 to 1μA/cm² [20-23] when compared to the nearly 10μA/cm² measured in the experiments in these chapter.

Passivity was clearly observed in the buffered 0M, 0.02M and 0.1M NaCl electrolytes, but only faintly in the buffered 0.5M NaCl; it is thought that this is due to the fact that the highest concentration of NaCl generates a highly aggressive solution, and the effect of the buffer is not enough to generate a well protecting passive layer. This is confirmed by the fact that during the OCP measurements for 0.5 M NaCl, a decrease of the potential in time is measured [6-9], as was seen for the unbuffered solutions, where no passivity at all was observed. However, the OCP value after 30 minutes was substantially higher than for the unbuffered solutions, suggesting that some film remained on the surface.

Breakdown of the passivity was observed by a sudden increase of current density and directly related to pitting, as widely found in literature. It was also confirmed that with increasing concentration of NaCl, the breakdown of the passive layer occurred closer to the OCP, i.e. a smaller passive region was observed, as also reported in [16, 24-26]. For 0.5 M NaCl, the faint passivating effect of the high pH, still leads to some localized attack, but without the presence of a distinct breakdown potential because general corrosion immediately starts when the very poor film is dissolving. For the buffered 0M NaCl electrolyte, a very stable passivity was obtained and no breakdown was identified in the polarization curve and no pits were observed on the surface of the samples after the experiments.

Another important issue that should be addressed is the “noise-like” behavior encountered around the corrosion potential for the buffered 0.02M and 0.1M NaCl electrolytes; the noise started on the cathodic branch of the polarization close to the corrosion potential and continued until a potential was reached well within the passivity range. Similar oscillatory behavior of the current in the passive-active transition state of iron in H₂SO₄ solutions has been reported [9, 26-30], where it was
explained by the presence of a “porous” not yet completely protective film (FeSO₄ being transformed into an oxide layer). It is also closely related to metastable pitting phenomena [31-33]. Our experiments can also be explained by the continuous formation of a passive film in competition with the dissolution of this film by substitution of the oxygen by chlorides, until at higher potentials the rate of oxide formation surpasses the rate of dissolution, resulting in a stable passive film.

It can be concluded that for the sample variations studied in this chapter, no significant variations in the electrochemical response was found as a function of the ferrite/martensite ratio.

6.5 Conclusions

The present study aims to elucidate the effect of microstructural variations of a thermally modified commercial grade DP steel. Different heat treatment regimens were applied in order to create phase ratios ranging from nearly fully ferritic to fully martensitic as developed in Chapter 3.

All microstructures studied showed an increase in anodic current densities with NaCl concentration in unbuffered electrolytes, resulting in a uniform corrosion attack. Potentiodynamic polarization curves for NaCl concentrations ranging from 0.02M to 0.5M showed no significant correlation with the microstructural variations present in the modified dual phase steel, i.e. the ferrite/martensite phase ratio.

Competitive action of passive layer formation and breakdown by a carbonate buffer and chloride, respectively, was observed for the samples in buffered sodium chloride electrolytes. A clear passive layer formation was observed in the polarization curves for a buffered 0M NaCl electrolyte, while very poor passive behavior was observed for the buffered 0.5M NaCl electrolyte. For the intermediate buffered electrolytes of 0.02M and 0.1M NaCl, a passive range was observed narrowing down with increasing NaCl concentration.

While a clear electrolyte effect was observed, it can also be concluded that also for the buffered electrolytes no significant variation of the electrochemical response with the ferrite/martensite phase ratio was found.
6.6 References


CHAPTER 7. LOCALIZED ELECTROCHEMICAL MEASUREMENTS WITH A MICRO-CAPILLARY CELL

7.1 Introduction

In this chapter, a Micro-Capillary cell technique is used in order to study the local electrochemical behavior of different dual phase grade model microstructures. Open Circuit Potential and potentiodynamic polarizations were performed under diverse electrolytes and experimental conditions, in the attempt of finding a correlation of the microstructure with the local electrochemical behavior.

A detailed description of the microcell technique is given. Results for various electrolytes are discussed while conclusions on the local electrochemical behavior of the Dual Phase alloys are put in context with the macroscopic measurements presented in Chapters 5 and 6.

7.2 The Micro-Capillary Cell Technique

Common practice concerning electrochemical tests involves the evaluation of an area in the centimeter range. When attempting to evaluate localized phenomena in relation with the microstructure, the use of macroscopic techniques provides only limited information, as shown in the comparison presented in Fig. 7.1. Taking this into account, several micro electrochemical techniques like the Scanning Reference Electrode Technique (SRET), the Scanning Vibrating Electrode Technique (SVET), Local Electrochemical Impedance Spectroscopy (LEIS), the Scanning Kelvin Probe (SKP), Scanning Kelvin Probe Force Microscopy (SKPFM) and the Micro-Capillary Cell (or microcell) [1] were developed. These techniques provide information on the electrochemistry of a corroding system on a micrometer or even nanometer range. With the use of these techniques, the electrochemical behavior of single microstructural features like inclusions or grain boundaries can be investigated [2-5].

The scanning techniques allow acquiring information about the local distribution of one or more parameters during corrosion experiments. These experiments can be performed under open-circuit conditions or under potential or current control. Obtaining a lateral resolution down to a nanometer range is possible, depending on the scanning technique and type of measuring micro-probes. However, most of the scanning methods cannot measure local corrosion currents, as the current flow of the complete immersed area (SRET, SVET, LEIS) is controlled by the potentiostat [2]. The measurement of the Volta potential maps with techniques like SKP and SKPFM are widely recognized and used in the electrochemical studies, but the limitations of the electrolyte (if any at all) and the number of variables that can affect the measurement and the interpretation of the results is an issue [1, 2].

On the other hand, the 3-electrode arrangement used in Micro-Capillary cell technique provides the opportunity of a wider range of common electrochemical
techniques: This not only enables the analysis of the surface of the sample, but also the preparation and structuring of thin film devices (galvanization, passivation, deposition, e.g.) [2, 6]. Micro-Capillary electrochemical measurements provide the possibility of studying the effect of microstructural features on the corrosion mechanisms in an aqueous environment [7]. As such, it can be said that the Micro-Capillary cell is used because it offers the best direct local corrosion information.

This technique was developed at the Swiss Federal Institute of Technology Zürich during the 90’s. It has the possibility of performing different micro electrochemical measurements on areas as small as 1 μm² [2-4, 8]. It has been used in different electrochemical studies in the last few years like: studies of pit initiation at single inclusions on stainless steel [9-14], aluminum alloys [1, 15] and Duplex Stainless Steels [16]. It has also been used in electrochemical analysis of welds and micro-electronics [4].

![Diagram of electrochemical measurement setup](image)

**Fig. 7.1**: Comparison of macro and micro-electrochemical evaluation: the mm range area provides a general overview of different characteristic of the microstructure, while the μm range area provides specific information of a localized microstructural feature [2]

### 7.2.1 Description of the Setup

The microcell technique is based on the miniaturization of the standard 3 electrode cell setup and as it works under the same principle, it can perform standard electrochemical measurements like Open Circuit Potential and potentiodynamic/potentiostatic polarizations [17].
The miniaturization idea consists of reducing the area of the working electrode exposed to the electrolyte from the mm (or even cm) to µm range. This is done by means of a glass capillary which holds a droplet of the electrolyte on the surface of the sample. The tip of the capillary is shaped to a determined size ranging from 1 to 1000µm, and even though nanometer diameters have been used, the most common sizes used for electrochemical experiments are found between 10 to 100µm [8].

Fig. 7.2: A) Micro capillary cell setup mounted in optical microscope. B) Detail (red circle) of A): Glass capillary approaching the surface of the sample
The glass capillary is supported by a plastic holder which is mounted on the carrousel of an optical microscope. The plastic holder also will be filled with the electrolyte, and is connected to a platinum wire (that acts as counter electrode) and a reference electrode, as shown in Fig. 7.2. During the experiments, the capillary, the plastic holder for the capillary, the glass holder for the reference electrode and the tube connecting the plastic holder and the glass holder are filled with electrolyte, as seen in Fig. 7.2c. It is important to mention here that any air bubble trapped in the setup must be removed before starting the experiment. The set is installed in the carrousel of the optical microscope, providing visual inspection of the surface at different magnifications prior to the experiment, while also enabling a fast and precise positioning. Furthermore, a camera gives the option of analyzing and recording images of the surface after the polarization with the advantage of not having to move the sample from the stage of the microscope, making it easy to find the position where the test was made. All this equipment is contained inside a Faraday cage to minimize noise effects on the polarizations.

Besides the equipment shown in Fig. 7.2, the microcell setup is controlled by a high resolution potentiostat (Jaissle 1002T-NC-3). This is a modified low-noise operated potentiostat, due to fact that at this level of resolution voltage noise and current noise are critical factors. When proper cable shielding and Faraday cage are used, this potentiostat is capable of measuring corrosion currents as low as 10fA. This value corresponds to a current density of 10µA/cm² when the exposed area is delimited by glass capillary with a tip diameter of approximately 1µm [18].

The complete setup consisting of micro electrochemical cell, microscope, camera, high resolution potentiostat and computerized controller can be seen schematically in Fig. 7.3
7.2.2 Micro capillary and silicon gasket

Besides the use of a high resolution potentiostat and proper isolation to avoid noise influencing the measurements, there is another critical factor that determines the quality and reliability of the experiment: the glass capillary and its seal.

The preparation of the capillary for electrochemical measurements starts by “pulling” the glass capillary. In this first stage, a borosilicate glass is mounted in a micropipette puller, where a heating resistance increases the temperature of the glass up to its transition temperature and then is pulled creating 2 capillaries with narrow or even closed tips. The borosilicate glass capillary has the advantage that, as it is pulled, it maintains its ratio of inside diameter to outside diameter over the total taper (“plastically deformed” part of the glass capillary) length [19].

After it has been pulled, the capillary is carefully ground and polished until the inner diameter of the tip has the desired size. At this stage, it is very important that the finished tip is as flat as possible. In order to keep the capillary clean and avoid blockage (by dirt, dust, residuals of glass or grinding paper), intermediate flushes with ethanol are performed.

![Fig. 7.4: Micro capillary a) after application of silicon sealant and b) in contact with surface [4]](image)

The next step is to apply the silicone gasket. The polished glass capillary is dipped in the silicone in order to create thin layers that stick to the tip of the capillary. Before it dries, the capillary is flushed again with ethanol to avoid the silicone from drying inside the capillary, and therefore blocking it. Then the silicone is left to dry, before repeating the process several times. This is done until the height of the silicone gasket over the tip is approximately half of the size of the diameter of the capillary. An example of a finished capillary with the silicone seal can be seen in Fig. 7.4.

This silicone gasket avoids leakage of the electrolyte during the measurements, while also providing a cushion while approaching the hard sample surface thanks to the high deformability of the silicone. This cushion also helps keeping leak tightness when the surface of the working electrode is not completely flat. When the gasket works properly, no electrolyte penetrates under the seal and therefore no crevice corrosion can be expected.
7.2.3 Advantages and Disadvantages of the Technique

Like any other technique, the Micro capillary cell has its advantages and drawbacks that can be summarized as follows:

Advantages:

The main advantage of the technique, when compared to a normal electrochemical cell, is that thanks to the miniaturization of the working electrode (exposed area of the sample); it can achieve a very high local resolution. Depending on the size of the tip of the glass capillary, measurements on specific grains, grain boundaries, inclusions or other particles can be performed [10, 13, 14].

Furthermore, as it uses 3 electrode setup, it allows a full range of electrochemical techniques. This enables not only surface analysis, but also preparation and structuring of the surface of the sample (e.g., galvanization, passivation, deposition of thin films) [10, 13, 15]. This is not possible with other techniques like SVET or LEIS.

Another advantage of the Micro-Capillary cell setup is that the plastic holder (where the capillary is supported) is mounted in a microscope carrousel replacing an objective. These enables the search of specific sites in the sample, as well as the precise and fast positioning of the capillary for the measurement [10].

Additionally, modification of the basic setup allows for measurements with pH monitoring, temperature control, applied mechanical stress, micro-tribology and fluid flow [10].

Limitations:

The following drawbacks of the Micro-Capillary cell technique have been discussed by some researchers:

- Detection limits of current [13]: the point here is that the resolution of the potentiostat is the limiting factor when performing electrochemical measurements, as current resolution down to pA and fA levels is required when the exposed area is in the μm² range. This issue is solved by the use of a high resolution potentiostat. In a similar fashion, Birbilis discussed in [16] the influence of capillary size on limiting current density.

- Oxygen reduction reaction (ORR) is strongly affected by the use of the silicone rubber: According to Oltra in [17], experiments under a surrounding argon gas shielding of the pulled capillary in contact with the metallic surface showed a large effect on the ORR, as higher currents were measured in the cathodic branch of the polarization when no gas shielding was used. This remark highlights the possible complications when interpreting micro electrochemical measurements to explain the corrosion
behavior of systems where ORR is the controlling step (e.g. metallic microstructures in neutral conditions).

A comparable drawback is discussed by Krawiek in [14], where the size of the Micro-Capillary has an effect on the transport of species to the substrate, such as oxygen and protons.

- Based on the fact that ohmic resistance (working/counter electrode) is a geometry dependent factor, measurements on a smaller working electrode will generate a higher resistance and therefore affect the current measurements [16]. However, even though this fact can certainly have an effect when comparing micro and macro electrochemical measurements, no influence was observed in the results presented in Chapter 7 when changing the capillary size from 30 to 150μm.

- The effect of scan rate on electrochemical results, Micro-Capillary cell experiments have a short duration to avoid leakage or corrosion product blocking the capillary [14, 16]; in order to neglect this effect, for all the experiments performed in chapters 5 to 7 in this study, a fixed scan rate of 1mV/s was used independent of the setup (macro or micro) or sample.

7.3 Experimental Details

7.3.1 Samples

The samples used for these experiments were the modified microstructures obtained with the dilatometer, as described in Chapter 3.5, where the 5 type of samples are referenced as base material BM, commercial DP600, A-100%M with small grains (SG), E-100%M with large grains (LG) and I-50%M. All the samples used for these measurements were previously ground with silicon carbide paper FEPA 1200 and 2400, and further polished with diamond paste cloth down to 9, 6, 3, and 1µm respectively, including intermediate ultrasonic cleaning baths in ethanol. All the tests were done at room temperature.

7.3.2 Experimental conditions

Potentiodynamic curves for the 5 groups of samples were measured using the Micro Capillary Cell. The experimental conditions and settings of the set of tests are presented in Table 7.1. Prior to the polarization, a 2 minute prepolarization at -500mV (measured against the SCE) was performed as done in [5, 14, 16, 20, 21]. These pre-treatments were done in order to obtain a stabilization of the electrochemical system prior to the polarization. Two sizes of capillaries were used (30 and 150μm) to evaluate the possible influence of the capillary size.

Four different sets of experiments were performed (Table 7.2). The difference between these sets of experiments was the electrolyte used, as the amount of chlorides and presence of a buffer was varied. The electrolytes were prepared in
Localized Electrochemical Measurements with Micro-Capillary Cell

deleonized water, while the carbonate buffer consisted of a mixture of Na$_2$CO$_3$ and NaHCO$_3$ (10.6 and 8.4 grams respectively) in one litre of deionized water.

**Table 7.1: Electrochemical conditions and settings for potentiodynamic scans**

<table>
<thead>
<tr>
<th>Range</th>
<th>-500mV to 1V*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan Rate</td>
<td>1mV/s</td>
</tr>
<tr>
<td>Tip diameter</td>
<td>30 or 150µm</td>
</tr>
<tr>
<td>Reference Electrode</td>
<td>Standard Calomel Electrode</td>
</tr>
<tr>
<td>Counter Electrode</td>
<td>Platinum</td>
</tr>
</tbody>
</table>

*Approximate upper limit for range of the scan

**Table 7.2: Electrolyte composition**

<table>
<thead>
<tr>
<th></th>
<th>Electrolyte composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1M NaCl</td>
</tr>
<tr>
<td>2</td>
<td>1M NaCl</td>
</tr>
<tr>
<td>3</td>
<td>0.1M NaCl with carbonate buffer pH 10</td>
</tr>
<tr>
<td>4</td>
<td>1M NaCl with carbonate buffer pH 10</td>
</tr>
</tbody>
</table>

The selection of these electrolytes was based on the following: First, different sodium chloride concentrations were used because a very aggressive electrolyte might dominate and mask the microstructural influence on the corrosion performance. Furthermore, a buffer solution with alkaline pH will generate a passive layer on the steel surface which might lead to an identification of differences based on the breakdown of that passivity by local microstructural variations.

In order to account for reproducibility, each electrochemical test was performed a minimum of 3 times.

**7.4 Results**

Besides the variations on the chloride concentration and the presence of the carbonate buffer, the effect of the size of the tip of the capillary was evaluated. In this chapter, the results of the polarization curves for all the samples under the mentioned electrolytes are presented. It is important to mention that in each graph, only one typical experiment for each type of sample is presented.

For the analysis of the graphs, three main characteristics of the potentiodynamic curve were observed: the corrosion potential, the current density prior to breakdown and the breakdown potential (pitting potential). These 3 parameters are represented in each graph (Fig. 7.5 to 7.8) as a shaded region; each shaded region covers the area of the curves where all the results of experiments are included for a determined parameter independent of the type of microstructure of the sample. The corrosion potential range is the shaded region in the graph where the corrosion potential for all the experiments is found. The current density range is the shaded region in the graph where the current density in the anodic branch showed passivity for all the experiments. The breakdown or pitting range is the shaded area of the graph where the passive behavior of the polarization was broken, if being the case, for all the experiments.
All the potential values presented in this chapter are measured against the SCE.

### 7.4.1 Electrolyte 1: 0.1M NaCl No Buffer solution

Fig. 7.5 shows the potentiodynamic curves measured in the electrolyte with the lowest concentration of chlorides and no buffer for both capillary sizes. In terms of the corrosion potential range (shaded vertical area in the graph were all corrosion potentials were found), when performing the experiments with the 30μm capillary, all the $E_{corr}$ values were found in a range of approximately 90mV (-360 to -270mV), while with the 150μm capillary the range was slightly smaller (-340 to -270mV).
On the other hand, the current density range (shaded horizontal area in the graph were all current density values in the passive region were found) for the small capillary was found between 20 and 70µA/cm², while with the 150µm capillary this range was from 20 to 30µA/cm². Furthermore, breakdown was measured from 700 up to over 1000mV with the 30µm capillary, while with the bigger capillary breakdown potentials where found in the range from 300 to 980mV approximately.

From these two graphs, the main conclusions that can be made are: first, the electrochemical behavior of different microstructures was similar. In other words, the potential and current values measured for all the experiments (before the break down potential region) showed slim differences between samples that could be attributed to the reproducibility of tests, and not to influence of microstructural features of the samples. Furthermore, the effect of the capillary size on these same parameters can be neglected.

However, it would appear that the bigger capillary would provide better reproducibility of the experiment; this can be said because the range of the corrosion potential values as well as the current density range is smaller for the 150µm capillary that the ones of the 30µm. Also, a wider spread of the breakdown potential range is clearly seen on the smaller capillary.

**7.4.2 Electrolyte 2: 1M NaCl No Buffer solution**

Fig. 7.6 shows the potentiodynamic curves measured in the electrolyte with the higher concentration of chlorides and no buffer for both capillary sizes. In terms of the corrosion potential range, when performing the experiments with the 30µm capillary, all the E_corr were found in a range of approximately 80mV (-380 to -300mV), while with the 150µm capillary the range was slightly smaller (-400 to -350mV).

On the other hand, the current density range for the small capillary was from 20 to 70µA/cm², while with the 150µm capillary this range was from 25 to 50µA/cm². Furthermore, pitting was measured from 250 up to 670mV with the 30µm capillary, while with the bigger capillary the breakdown potentials were found in the range from -120 to 200mV approximately.

Like with the 0.1M NaCl electrolyte, the polarization curves performed with the 1M NaCl solution showed no correlation between the electrochemical behavior of the sample and its microstructure. The values of both the corrosion potential and current density for the experiments performed with the two capillary sizes appear to be similar; however, the range of the results obtained with the large capillary was slightly smaller for these two parameters, than obtained with the 0.1M NaCl solution.

Moreover, the values for the breakdown potential obtained with the large capillary were significantly lower, as all the measurements performed with this capillary had values below 200mV, while the ones obtained with the small capillary only started above the 250mV.
Fig. 7.6: Typical potentiodynamic curves for the dilatometer samples in 1M NaCl with a 30(top) and a 150µm (bottom) capillary.

### 7.4.3 Electrolyte 3: 0.1M NaCl with Carbonate Buffer pH10

Fig. 7.7 shows the potentiodynamic curves measured in the electrolyte with the lower concentration of chlorides in carbonate buffered solution (to adjust the pH to 10) for both capillary sizes. In terms of the corrosion potential range, when performing the experiments with the 30µm capillary, all the $E_{corr}$ values were found in a range of approximately 100mV (-390 to -290mV), while with the 150µm capillary the range was slightly smaller (-320 to -250mV).

On the other hand, the current density range for the small capillary was found between 15 and 70µA/cm², while with the 150µm capillary this range was between 30 and 60µA/cm². Additionally, no breakdown potential was obtained for either capillary
size; the passive behavior of the anodic branch of the polarization was continued until the reaction reached oxygen evolution levels.

![Graph showing potentiodynamic curves](image1.png)

![Graph showing potentiodynamic curves](image2.png)

Fig. 7.7: Typical potentiodynamic curves for the dilatometer samples in carbonate buffered 0.1M NaCl with a 30(\text{top}) and a 150µm (\text{bottom}) capillary.

Independent of the microstructure of the sample, all the polarizations performed were found to have comparable electrochemical response. The addition of the carbonate buffer induced a stable passive layer clearly shown in the anodic branch of all polarizations.

The values of corrosion potential and current density are similar for both capillary sizes, but for both these parameters the range of the results was smaller for the experiments performed with the 150µm capillary.
7.4.4 Electrolyte 4: 1M NaCl with Carbonate Buffer pH10

Fig. 7.8 shows the potentiodynamic curves measured in the electrolyte with the higher chloride concentration with the addition of the carbonate buffer for both capillary sizes. In terms of the corrosion potential range, when performing the experiments with the 30µm capillary, all the $E_{corr}$ were found in a range of approximately 60mV (-410 to -350mV), while in the 150µm capillary the range was slightly smaller (-310 to -260mV).

Fig. 7.8: Typical potentiodynamic curves for the dilatometer samples in carbonate buffered 1M NaCl with a 30(top) and a 150µm (bottom) capillary.
On the other hand, the current density range for the small capillary was found between 15 and 70µA/cm², while with the 150µm capillary this range was from 25 to 60µA/cm². No pitting behavior was measured when using the 30µm capillary, while with the bigger capillary all experiments showed breakdown in the range from 300 to 800mV approximately.

Like with the previous electrolytes, no clear relation between the microstructure of the sample and the electrochemical behavior was identified.

However, in this electrolyte the main difference was found when comparing the exposed area of the working electrode: with the small size capillary, the stability of the passive range was kept throughout the curve until reaching the oxygen evolution range. Still, some perturbations (like in the 100%M_SG curve in Fig.7.8) were seen in approximately 10% of the experiments performed. Other researchers describe this behavior as the initiation of metastable pitting [22-29] or even the initiation of a crevice [30]. With the 150µm capillary all the experiments presented a clear breakdown potential.

Table 7.3 shows a summary of the maximum and minimum values for the $E_{corr}$, current density in the passive range, and breakdown potential for the carbonate buffered and unbuffered electrolytes, with high and low concentration of chlorides (0.1 and 1M) and two different exposed areas—capillary tips (30 and 150µm) for the 5 types of microstructures.

7.5 Discussion

The potentiodynamic scans with the micro capillary cell technique show that no significant variations in the electrochemical response was found as a function of the ferrite/martensite (or ferrite/cementite in case of the Base Material sample) ratio. All the experiments (microstructure independent) performed in this chapter lie within the shaded area (per experimental condition); it can be said this shows two things: The first one is that the corrosion potential and passive current are fairly reproducible, while the breakdown potential was a random parameter spread on a wide range for every microstructure.

The second thing is that it can be seen that with the increase of the diameter of the capillary, the shaded areas in the graphs become narrower, which would suggest a better reproducibility.

The differences reported in prior literature studies [31-48] can be considered to be in the reproducibility range of the tests, which was not taken into consideration carefully. Even more, contradictory conclusions reported by different authors might be due to the selection of different electrolytes: an aggressive electrolyte (for example one with high concentration of NaCl, no buffer) may overrule and dominate any effect (if so) of the microstructure.

However, the variations of the experimental parameters used, enable a more detailed interpretation of the polarization curves. The variations in the exposed area, the chloride concentration and the presence of a buffer solution (with a basic pH) are discussed in the following paragraphs:
Table 7.3: Summary minimum and maximum values for corrosion potential, passive current density and breakdown potential independent of sample microstructure in 4 different electrolytes and 2 capillary diameters, as shown in Figs 7.5 to 7.8. These values do not correlate in any way with the martensite content of the different samples

<table>
<thead>
<tr>
<th>NaCl Conc</th>
<th>Capillary Diameter</th>
<th>Ecorr Min (mV vs SCE)</th>
<th>Ecorr Max (mV vs SCE)</th>
<th>Current density Min (μA/cm²)</th>
<th>Current density Max (μA/cm²)</th>
<th>Break Min (mV vs SCE)</th>
<th>Break Max (mV vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Buffer</td>
<td>0.1M 30μm</td>
<td>-360</td>
<td>-270</td>
<td>20</td>
<td>70</td>
<td>700</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>150μm</td>
<td>-340</td>
<td>-270</td>
<td>20</td>
<td>30</td>
<td>300</td>
<td>980</td>
</tr>
<tr>
<td></td>
<td>1M 30μm</td>
<td>-380</td>
<td>-300</td>
<td>20</td>
<td>70</td>
<td>250</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td>150μm</td>
<td>-400</td>
<td>-350</td>
<td>25</td>
<td>50</td>
<td>-120</td>
<td>200</td>
</tr>
<tr>
<td>Buffer</td>
<td>0.1M 30μm</td>
<td>-390</td>
<td>-290</td>
<td>15</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>150μm</td>
<td>-320</td>
<td>-250</td>
<td>30</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1M 30μm</td>
<td>-410</td>
<td>-350</td>
<td>15</td>
<td>70</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>150μm</td>
<td>-310</td>
<td>-260</td>
<td>25</td>
<td>60</td>
<td>300</td>
<td>800</td>
</tr>
</tbody>
</table>

7.5.1 Capillary size effect

In three out of the four different electrolytes used in the experiments a clear effect of the size of the capillary could be seen: when the experiments were performed with the large capillary, the range of the values of the breakdown potential started at a lower potential (only in one of the electrolytes tested – Buffered, 0.1M NaCl, Fig. 7.7-, no breakdown of the passive layer was observed on either capillary sizes). In other words, larger exposed areas have a tendency to present breakdown of the passive layer at lower potential values of the anodic polarization. This behavior has been reported in other studies [2-4, 49, 50], and can be explained by the diagram presented as Fig. 7.9:

![Fig. 7.9: Effect of capillary size on the steel surface during electrochemical testing](image)

The “weak” spots shown in Fig. 7.9 represent areas where the homogeneity of the passive film is compromised; depending on the type of sample [51], electrolyte and electrochemical cell, these instabilities or heterogeneities in the oxide film can be caused by many mechanisms, among them:
Localized Electrochemical Measurements with Micro-Capillary Cell

- chemical compositional differences on the surface of the sample, like chromium depleted areas in stainless steels [52-57]
- microstructural features like grain boundaries, inclusions/impurities or grain orientation [14, 16, 20, 21, 58-61]
- surface and/or surface preparation defects

Taking into account the presence of these weak spots, the probability of finding defect free areas on the surface of the sample decreases with the increasing size of the exposed area.

### 7.5.2 Chloride concentration effect

The effect of chlorides on the breaking down of passive layers has been extensively reported in literature. The mechanism can be summarized as follows: aggressive ions (chlorides) penetrate the passive film. This penetration creates instability of the film, and “weak” spots (as described in section 7.5.1) will increase the vulnerability of the film and may result in pit initiation and metastable pitting. If the shallow pits are covered with corrosion products, an occluded cell results where no exchange of ions with the electrolyte takes place with the exception of the very mobile chloride ions. This results in good conductivity in the occluded cell. The onset of corrosion in the occluded cell will result in the production of H⁺ ions; this will then locally lower the pH, inducing a faster dissolution of the Fe.

The increase of the concentration of chlorides will facilitate the breakdown of the passive layer; as reported by other authors [62-65], this results in lower values of the pitting or breakdown potentials.

![Diagram](image)

**Fig. 7.10: Effect of chloride ion concentration on pitting evolution during electrochemical testing**

In Fig. 7.5 and 7.6 without a buffer it was clear that a higher chloride concentration resulted in a lower pitting potential range value. This was also seen with the buffer solution: in the 0.1M NaCl case, no breakdown of passivity was found at all, while in the 1M experiments, all the samples showed pitting above 300mV.
7.5.3 Carbonate buffer effect

The effect of the carbonate buffer was clearly seen in all the experiments performed: when the solution was buffered, breakdown of the passive layer was absent completely except for the large capillary size with high concentration of chlorides. In this case pitting took place but the potential values of the pitting range were increased.

This suggests that the carbonate buffer has an effect on the corrosion resistance of the sample. Fig. 7.11 shows a sketch that shows the proposed explanation of the effect of the carbonate buffer on the sample.

![Unbuffered vs Carbonate Buffer pH10](image)

Fig. 7.11: Effect of carbonate buffer on sample

Due to the experimental conditions, it can be assumed that formation of a natural oxide layer on the surface of the sample as a result of the exposure to air after surface preparation and immersion in an aerated solution takes place [51, 66, 67]. This model was assumed as shown in Fig. 7.9 to 7.11. As such, it is proposed that between the steel sample and the micro capillary with the electrolyte lays a thin natural oxide layer. With the presence of the carbonate buffer, the experiments showed that the breakdown of the passive layer was avoided or at least delayed; this is in agreement with the information found in literature and summarized in Chapter 4.2.1. This effect could be explained by two theories: the first one could be that the carbonate buffer further enhances the growth and stabilisation of the natural oxide layer. With the increase in thickness of the oxide, a more protective layer is formed on the surface, therefore delaying the breakdown [68-71]. The second theory relays on the deposition of carbonate compounds over the existing oxide layer, creating a double layer that protects the surface from the chloride effects [70, 72-79].

7.5.4 Capillary/Seal effect

There is another aspect that was discovered while performing the experiments that is important to mention. As described in the summary of the micro capillary cell electrochemical setup, one of the most critical factors of the technique is the silicon seal that is placed on the tip of the capillary. The magnitude of this effect is shown in Fig. 7.12.
Localized Electrochemical Measurements with Micro-Capillary Cell

Fig. 7.12: Polarizations on 0.1M NaCl with carbonate buffer, 2 different capillaries of the same size

In the graph shown above, two different sets of experiments were performed: the only difference in the experimental conditions was the capillary used. Both capillaries had a tip diameter of 30µm. Because of the nature of the procedure to create the silicon gasket on the tip of the capillary, it is extremely complicated to have identical capillaries and seals. In this specific case, the first capillary (Cap 1 in Fig. 7.12) had a slightly smaller silicone tip than the second capillary (Cap 2). As it can be seen in the polarizations, the experiments done with Cap 1 had higher current values and showed break down of the passive layer in all cases. What is more, the experiment had similar behavior around the corrosion potential.

The problem with the results of the experiments with Cap 1 is that they can be misleading; the difference between the results was a consequence of the thinner silicone seal; due to the fact that it was very thin, it appears that the glass tip of the capillary was making contact with the surface of the working electrode. This generated a crevice which would explain the high current values and presence of a pitting potential behavior on the experiments with this capillary, and furthermore the differences between two “identical” capillaries. However, because of the size of the capillary, any crevice generated at this size range is difficult to detect and might be missed while analyzing the surface. The electrochemical behavior caused by the imperfection of the silicone tip can lead to wrong interpretations of the electrochemical system.

Other researchers [30, 80-84] have previously discussed the influence of crevice on the interpretation of data obtained from electrochemical testing: in general terms, they conclude that not only the interpretation is difficult, but that the effect of crevice can mask the test results making them questionable, or simply irrelevant.
7.6 Conclusions

After performing the electrochemical experiments with micro capillary cell technique, several important remarks can be done:

The electrolyte, like in Chapter 6, proved to be the source of fundamental differences in the electrochemical behavior of the system. It was clearly seen that the concentration of chlorides has a direct relation with the stability of the passive system: as the chloride concentration increases, the values of pitting (or breaking of passivity) potential become lower.

It was also clearly seen that the presence of the carbonate buffer in the electrolyte has a beneficial effect on the corrosion resistance of the sample. The carbonate buffer seemed to enhance the growth and stability of the oxide layer, preventing or at least delaying the breakdown of passivity by the chloride ions. Although the mechanism is still not clear, the added protection of the carbonate buffer is reached by growth of the existing natural oxide on the surface of the sample, or the deposition of a protective layer with carbonate components.

Furthermore, differences in the size of the exposed area showed significant influence on the electrochemical data. Even though both capillary sizes studied were in the micrometer range, it was clearly seen that the larger exposed area showed lower breakdown potentials. This effect was explained by the presence of different pitting inducing factors like inclusions, surface/oxide defects or heterogeneities of the surface. As the studied area becomes larger, the possibility of finding these pitting inducing elements also increases, therefore generating breakdown potentials at lower values in the anodic branch of the curve.

But beside the influence on the breakdown potentials, the exposed area also showed another effect on the experiments performed: the polarizations done with the larger capillary showed smaller ranges for passive current and corrosion potential. In other words, the reproducibility of the polarizations was improved with an increase of the exposed area. There are two possible reasons for this effect: the first one is the differences found on different spots of the exposed area generated by the 30µm capillary. Due to the small area, any heterogeneities or differences on the surface/oxide have a significant influence on the electrochemical response. While when using a 150µm capillary, a more general surface covering a wider range of differences is studied, providing then values that represent the averages electrochemical response of all the features encountered.

The second possible explanation is not related to the electrochemical system itself, but to the experimental technique: as mentioned previously, one of the critical factors of the technique is the capillary together with its silicon gasket. The capillaries and the gasket are hand-made, making it very difficult to make two identical capillaries. This becomes even more critical when attempting to make smaller sized capillaries. Not only the complexity when polishing capillaries to a size under 30µm is high, but also the addition of the silicone gasket becomes more difficult in this size range. Furthermore, as the silicone tip is deformable, it is also possible to have small
differences in the exposed area when doing the experiment with the same capillary: when approaching the surface with the capillary, the silicone tip is deformed. This process is also done manually; therefore having the same pressure on the surface with the capillary’s tip (and therefore deformation) is difficult to reproduce accurately. Assuming the deformation varies the capillary size in a few micrometers, the exposed area will also be different. Naturally, this effect is more significant when using smaller capillaries, and because of this, the reproducibility in this range is more difficult to obtain.

However, the micro electrochemical technique proved to be a valuable resource to identify differences in the electrochemical systems related to chloride concentration, carbonate buffer and exposed area. Even though the reproducibility with the smaller tip capillaries was not as good as with larger capillaries, the results obtained were very reproducible and gave a reliable description of the electrochemical system under various electrolytes.

With this in mind, the most important conclusion that can be made from the experiments in this chapter is that no significant correlation with the microstructural variations present in the modified dual phase steel, i.e. the ferrite/martensite phase ratio, and the electrochemical behavior of the system were identified. Like in Chapter 6, while a clear electrolyte effect was observed, it can also be concluded that for the buffered and unbuffered electrolytes and sample variations studied, ranging from nearly fully ferritic to martensitic, no significant variation in the electrochemical response with the ferrite/martensite phase ratio was found with the micro capillary cell technique.

### 7.7 Acknowledgment

The author would like to acknowledge the participation of Dr. Nicolas Mary (INSA-Lyon/ TUDelft), Dr. Thomas Suter and Dr. James de Rose (EMPA Zurich) for their help and guidance with the experimental technique used throughout this chapter.
7.8 References

Localized Electrochemical Measurements with Micro-Capillary Cell


CHAPTER 8. EXPOSURE TESTS AND SURFACE OXIDE ANALYSIS

8.1 Introduction

The main conclusion of chapters 5, 6 and 7 can be summarized as follows: no significant difference could be found in the electrochemical behavior of the different model dual phase steel specimens, regardless of the amount of the phases present in their microstructure; this fact was true for experiments carried out on both macro and micro scale. However, visual inspection of the surface of the samples after exposure showed minor differences on the degradation of the surface related to the type of microstructure.

In order to attempt to explain the differences observed, immersion tests were performed on the dilatometer samples with different electrolytes. After exposing the samples, the surfaces were inspected, and specific experimental conditions were chosen to further analyse the oxide layer formed.

The contents of this chapter cover a first approach to identify the oxide layer and its influence on the corrosion resistance of the samples; this is performed by means of Auger Electron Spectroscopy (AES). The surface of the samples was analyzed before and after immersion in selected electrolytes. The differences found by visual examination and AES analysis are discussed in this chapter.

8.2 The Technique

Auger electron spectroscopy is one of the most widely used surface-sensitive analytical techniques which offer the possibility of identifying the elemental composition of the outermost atomic layer of a solid. It is characterized by using a focused beam of electrons to interact with atoms in the surface layer, which provides chemical information on this layer.

AES is based on the accurate measurement of the number of emitted secondary electrons as a function of kinetic energy. The electron beam is used to excite atoms, generating a core hole. This hole can be filled by an outer electron and the extra energy can be released to a third electron (an Auger electron). If the target atom was very near the surface (nm range), the Auger electrons can escape the solid and be energy analyzed and counted to yield a spectrum of the number of electrons emitted as a function of energy. The Auger electrons are characteristic of the specific element emitting them, making them useful for qualitative analysis [1], as they are emitted at discrete energies that allow the atom of origin to be identified [2]. In some circumstances it is also possible to derive more detailed chemical information from the peak position and/or the peak shape. The intensity of an Auger peak can be related to the amount of that element present in the analyzed volume by applying appropriate sensitivity corrections [3-7].
By combining AES with ion beam sputter-etching the elemental composition can be determined as a function of depth. The intensity of particular Auger peaks is monitored as a function of sputter time. The intensity scale can be converted to composition and the time scale converted to depth. [6, 8]

![Auger process diagram](image)

Fig. 8.1: Representation of the Auger process. Taken from [9].

### 8.3 Experimental

#### 8.3.1 Samples

The samples used for these experiments were the modified microstructures obtained with the dilatometer, as described in Chapter 3.5, where the type of samples are referenced as base material BM, commercial DP600, A-100%M with Small grains, E-100%M with Large grains and I-50%M. All the samples used for these measurements were previously ground with silicon carbide paper FEPA 1200 and 2400, and further polished with diamond paste cloth down to 9, 6, 3, and 1µm respectively, including intermediate ultrasonic cleaning baths in ethanol. All the tests were done at room temperature.

#### 8.3.2 Experimental conditions and equipment

For visual examination, all samples were immersed for 1 hour in 4 different electrolytes:
1. 0.1M NaCl
2. 0.1M NaCl with carbonate buffer pH 10
3. 1M NaCl
4. 1M NaCl with carbonate buffer pH 10

After immersion, the samples were cleaned with distilled water and dried.

For the AES analysis, 4 different scenarios were selected for the study:
A. As polished (immediately after polishing the sample, with no polarization or immersion involved)
B. After immersion (1 hour in 1M NaCl with carbonate buffer pH10)
C. After polarizing until 400mV vs. SCE in 1M NaCl with carbonate buffer pH 10 (*details of the procedure are presented in the following paragraph)
D. After polarizing until -100mV vs. SCE in 1M NaCl (*details of the procedure are presented in the following paragraph)

*In scenarios C and D, where the samples were polarized, the procedure followed was similar to the one presented in Chapter 7: after preparation (polishing), the sample was polarized in the Micro capillary cell setup using a capillary with a tip diameter of 100µm. The polarization consisted of 2 steps: a prepolarization at -500mV wrt SCE followed by a potentiodynamic scan starting from -500mV at a scan rate of 1mV/sec until reaching the established limit for each scenario (400mV in C, -100mV in D): these limits were chosen because they represented a limiting value in polarization prior to breakdown of passivity for each electrolyte respectively. After this, the samples were cleaned with distilled water and dried, and after were analyzed with AES.

<table>
<thead>
<tr>
<th>ELECTROLYTE / SCENARIO</th>
<th>SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M NaCl</td>
<td>BM X DP X* A X* I X* E</td>
</tr>
<tr>
<td>0.1M NaCl pH 10</td>
<td>X X* X X* X* X*</td>
</tr>
<tr>
<td>1M NaCl</td>
<td>X X* X X* X* X*</td>
</tr>
<tr>
<td>1M NaCl pH 10</td>
<td>X X* X X* X* X*</td>
</tr>
<tr>
<td>As Polished</td>
<td>BM X X* X</td>
</tr>
<tr>
<td>After Immersion (1h in 1M NaCl pH 10)</td>
<td>X X* X</td>
</tr>
<tr>
<td>After polarizing until 400mV vs. SCE in 1M NaCl pH 10</td>
<td>X X* X</td>
</tr>
<tr>
<td>After polarizing until -100mV vs. SCE in 1M NaCl pH 10</td>
<td>X X* X</td>
</tr>
</tbody>
</table>
Auger Electron Spectroscopy (AES) measurements were performed using a PHI 650 SAM with a LaB6 cathode. A cylindrical mirror analyzer (CMA) and a 5 keV ion-gun (PHI 04-303) were used. The base pressure in the analysis chamber was $3 \times 10^{-10}$ Torr. A primary electron beam with energy of 5 keV and a current of 1μA was incident on the sample surface at 30° to the normal. Ion sputtering was performed to obtain the depth profile. The surface was rastered using a 2 keV Ar ion beam over an area of $4 \times 4$ mm². The emission current was 20mA and Ar pressure was 10mPa. The ion beam was used at intervals of 1 minute and impinged on the sample surface at 50° to the normal. The recorded spectra were analyzed with Multipak 6.1A software.

8.4 Results

8.4.1 Immersion tests:

The following figures show a comparison of the surface of the samples exposed to the four different electrolytes. Even though five types of samples were studied, only two types are presented: the Base Material (BM) and A-100%M with Small grains (A). The reason for this is the fact the no significant differences could be identified (after visual examination) between the samples commercial DP600, A-100%M with Small grains, E-100%M with Large grains and I-50%M.

![Fig. 8.2: BM (Left) and sample A (right) after one hour immersion in 0.1M NaCl](image-url)
Fig. 8.3: BM (Left) and sample A (right) after one hour immersion in 0.1M NaCl with Carbonate buffer pH 10

Fig. 8.4: BM (Left) and sample A (right) after one hour immersion in 1M NaCl
From Figures 8.2 through 8.5 it can be seen that in general terms the surface of the samples present different levels of corrosive attack depending on the electrolyte that they were exposed to. Also some minor differences for the two types of surfaces were visible.

The BM samples immersed in the unbuffered solutions (Fig. 8.2 and 8.4) showed a more distributed corrosion behavior throughout their surfaces when compared to samples A; it is possible to identify more attack points in the surface of samples BM than in the surface of sample A. This effect is particularly noticeable when immersed on the 0.1M NaCl solution (Fig. 8.2), where the BM sample appears to present what could be considered a general corrosion attack, while sample A showed a more localized behavior.

When comparing the samples immersed in the buffered solutions (Fig. 8.3 and 8.5), the first thing that can be pointed out is that none of the samples presented any kind of corrosion marks when immersed in the 0.1M NaCl solution; no attack could be identified on the surface of the samples even when increasing the exposure time over 3 hours. However, when increasing the Cl\(^-\) concentration it was possible to identify corrosion spots in the surface of all the samples. Furthermore, the BM showed more spots (of apparent minor depth) when visually compared to the few spots (more localized, arguably deeper) of the A sample.

### 8.4.2 AES tests

In line with the procedure followed on the immersion tests, only 2 types of samples were treated and analyzed with AES: BM and A type. As mentioned in section 8.1.2,
4 different treatment routes were followed prior to the measurement. A sputter rate of 5nm/min is used for these experiments.

After being polarized by route C (until 400mV vs. SCE in 1M NaCl with carbonate buffer solution), the atomic concentration (%) iron, carbon and oxygen were recorded for both samples, as shown in Fig. 8.6.

The atomic concentration of the AES analysis as shown in Fig. 8.6 reveals some characteristics of the state of the surface: the carbon content on the surface after being polarized is approximately 70%, which is reduced to approximately 10-15% after 30sec sputtering. This very high concentration can only be a measurement of the contamination on the surface of the sample, which may have been caused by the CO/CO₂ in the air, as well as electrolyte used during the polarization (carbonate buffered solution). In this experiment, the drastic reduction of carbon comes together with an increase of the iron and oxygen content (up to a maximum concentration of approximately 45% for the oxygen). This suggests the presence of an iron oxide layer (most likely Fe₂O₃) on the surface of the sample.

After one minute sputtering, the oxygen concentration has been practically removed, while the iron concentration reached its maximum and stabilized. This suggests the sputtering has removed the oxide layer (after having already removed the contamination on the surface), reaching the steel substrate.

As described by De Laet in [10], factors like surface roughness and the settings of the sputtering parameters have an influence on the depth resolution of the AES; furthermore, De Laet also presented a model where a double layer barrier is present on the surface of the substrate. The two layers are the oxide film and an intermediate
interface. For the estimation of the thickness of the oxide layer, in this work the following assumptions were taken:

- The carbon contamination layer is assumed to be removed when the carbon concentration is below 20%.
- Due to the low thickness encountered, the oxide layer is going to be composed by the oxide layer and the intermediate interface. This assumption can be done taking into account that the sputtering settings are fixed for all measurements, and the surface roughness can be considered to be the same for all samples.
- The extent of the oxide layer is assumed up to the moment where the iron concentration reaches a value of 80%, where it is assumed that the steel substrate is reached.

The measurements performed on both samples showed (Fig. 8.6) similar results: an approximate 20% oxygen concentration is found on the oxide layer in the surface of the sample, rising up to around 45% after 15 sec sputtering (assumed to remove most of the contamination on the surface). The thickness of the oxide layer is approximately 4nm for both samples.

Here it is important to emphasize that the results shown in Fig. 8.6 are in general terms identical for both samples when measured after treatment route D (until -100mV vs. SCE in 1M NaCl solution).

![Graph showing atomic concentration](image1.png)

**Fig. 8.7: Atomic Concentration for base material (BM, top) and fully martensitic sample (A, bottom) immediately after polishing (no polarization or immersion involved, Route A)**

The results measured on the samples after being exposed to treatment route A (As polished, no polarization or immersion involved) are presented in Fig. 8.7. Unlike the results encountered when following routes C and D (as shown in Fig. 8.6), the results were influenced by the type of sample exposed. In this case, it can be noticed that
both samples had a very low carbon concentration on the surface, which means that even though they were immersed in the carbonate buffered electrolyte, no carbon contamination was detected. This suggests that the carbon contamination seen in Fig. 8.6 was an effect of the CO/CO$_2$ exposure. Also, particularly in the BM sample, there was no development of an oxide layer.

The results of the test on the BM sample showed that the oxygen concentration on the surface was estimated to be around 12%, while on the sample A the surface oxygen atomic concentration was nearly 50%. Furthermore, the atomic carbon concentration was below 20% (down to nearly 10% on the A sample), while this same parameter reached approximately 75% on the surface of both samples after being polarized (Fig. 8.6). The oxygen concentration on the surface was removed after sputtering for 12 seconds for sample BM, while it took 24 seconds to reach the same limit on sample A; this results in an oxide layer of approximately 1nm thickness.

The atomic concentration after immersing the samples for one hour in the 1M NaCl buffered solution (route B) are presented in Fig. 8.8. Like with the polarized samples, the immersed samples showed a higher concentration of atomic carbon on the surface when compared to the samples that were not exposed to any electrolyte. Concentrations of approximately 60 and 40% were recorded for samples BM and A respectively, although not as high as the 75% seen on both samples polarized in the two electrolytes. As mentioned for the other experiments, the carbon is attributed to contamination by CO/CO$_2$.

![Fig. 8.8: Atomic Concentration for base material (BM, top) and fully martensitic sample (A, bottom) after immersion in 1M NaCl with Carbonate buffer for 1hour (Route B)](image)

Like with the samples that were measured directly after polishing (route A), these results show that different samples presented different behavior: the first issue that could be noticed was that oxygen atomic concentration on the surface was around 25% for the BM sample. This value increased up to 50% a 40 seconds of sputtering, and removed after almost 5 minutes sputtering, resulting in an oxide thickness of
approximately 24nm. On the other hand, sample A’s surface measured oxygen atomic concentration of almost 45%, peaking at 60% after 6 second sputtering, and removed after less than 1 minute sputtering (oxide thickness approximately 5nm).

8.5 Discussion

Both kinds of tests showed interesting results concerning the corrosion behavior of different kinds of samples. These are discussed in the following paragraphs:

8.5.1 Immersion tests

Visual inspection of the samples after the immersion tests showed 3 main aspects as a general rule for all the samples studied: the first aspect is that the increase of chloride concentration in the electrolyte had a detrimental effect on the surface sample. When having a higher concentration of chlorides, it was clearly seen that the surface of all the samples presented a higher number of corrosion spots, or deeper/bigger corrosion points. This effect becomes evident when comparing the samples exposed to the buffer solution with low and high concentration of chlorides (Fig. 8.3 and 8.5). When the chloride concentration is low, no corrosion attack could be seen on the surface of the sample, even after longer exposure times.

The second issue is the effect of the carbonate buffer on the protection of the surface of the sample. It was seen that the samples exposed to the buffered electrolyte presented a less damaged surface after exposure, which was particularly clear when the chloride concentration was low. In this case, the buffer protected the surface from any visible corrosion attack (Fig. 8.3).

The third aspect is a combination of the first two: even though it was proven that the carbonate buffer had supported the surface in limiting the degradation, this effect has a limit. When the chloride concentration is high, it suppresses the protective characteristics of the buffer generating localized corrosion spots, as seen in Fig 8.5.

However, another feature was noticed while performing the tests: as mentioned in section 8.4.1, the immersion tests showed that BM sample presented a slightly dissimilar behavior from the rest of the group, noticeable by visual inspection after exposed to three of the four chosen electrolytes; the corrosive effect of the 0.1M NaCl buffered solution was not significant enough to generate any degradation on the surface of the samples, therefore no differences could be identified.

The BM sample (base material) appeared to have a more generalized distribution of corrosion attack points over its surface, while the other 4 samples presented a more localized phenomena (fewer damage spots over the surface, arguably deeper and/or with larger diameter).

This last difference found only in sample BM points to the fact of an effect of the underlying microstructure on the development of passivity on the surface of the sample. However, even though the 5 microstructures are different to each other, the BM sample is characterized by having a highly deformed ferritic matrix with cementite/pearlite islands while the other 4 samples consist of a ferrite and/or
martensite mixture (as explained in Chapter 3). The four ferritic and/or martensitic samples presented a similar behavior after exposure, independent of the phase ratio present on their underlying microstructures.

8.5.2 AES analysis

Four different routes were applied to the two types of samples in order to analyze its surface characteristics. Even though the nature and composition of the oxide layer on the surface of the samples was not determined, some conclusions can be drawn from the AES results.

The first thing that can be mentioned is that independent of the underlying microstructure as well as composition of the electrolyte, no differences were identified on the surface of the samples after being polarized. In general terms, it could be seen that polarizing the samples anodically up to potential values before breakdown showed that the oxides on the surfaces were basically identical. This fact boosts the effect of the polarization itself, as it was independent of the underlying microstructure and the presence of carbonate on the buffer solution. As such, the adequate description of the analysis of the development of the oxide on the surface during the complete polarization (from the pre-polarization and up to the “pre-breakdown” point as described in paragraph 8.3.2) of the samples becomes critical.

Furthermore, the results seen on the polished and the immersed samples showed that unlike the polarized ones, differences could be identified on their surfaces: not only differences when comparing to the polarized samples, but also among the two samples subjected to the same treatment route.

On the polished samples (Fig. 8.7), the small time the sample was exposed to air while preparation for the AES generated a very thin oxide layer (around 1nm) and marginally no contamination (no carbon). Even though the concentration of oxygen in the surface of sample A suggested a slightly thicker layer or even a different stoichiometry, it is difficult to reach this conclusion due to the very thin oxide layer, where any difference in surface roughness or exposure to air of the samples can be the reason for such a difference.

But probably the most significant feature was the differences found after immersing the samples for one hour in 1M NaCl carbonate buffer solution: the first thing that can be noticed, as shown in Fig. 8.8, is that the contamination of carbon is present like on the polarized samples. This can be attributed to the longer exposure to air and cleaning after immersed on the electrolyte. Furthermore, not only the atomic oxygen in the surface was different for both samples in similar fashion as when only polished (where sample A presented a higher concentration), but also one of the surface oxide layers was found to be clearly thicker than the other. This was the case for the BM sample, where almost 5 minute sputtering was required to remove the oxygen from the surface, giving an approximate oxide thickness of over 20nm and almost 5 times as much as the one calculated for the A sample. This value is significantly higher than the ones found for the only polished and the polarized samples.
In general terms, it can be said that the natural oxide layer of the 5 different types of samples seems to be different depending of the underlying microstructure; although the quantification of the thickness appeared to show similar sizes, the concentration of the atomic elements suggests a different stoichiometry, therefore a different type of oxide. Even though it has not been determined which type of oxide corresponds to either kind of microstructure, existing literature has covered the differences on oxides layers based on microstructural characteristics like grain orientation, internal stresses and chemical composition (Chapter 7.5.1). As described in Chapter 3, the combination of a highly deformed ferritic structure and cementite (on its way to become martensite) from the BM sample appeared to be the reason for having a different oxide layer when compared to the other 4 samples.

As such, the difference on the natural oxide layer can explain then the difference of the exposed samples: under the same buffered electrolyte, it is natural to assume that the development and growth of the oxide layers is different as well. However, it is important to mention that the electrochemical polarizations (independent of the electrolyte) seemed to overrule the microstructural effect on the oxide layer.

### 8.6 Conclusions

A first optical inspection and comparison overview of the specimens immersed in the electrolytes showed that:

- Increasing the chloride concentration brought a deleterious effect on the samples.
- The carbonate buffer provides/prevents the corrosion effect for longer times (no pits/corrosion was seen on the surface of all the samples when immersed in 0.1M NaCl with Buffer after even 3 hours)
- High concentration of chlorides overruled the buffering effect

These conclusions are in agreement with the results obtained after the polarization tests in Chapter 7, and are on essence, not surprising. However, unlike the results of the previous chapters, a microstructural influence on the corrosion resistance of the samples was noticed on both types of experiments performed in this chapter. Still, this difference was only identified in 1 of the five different types of samples tested. Sample BM presented a different kind of behavior when immersed in the electrolytes, as well as different characteristics when evaluated with AES; the other four types of samples had arguable identical results after the experiments.

As described in Chapter 3, the five kind of samples have the same chemical composition; the main difference lies on the fact that the sample BM did not go through the final annealing procedure that the other samples had. Even though all the samples were subjected to different heat treatment routes, only sample BM had a microstructure composed of a highly deformed ferrite matrix with cementite/pearlite islands, while the other four types of sample had microstructures consisting of ferrite and/or martensite.
Visual inspection of the immersion tests showed that the BM sample had a slightly different corrosion resistance when compared to the other types of samples; the AES analysis showed that characteristics as thickness and/or stoichiometry of the natural oxide layer and the developed oxide layer (oxide after immersion) of sample BM were also different than the ferritic/martensitic microstructures.

It can be concluded that the underlying microstructure of the BM sample influenced the characteristics of the oxide layer growing on the sample; the differences generated by this specific microstructure are the reason for the minor alterations of the corrosion resistance of the sample when compared to the other type of microstructures.
8.7 References

CHAPTER 9. DISCUSSION AND CONCLUSIONS

9.1 Background and Approach

The main goal of the project was to study the influence of the microstructure on the corrosion behavior of a Dual Phase steel; in order to reach this objective, the approach was first to obtain a microstructure that would ideally allow to isolate phases in order to study individual electrochemical performance. It was intended to control critical characteristics like homogeneity, optimum grain size and phase percentage prior to the corrosion studies.

Furthermore, as the influence of microstructural features on electrochemical behavior was to be studied, a technique with high spatial resolution like the Micro-Capillary cell seemed to provide the necessary tool. Nevertheless, a standard non-localized electrochemical approach was performed as well in order to study differences between macro (exposed area in mm-cm range) and micro (exposed area µm range) techniques.

Unfortunately, both parts of the approach (obtaining the desired microstructure, and reliable and reproducible macro and micro electrochemical measurements) proved to be quite complicated and consumed more time than initially planned; therefore only the onset of a complete analysis of the development of the oxide layer on the dual phase alloys and its relation with the microstructure could be done. Nevertheless these last results seem to provide a good starting point for further elaboration of the corrosion mechanism of the dual phase alloy.

9.2 Microstructure

The first part of the research project was dedicated to obtain the proper microstructures for the electrochemical testing; the idea was to develop microstructures in which the amount of the phases present was controlled and measured in order to observe the influence of the microstructural differences on the electrochemical behavior.

After heat treatment trials with the CASIM and salt bath techniques, trials with the dilatometer brought samples that have optimal microstructures for the comparison: not only the differences between martensite and ferrite were well defined in these samples, but it was also possible to obtain fully martensitic microstructures without decarburization. Furthermore, fully martensitic microstructures were obtained with different grain size; one of those samples provided the theoretical possibility of performing single grain electrochemical measurements.

However, even though the dilatometer provided the microstructural control ideally required for the corrosion analysis, the samples generated restrictions for the electrochemical testing due to their small size: too small for the macro
Discussion and Conclusions

electrochemical technique. For this reason the CASIM samples were also used for electrochemical analysis.

9.3 Electrochemistry

9.3.1 Crevices

Three different 3-electrode cell setups were tested in the macro level as well as one in the micro level to perform electrochemical polarization curves. During the experimental procedures, crevices proved to be a major issue. With the macro level setups, it was basically not possible to perform and measure potentiodynamic polarization curves without having crevice corrosion. The crevice effect was identified visually on the surface of the sample and/or by the behavior of the OCP curve (for buffered electrolytes). A modified version of the Avesta cell managed to apparently perform the polarization measurements without disturbance by crevice corrosion, but the peristaltic pump used during the procedure probably affected the current measurements at its lowest levels, making it impossible to identify the corrosion potential and current density.

In the micro capillary cell setup, it was necessary to analyse the OCP curve in order to identify crevices (possible only in the buffered solutions); nevertheless, with this technique the crevice could be avoided by having a well formed capillary tip and silicon gasket. The thickness and shape of the gasket proved to be critical. As briefly discussed in Chapter 7.5.4, crevices have a significant influence on the results obtained by electrochemical testing; this has been discussed as well by other authors in [1-6]. It was clearly shown there that not taking into account the crevice effects would lead to a completely different interpretation of the data obtained and therefore a deceitful description of the electrochemical system being studied.

Unfortunately, as seen in [7, 8], it can be argued that it is possible that some researchers have ignored the effect of crevices while performing electrochemical testing. The adequate link between electrochemical work and surface analysis is, whenever investigated at all, not always performed and reported in detail. Particularly when doing experimental work at micro and nano ranges, this can be very easily ignored: optical microscopy (used in the micro electrochemical systems) does not provide enough magnification and the exact position of the tested area and the boundary limits of the capillary are not easily defined and traceable when studying the surface of the sample after electrochemical experiments ex situ with SEM and AES.

9.3.2 Micro-Capillary Cell

The technique:

In the last 20-30 years, an important development of localized electrochemical techniques has taken place. The birth of new techniques and the further development of existing ones has provided the necessary tools to obtain information on the electrochemistry of a corroding system on a micrometer level, and under ideal
conditions, even nanometer range. With the use of these techniques, the electrochemical behavior of single microstructural features like inclusions or grain boundaries can be investigated [9-12].

A brief overview of some localized techniques was done in Chapter 7.2; all of the techniques mentioned have advantages as well as limitations which have been discussed in literature. A more detailed outline specifically on the micro capillary cell is summarized in the mentioned chapter.

The crevice-free environment and the high reproducibility of the tests gave a strong argument to assume that the results obtained with this technique are an adequate reflection of the electrochemical systems under study. As such, the electrochemical experimental results can be summarized as follows

**The experimental results:**

The development of electrochemical setups like the Avesta cell and the Micro-Capillary cell were proposed for the study of localized attack studies; more specifically, the Avesta cell design was used mainly to avoid the presence of crevice in order to study pitting corrosion [2, 18-21], while the Micro-Capillary cell was designed with the aim of studying single microstructural features and their influence on electrochemical behavior [9-11, 22-28]. However, one important aspect to take into account is the fact that all these studies were performed on aluminium or stainless steel samples; the localized studies are linked to the existence of a stable passive layer, which is characteristic of aluminium or stainless steel, but not the case for bare steels like the DP.

Nevertheless, the use of a basic carbonate solution with pH 10 aids in the formation of an oxide layer which, even though it does not create a stable passive effect comparable to the one of a chromium oxide (in stainless steel grades) or aluminium oxide, proved to provide suitable conditions for the electrochemical testing particularly with the Micro-Capillary cell.

When the crevice effect was finally avoided in the Micro-Capillary cell, polarization curves were measured for both the CASIM and dilatometer samples. The parameters for the electrolyte used for the polarizations (Cl concentration and use -or not- of buffer) were varied. The results of the electrochemical testing showed that the electrolyte conditions had an effect on the polarization curves, but the microstructures showed no significant difference or trend among themselves for a fixed experimental condition.

The small differences identified in terms of corrosion potential, current density, passivity current and break down potential for different samples were just statistical changes within the range of experimental errors, and not an electrochemical feature due to microstructural variations. This increases the necessity of an adequate statistical study and data recollection while performing this type of electrochemical measurements.
It is believed that the results obtained with the Micro-Capillary cell (shown in Chapter 7) reflect the behavior of the electrochemical system studied; this means that the influence of the microstructure on the corrosion behavior of the complete set of samples studied can be considered to be negligible.

As such, based on the experimental curves from the Micro-Capillary setup and the information found in literature summarized in Chapter 4, the polarization curve, independent from the type of microstructure, can be described as follows (in the carbonate buffered electrolyte):

![Polarization curve](image)

**Fig. 9.1: Region 1: Polarization curve in carbonate buffered electrolyte.**

In the first (I) region of the curve shown in Fig. 9.1, the cathodic branch of the polarization can be seen. Here, the main reaction is the Oxygen Reduction Reaction (ORR) (Eq. 9.1):

$$
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (9.1)
$$

After the corrosion potential has been reached at approximately -300mV (vs. SCE), the second (II) region of the curve begins: at this point, active dissolution of the metal and hydroxide formation and deposition take place. The first step is the formation of FeOH$^+$ or the direct precipitation of Fe(OH)$_2$ (Eq. 9.2), where further oxidation to form FeOOH or Fe(OH)$_3$ may take place (Eq. 9.3):

$$
Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \quad (9.2)
$$
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\[
\text{Fe}^{2+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 + e^- \quad (9.3)
\]

Due to the carbonate buffer solution, the formation of insoluble iron species FeCO\(_3\) can also occur simultaneously with the development of the ferrous hydroxide (Eq. 9.4) [29]:

\[
\text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{H}^+ + 2e^- \quad (9.4)
\]

In this area, the ferrous carbonate and Fe(OH)\(_2\) create a first protective film on the surface [30-41]. According to [36], the mechanism is a dissolution/precipitation reaction of the Fe(II) species. The precipitation process is further stimulated at high pH and CO\(_3^{2-}\) / HCO\(_3^-\) concentration[35].

In the third (III) region of the curve, after the hydroxy-carbonate layer has been formed, passivity is obtained based on an oxide layer developed following these oxidation reactions (Eq 9.5 and 9.6) [30] :

\[
2\text{FeCO}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{CO}_3^{2-} + 6\text{H}^+ + 2e^- \quad (9.5)
\]

or

\[
3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2e^- \quad (9.6)
\]

Even though several authors also present models where the passivity is obtained by a single oxide layer [32, 34, 36], the double oxide compound layer theory seems to have a more general acceptance in literature [29, 30, 33, 37, 40, 42-45]. In this region, further conversion and growth of the oxide structure takes place.

An important aspect to remark is that this area is divided in two cases dependant on the chloride concentration of the solution: as established in Chapter 4, even though the chloride concentration did not have any influence on the formation and/or composition of the passive films, a higher concentration of these ions generated an earlier break down of the passive layer. This breakdown was identified in the polarization diagrams by sudden increase in current density (vertical dashed line in region III), and localized attack on the surface of the steel sample [46]. When no aggressive ions were present in the solution, anodic polarization could continue up to high values corresponding to oxygen evolution potentials. If breakdown occurred during the polarization, it was found randomly throughout region III; the breakdown was influenced by the chloride concentration and the size of the tip of the capillary, but not by the microstructural difference among the samples.

The last region of the curve, IV, the anodic currents start to increase due to the evolution of oxygen, shown in Eq. 9.7

\[
2\text{H}_2\text{O} \rightarrow 4e^- + 4\text{H}^+ + \text{O}_2 \quad (9.7)
\]

9.4 Exposure and Oxide Analysis

Immersion tests were performed on the dilatometer samples. Visual inspection of these showed that the samples without the final annealing procedure (a highly
deformed ferrite matrix with cementite islands) had a slightly different corrosion attack when compared to the other 4 types of dilatometer samples: this sample seemed to have a more general attack (general corrosion), while the other samples had a more localized attack (pitting) on the surface.

Subsequently, the oxides formed on the surface (after polishing and after immersion) were analysed with AES; it was discovered that both the natural oxide and the oxide after immersion was different for the not-annealed sample than for the others. Only this sample showed differences in the oxides, both in thickness and stoichiometry.

These differences could be the reason for the observations derived from the immersion tests; the level of deformation and/or internal stresses and grain orientation appear to have an influence on the oxide layer (effect that has been mentioned in other studies in literature), and this is the reason for the samples to have a different corrosion attack after immersion.

9.5 Comparison between Macro and Micro Electrochemistry

Chapter 6 and Chapter 7 discuss the electrochemical work performed in a Macro (Avesta cell) and a Micro (Micro-Capillary cell) level respectively. Even though different experimental parameters were used, important aspects can be highlighted when comparing the results obtained with both techniques.

General aspects like the influence of the carbonate buffer on the passivation of the surface and the detrimental effect that the chlorides have on the corrosion of the sample (or stability of the passive layer) are clearly seen in the results obtained with both experimental techniques. Furthermore, no influence on the microstructure on the corrosion performance of the model DP samples was identified with either setup. Also, the reproducibility of the Micro-Capillary experiments was better (less scatter) than the ones obtained with the Avesta cell, and the noise-like behavior seen on some of the Avesta polarizations was not recognized on the Micro-Capillary cell results.

However, a more detailed comparison reveals significant differences between the results: Fig. 6.6 and. 7.5 show the polarization curves for the DP samples in a 0.1M NaCl solution (no buffer) for the tests done with the Avesta and the Micro-Capillary cell respectively. While the Avesta cell recorded $E_{corr}$ values in the range of -700 to -600mV (wrt SCE), the ones seen in Micro-Capillary cell were found around -300mV. The anodic current ranges were also higher on the macro results, while the micro showed that even though no buffer was used, a passivation effect and breakdown potential appeared to be reflected on the experiments. This was not the case for the Avesta samples.

This behavior can be explained by the difference on the experimental parameters: the macro experiment had a 30min OCP measured prior to the potentiodynamic polarization. As shown in Fig. 6.6a, the decreasing value of OCP to a more negative value indicates that dissolution on the surface started before the potentiodynamic scan. The 30min OCP was not applied on the Micro-Capillary setup. This confirms
that there is a natural oxide layer formed in the surface of the samples after preparation and exposure to the electrolyte, but it is only stable enough for small areas.

On the other hand, when the buffer solution was used, both setups had a more similar behavior: Fig. 6.12 and 7.7 show the polarization curves for with the 0.1M NaCl with carbonate buffer solution for the Avesta and the Micro-Capillary cell respectively. Although the $E_{corr}$ was not clearly identified for the Avesta experiments due to the noise-like behavior around the corrosion potential, the range was found to be around -400 and -250mV (wrt SCE); for these experiments, the potential was found to be around -300mV with the Micro-Capillary cell. The Micro-Capillary experiments showed a very clear passive behavior that was not seen in the Avesta experiments, but a clear breakdown was identified. The fact that the macro samples had breakdown not seen in the micro samples can be attributed to the larger area effect: the larger area has a higher probability of having a weak spot in a not very stable passive layer (like the capillary size effect described in Chapter 7.5.1).

Furthermore, the current density level around the corrosion potential is lower for the Avesta experiments; this is most likely due to the ohmic resistance difference because of the different geometries between both electrochemical cells as mentioned in Chapter 7.

9.6 General Remarks

One of the main conclusions that can be made from this research is that the modification of the microstructure of a commercial grade DP600 showed no influence on the electrochemical behavior of the steel. Characteristics like ferrite/martensite phase ratio and grain size did not appear to affect the electrochemistry of the system.

This can also be concluded from the immersion and brief oxide analysis performed on the samples, where all the ferritic/martensitic samples showed arguably identical results. The only difference identified was found on the sample with a highly deformed ferritic matrix with carbides (Base Material sample, BM). It is suggested that the highly deformed microstructure had an influence on the type and/or size of the naturally grown oxide layer, which also proved to generate differences on the development of this layer when exposed to different electrolytes.

However, the difference found on the exposure and AES tests for only the BM sample was not identified in the electrochemical work; this leads us to state that the electrochemical characteristics of the tests mask whatever minor difference that might be found on the corrosion behavior of the sample. This implies possible complications not only on selection of adequate parameters and setups for electrochemical testing, but also on the conclusions derived from experimental work.

Furthermore, reproducing identical conditions of the samples for AES testing is expected to be not an easy task: first, polishing of the samples up to a fixed roughness is difficult because of their inherent different hardness due to the range of ferrite-martensite phase ratios. Second, the process of cleaning-drying, as well as the time spent for preparation of the sample for AES is a completely “manual” task, and
getting identical conditions and time frames is decidedly unlikely. As the apparent
differences of the electrochemical behavior due to microstructural effects seem to be
very small, any of these situations might present an influence that masks the effect
that wants to be measured.

Additionally, the proper establishment of parameters to determine reproducibility and
accuracy of the tests proved to be of vital importance, but also very difficult to
develop: it is thought that when researchers with similar work conclude that a clear
difference was found when corrosion potentials change in the order of 20-30mV due
to an increase of the ferrite/martensite phase ratio of 10%, this interpretation is
certainly debatable.

Contradictory conclusions reported by different authors [47-55] might be due to the
selection of electrolyte: an aggressive electrolyte (for example one with high
concentration of NaCl, no buffer) may overrule and dominate any effect (if so) of the
microstructure.

Another very important aspect to take into account, particularly while working on
micro ranges, is that the risk of neglecting the effect of crevices is high due to the
difficulties on the identification of it on the first place. It is clear that crevices have a
significant effect on the electrochemistry of the system and therefore the
interpretation of results. However, avoiding the presence of crevices during
experimental work proved to be a challenging task, and crevices can easily be
missed. Very careful analysis of both the surface after the experiments and the
results is necessary to ensure that crevices are not the dominant factor.

9.7 Further development

The results obtained showed that there are other microstructural features (other than
the phase percentage and size of the grains) that would be worth investigating in the
attempt to enhance the corrosion resistance of high strength steels.

Recommended future research could be focused on one of the following topics:

- Evaluation of corrosion performance of DP600 with different base chemical
  compositions
- Evaluation of the effect of internal stresses on the corrosion performance of
  DP600
- Evaluation of the effect of grain orientation on the corrosion performance of
  DP600
- Studies of these factors (chemical composition, internal stresses and grain
  orientation) on the corrosion behavior of other higher grades of DP and other
  type of (U)HSS like TRIP and TWIP steels.
- Microstructural influence on (U)HSS on the bonding properties of protective
  coatings.
9.8 References

Discussion and Conclusions

Summary

Weight reduction of car bodies can be achieved by application of steel components with a lower thickness; however mechanical properties (for constructive and safety reasons) must be maintained, which can be achieved by using (U)HSS steels. These steels have been designed and optimized for improved mechanical behavior and therefore normally have a poorer or at least not well documented and understood corrosion resistance. One of these HSS steels are the so called Dual Phase steels, or DP steels.

The aim of this work is to investigate the effect of the individual and combined ferrite and martensite phases in model DP steels on the corrosion performance and electrochemical behavior. For this, the first part of this work consisted in the development of a range of dual phase microstructures with different ferrite-martensite ratios ranging from virtually fully ferritic to fully martensitic. Controlled heat treatments were developed with the CASIM (Continuous Annealing SIMulator) and the dilatometer in order to obtain the desired microstructures.

After the microstructures were developed, standard 3 electrode electrochemical setups were used to perform open circuit potential and potentiodynamic polarization measurements, approach which was then complemented by the use of Micro-Capillary cell. The use of the localized technique was focused on the possibility to perform single phase measurements which are not possible with the standard setups. The influence of the individual and relative amounts of ferrite and martensite on the electrochemical response of model DP steels was discussed.

The first conclusions that were drawn from the electrochemical work was that due to the absence of a stable passive layer, performing measurements on standard setups proved to be a challenge because crevice was a dominating factor in the system. Modifications to standard cell and Avesta cell were done in the attempt to avoid the presence of crevice.

With the Micro-Capillary setup, even though crevice can also be an issue, reliable and reproducible polarization curves were obtained. A clear effect of sodium chloride concentration and the presence of a carbonate buffer on the electrochemical response of the model DP steels was observed. However, it was also found that the differences in the electrochemical behavior induced by the amount of martensite present are not significant enough to be distinguished from the reproducibility of the polarization curves. This was also the case for the base material sample, which even though composed of a highly deformed ferritic matrix with cementite-carbides islands, showed a similar response in the polarizations.

The influence of the polarization system (setup, electrolyte, and microstructure) was discussed, as well as the importance of acknowledging the influence of crevice and reproducibility while performing electrochemical measurements.
Samenvatting

Het lichter maken van de carrosserie van een auto kan men realiseren door dunnere stalen delen toe te passen. Voor constructieve- en veiligheidsdoeleinden moeten de mechanische eigenschappen echter worden gegarandeerd. Dit kan worden bewerkstelligd door het gebruik van zogenaamde Ultra High Strength Steels - (U)HSS. Eén categorie van (U)HS staal is het zogenaamde “Dual Phase” (DP) staal. Deze stalen zijn ontworpen en geoptimaliseerd voor mechanisch gedrag, en hebben normaal gesproken slechter corrosieweerstand, of ten minste slechter gedocumenteerde en begrepen corrosiemechanismen.

Het doel van dit onderzoek is het bepalen de corrosieweerstand en het elektrochemisch gedrag van de individuele en de gecombineerde ferriet- en martensietfasen in model-DP stalen. Het eerste deel van dit werk beslaat de ontwikkeling van een reeks van “dual phase” microstructuren met uiteenlopende ferriet-martensietverhoudingen, variërend van volledig ferritisch tot volledig martensitisch. Geregelde warmtebehandelingen werden ontwikkeld met de CASIM (Continuous Annealing SIMulator) en de dilatometer om de gewenste microstructuren te krijgen.

Na het vervaardigen van de microstructuren zijn conventionele “3-elektrode” elektrochemische opstellingen gebruikt om de vrije corrosiepotentiaal te meten en potentiodynamische polarisatiemetingen te doen. Deze methoden zijn daarna aangevuld met de microcapillaire techniek. Het gebruik van deze plaats specifieke techniek was gericht op metingen aan één enkelfasige korrel, iets wat niet mogelijk is met de conventionele technieken. De invloed van de individuele korrels en relatieve verhoudingen ferriet en martensiet op het elektrochemisch gedrag wordt besproken. De eerste conclusies die werden getrokken uit het elektrochemische werk waren dat, door de afwezigheid van een stabiele passieve laag, het doen van metingen een grote uitdaging was omdat spletten van dominante invloed waren in het systeem. Modificaties werden doorgevoerd aan de standaard corrosiecel en de zogenaamde Avestacel in een poging om spletten te vermijden.

Met de microcapillaire opstelling werden, ondanks dat ook hier spltten problematisch kunnen zijn, betrouwbare en reproducierbare polarisatiecurven gemeten. Een duidelijk effect van chlorideconcentratie en van de aanwezigheid van een carbonaatbuffer op de elektrochemische respons konden worden aangetoond. De verschillen die werden gevonden in het elektrochemische gedrag door de hoeveelheid martensiet waren echter niet significant ten opzichte van de reproduceerbaarheid van de polarisatiecurven. Dit gold ook voor het specimen van het onbehandelde uitgangsmateriaal dat, ondanks dat het bestond uit een sterk vervormde ferritische matrix met cementiet-eilanden, een soortgelijke meting tijdens de polarisatie te zien gaf.

Zowel de invloed van het polarisatiesysteem (opstelling, elektroliet en microstructuur) als de invloed van spletten en reproduceerbaarheid tijdens het uitvoeren van elektrochemische metingen wordt besproken.
Conference Presentations and Proceedings

- **D. Farias, J.M.C. Mol, H. Terryn, J.H.W de Wit, F. Hannour**, Microelectrochemical measurements to Evaluate Corrosion Performance of model DP steels, Eurocorr 2010, Moscow, Russia


Journal Paper

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Or simply,

GRACIAS, TOTALES!
About the Author

David Farias was born in Bogota (Colombia) in 1978. In 2002, he obtained his BSc. in Mechanical Engineering from Los Andes University (Bogota). During most of his studies, he worked as a Mathematics teacher in a prestigious high school. After working for one year as a Maintenance Engineer in a military base, he moved to the Netherlands to pursue further academic development. In 2006, he obtained his MSc. degree in Mechanical Engineering (Automotive Engineering - Vehicle Safety track). He did his internship and graduation project at Tata steel R&D (then Corus R&D), investigating in service performance of High Strength Steels. From October 2006 until the end of 2010, he was part of the Corrosion Technology and Electrochemistry group at TU/Delft, while carrying out his PhD research on “Influence of the microstructure on the corrosion performance of DP steels”. As from the beginning of 2011 he has been working at Fluor B.V. as a Corrosion and Materials specialist, being involved in material selection and corrosion control advice in several projects mainly in the petrochemical business.

During his PhD studies, he presented his work in several international conferences.
About the Cover

The cover of this book was designed by Camila Farías Torres.