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AN EVALUATION OF GALVANIC CORROSION OF SHEET METAL REINFORCED HYBRID STRUCTURES MANUFACTURED BY HIGH-PRESSURE DIE CASTING

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"Good parents give their children Roots and Wings.

Roots to know where home is,

Wings to fly away and exercise what's been taught them."

Dr. Jonas Salk

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Compendio

I. Introduzione

Questo lavoro è stato sviluppato con lo scopo di analizzare il comportamento a corrosione di diverse leghe di alluminio a magnesio e, in particolare, di studiare il processo di corrosione galvanica quando esse si trovano accoppiate in strutture ibride, al fine di capire quale coppia presenta la miglior resistenza contro tal processo degenerativo.

L'alluminio e il magnesio, infatti, quali materiali da costruzione di minore densità, sono sempre più utilizzati nell'industria dei trasporti con lo scopo di ridurre il peso delle strutture e risparmiare carburante, e la combinazione dei due in strutture ibride rappresenta la miglior soluzione a tale fine. Le strutture ibride Al-Mg registrate come VarioStruct® da Imperia GmbH permettono attualmente una riduzione del peso del 45-55% in comparazione all'uso dell'acciaio.

Per la produzione di massa di componenti in leghe leggere, il metodo più efficiente in termine di costi è il processo di pressocolata che permette di ottenere componenti di alta complessità e precisione, mentre nel caso in cui siano necessarie delle combinazione di leghe, il compound casting permette di colare direttamente una lega metallica su un substrato metallico solido. Le strutture ibride in alluminio e magnesio prodotte per compound casting in pressocolata sono quindi la soluzione per ottenere una buona riduzione di peso ma il problema più consistente è rappresentato dalla corrosione galvanica che entra in gioco a causa dell'alta differenza di potenziale elettrochimico tra i due elementi (Al = -1,67 V, Mg = -2,37 V) e alla presenza di un elettrolita.

Diversi test sono stati eseguiti per capire il comportamento a corrosione delle leghe d'interesse: quando si trovano situate da sole in un elettrolita, tramite l'utilizzo di tecniche elettrochimiche, o quando si trovano in contatto tra di loro, quindi in presenza di corrosione galvanica. I materiali analizzati sono per l'alluminio: EN AW 5083 e EN AW 6082, e per il magnesio le leghe: AZ91 HP, AM50 HP e AM60 HP, con

riferimento poi alle coppie formate da EN AW 5083 + AZ91 HP e EN AW 6082 + AM50 HP.

La coppia che minimizza gli effetti della corrosione galvanica sarà, come dimostrato, la combinazione di EN AW 5083 + AZ91 HP ma successivi studi sono necessari per trovare metodi che proteggano completamente le strutture ibride Al-Mg dall'inevitabile corrosione.

II. Pressocolata e compound casting

La pressocolata è una tecnica di colata in stampo permanente che si differenzia dalle altre per la velocità di riempimento della cavità e l'alta pressione applicata. Si distingue in pressocolata a camera fredda o calda. L'alluminio richiede l'utilizzo della camera fredda perché può erodere il sistema e il ferro può contaminare la lega; nel caso del magnesio si utilizza in genere la camera fredda ma per le leghe AZ e AM può essere utilizzata anche la camera calda.

La pressocolata permette una forte automazione del processo e una grande produttività ma due caratteristiche peculiari sono l'estrema turbolenza sperimentata dal metallo fuso quando viene forzato nello stampo e l'alta velocità di solidificazione. Per queste motivi, i pezzi ottenuti per pressocolata presentano porosità interna dovuta a gas quali aria, idrogeno o vapori, oppure difetti derivanti da ritiri di solidificazione.

La differenza nella velocità di solidificazione fa si che i getti presentino differenze significative rispetto quelli ottenuti con altre tecniche di colata; in particolare la macrostruttura presenta tre diverse regioni: la pelle superficiale densa e fine, il corpo centrale e il cuore che in genere contiene difetti e cavità da ritiro. La macro e microstruttura influenza il comportamento meccanico e anche il comportamento a corrosione, che sono inoltre entrambi meno prevedibili rispetto al caso di componenti prodotti con altre tecniche. La microstruttura è infatti fortemente influenzata dalle condizioni a contorno della colata e una geometria complessa può esibire un range molto alto di proprietà diverse.

Il compound casting ottenuto per pressocolata è il processo d'interesse in questo lavoro in quanto permette di unire metalli leggeri semplicemente colando un metallo liquido su un inserto solido, formando uno strato di transizione continuo. Questo permette di evitare la formazione di fasi o strutture fragili nel punto di contatto. Gli studi fatti fino ad ora riportano casi di compound casting con la colata di magnesio liquido su inserti in magnesio, o di alluminio su inserti di alluminio o ancora la creazione di componenti alluminio-magnesio.

Diverse tecniche vengono usate nei vari casi per eliminare lo strato di ossido e migliorare la bagnabilità della superficie durante la colata per permettere la creazione di una zona continua di transizione. Nel caso dei componenti alluminio-magnesio si è scoperto che solo la colata di leghe di magnesio liquido su inserti di alluminio permette una buona creazione di strutture ibride tramite compound casting.

III. Corrosione galvanica

La corrosione è un attacco distruttivo del materiale dovuto alla sua reazione con l'ambiente, di solito per reazione chimica o elettrochimica. Nello specifico, la corrosione galvanica, è definita come un'accelerazione della corrosione di un metallo dovuta al contatto elettrico con un altro metallo o conduttore più nobile, in un ambiente corrosivo. Per avere

Figura 1: Elementi per la corrosione galvanica.

corrosione galvanica dunque è prevista la presenza di: almeno due materiali, uno in cui avviene l'ossidazione, detto anodo, e uno in cui avviene la riduzione, detto catodo, un contatto elettrico tra i due e un elettrolita conduttivo. Se uno dei quattro fattori è assente, non avviene corrosione galvanica.

Per spiegare tutti i processi che avvengono durante la corrosione galvanica, si fa riferimento alla teoria elettrochimica e, in particolare, per lo studio dei potenziali di corrosione di ogni metallo, si analizzano le curve di polarizzazione e il diagramma di Evans. L'intensità della corrente che si misura quando due elementi sono accoppiati in

un elettrolita, e l'aumento nel tasso di corrosione dovuto a tal corrente, è determinato dalla tendenza di ogni elemento di creare una corrente quando il suo potenziale è forzato ad un cambiamento e tal fenomeno è chiamato polarizzazione. Le curve di polarizzazione rappresentano proprio questo: riportano la variazione della corrente in funzione del potenziale applicato. Ogni curva presenta due parti distinte: una parte catodica e una anodica, mentre il punto rivelato dal diagramma di Evans indica la corrente e il potenziale di corrosione.

Riconoscere e predire la corrosione galvanica non è così facile ma esistono diversi tipi di test sviluppati a tale scopo, inoltre si possono ricorrere anche a diversi metodi per ottenere le curve di polarizzazione sopra citate, in particolare metodi potentiodinamici o potentiostatici. Ogni tipo di test ha una serie di condizioni al contorno da tenere sotto controllo o impostare e la difficoltà consiste nel rendere questi test il più vicino possibile alle reali situazioni di utilizzo dei materiali per verificare il loro comportamento e la loro resistenza alla corrosione galvanica nell'ambiente d'interesse.

IV. Alluminio e magnesio

L'alluminio è conosciuto come materiale da costruzione grazie alla sua leggerezza. Possiede un'alta resistenza a corrosione rispetto altri materiali, conferitagli dal film di ossido autorigenerante sempre presente sulla superfice in atmosfera ossidante. L'acidità o la basicità di una soluzione o di un ambiente cambia però notevolmente le proprietà a corrosione dell'alluminio: in condizione alcaline, il metallo può corrodersi e quando il film è localmente perforato, la corrosione procede più velocemente perché l'alluminio si corrode prima del suo ossido; in condizioni di acidità, l'ossido si corrode prima e si può avere un attacco corrosivo più diffuso sulla superficie. L'alluminio è comunque un elemento molto reattivo e quasi tutti i metalli sono catodici a esso e alle sue leghe, in quanto presenta un potenziale elettrochimico di -1,67 V, quindi diventa sacrificale in presenza di un elettrolita, tranne per le eccezioni di magnesio, cadmio e zinco, che risultano anodici nei confronti dell'alluminio.

Le leghe di alluminio d'interesse per i test eseguiti sono EN AW 5083, una lega alluminio-magnesio, e EN AW 6082, una lega alluminio-magnesio-silicio. La prima è

composta nominalmente dal 4,5 % di magnesio, 0,7 % di manganese e altri elementi in lega, e conosciuta per le eccezionali performance in ambienti estremi. La seconda lega è composta dall'1 % di silice, 0,6-1,2 % di magnesio e altri elementi come il manganese; è conosciuta come lega per la costruzione di strutture e presenta un'eccellente resistenza a corrosione.

Il magnesio è il materiale da costruzione più leggero conosciuto e presenta alcuni ottimi vantaggi ma i lati negativi ne hanno limitato l'utilizzo fino a ora. Tra questi in particolare il basso modulo elastico, l'alto ritiro durante la solidificazione, l'alta reattività chimica e la bassa resistenza a corrosione. Infatti, a differenza dell'alluminio, il magnesio presenta un film di passivazione molto instabile in alcuni tipi di ambienti, inoltre, con un potenziale elettrochimico di -2,37 V, risulta anodico alla maggior parte dei materiali usati nell'ingegneria e quindi soggetto a grave corrosione. Lo sviluppo di varie leghe ha permesso un miglioramento: l'aggiunta di alluminio, zinco e manganese migliora la resistenza a corrosione, come pure lo sviluppo di processi per eliminare le impurità quali ferro, nickel, rame che anche in bassissime percentuali accelerano enormemente i processi di corrosione.

Le leghe di magnesio testate sono AZ91, la più comune, AM50 e AM60, tutte prodotte per pressocolata. La lega AZ91 HP è nominalmente composta dal 9 % di alluminio, 1 % di zinco e altri elementi ed è la più popolare commercialmente disponibile, presenta buone proprietà meccaniche e resistenza a corrosione. La lega AM50 HP contiene il 5 % di alluminio e 0,28-0,50 % di manganese, ed è tipicamente utilizzata nell'automotive, come pure la lega AM60 (6 % alluminio e 0,21-0,35 % manganese).

V. Metodo sperimentale

I test eseguiti sulle leghe d'interesse sono in tutto cinque, qui brevemente riassunti.

I primi due utilizzano un metodo potentiodinamico per ottenere le curve di polarizzazione delle singole leghe analizzate. Il primo setup prevede l'uso del Rotating Disk Electrode (RDE), un elettrodo rotante su cui viene montato il provino da testare e immerso nella soluzione di interesse, nel caso specifico un soluzione acquosa a 0.1M di

cloruro di sodio. Il secondo setup è quello standard con l'utilizzo di tre elettrodi, in cui l'elettrodo con il materiale da testare rimane fisso e immerso nella soluzione. I test presentano un setup molto simile, con le uniche differenze nella rotazione o meno del provino d'interesse (working electrode) e delle dimensioni del provino stesso, e il risultato di tali test sono rappresentai dalle curve di polarizzazione che riportano la variazione di corrente al variare del potenziale applicato.
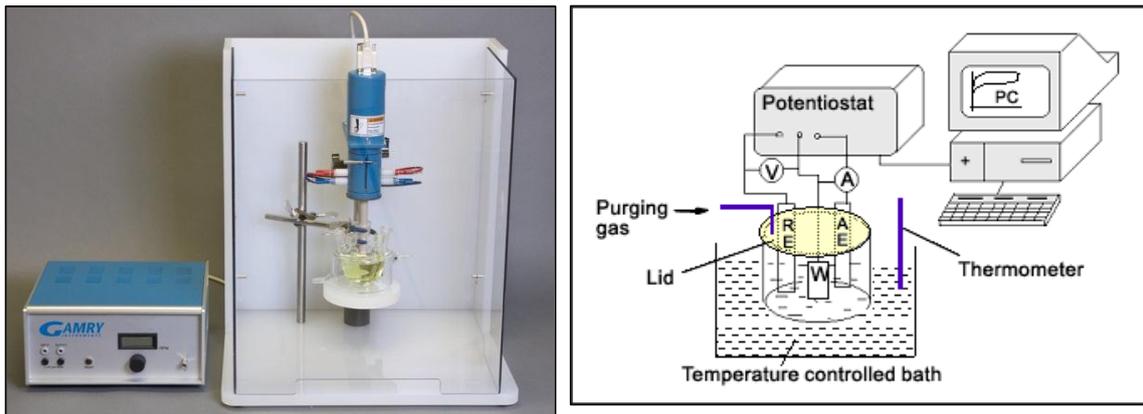
Figura 2: (sinistra) Rotating disk electrode setup e (destra) Standard setup per ottenere le curve di polarizzazione.

Gli altri tre test si concentrano sullo studio della corrosione galvanica, nelle coppie d'interesse EN AW 5083 + AZ91 HP e EN AW 6082 + AM50 HP.

Il primo test utilizza una cella galvanica in cui sono immersi i due elettrodi (uno rappresentato da una lega di alluminio e l'altro da una lega di magnesio) collegati in un circuito, e vengono misurati diversi valori, come il potenziale dell'anodo e del catodo a circuito aperto o chiuso, ma con lo scopo finale di misurare la corrente galvanica che si crea tra i due materiali. I vari valori rappresentati da tensioni sono misurati con un voltmetro ma, essendo lo strumento troppo poco sensibile per misurare valori piccoli, si preferisce non ricavare la corrente galvanica dalle tensioni, ma utilizzare un potentiostatometro utilizzato con resistenza zero. Inoltre la corrente viene misurata per otto ore per
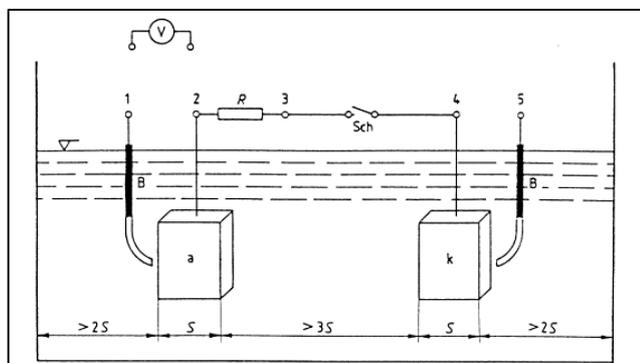
Figura 3: Setup con cella galvanica e i due elettrodi.

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capirne l'evoluzione nel tempo e il procedere della corrosione.

Il successivo test prevede l'uso di provini in cui le leghe di alluminio e magnesio presentano una forma di 1 cm x 1 cm e sono a contatto in uno dei lati. Il provino così realizzano viene immerso nella soluzione, identica ai test precedenti, e un particolare setup permette di raccogliere l'idrogeno che si sviluppa dalla reazione chimica del magnesio con l'acqua. Tale

Figura 4: Setup per la misurazione dell'evoluzione di idrogeno.

quantità d'idrogeno prodotta nel tempo è direttamente correlabile alla quantità di magnesio dissoltasi e quindi alla percentuale di avanzamento della corrosione. La raccolta d'idrogeno viene fatta per otto ore consecutive e i risultati riportati su un grafico per confrontare le due coppie.

L'ultimo test eseguito è di nuovo un test d'immersione ma i provini utilizzati sono formati da fogli di puro magnesio e puro alluminio connessi tramite diffusion bonding cioè tramite processo di diffusione nella superficie di contatto tra i due. I provini usati sono due, sottoposti a stesse condizioni di temperatura e pressione, uno per la durata di sei giorni e l'altro per sette giorni. I provini vengono immersi nella soluzione ed estratti a intervalli di 10, 20 , 40 e 100 minuti per essere osservati a microscopio e capire come la corrosione procede nei due materiali e nell'interfaccia.

Figura 5: Provini usati nel test di immersione formati da fogli di puro alluminio e magnesio connessi con diffusion bonding.

VI. Risultati dei test e discussione

I risultati ottenuti con l'uso del Rotating Disk Electrode presentano curve di polarizzazione poco definite a causa della passivazione dello strato esterno nelle leghe di alluminio, mentre per il magnesio i risultati sono più chiari e lineari. Questo setup è relativamente nuovo e utile soprattutto per il magnesio in quanto la rotazione dell'elettrodo e il ricircolo della soluzione fanno si che l'effetto di alcalinizzazione della soluzione vicino alla superficie del provino influenzi meno i risultati. Purtroppo risulta necessaria un'ulteriore sperimentazione per capire come la velocità di rotazione dell'elettrodo influenzi i risultati e il valore del potenziale di corrosione dei vari materiali. Per questo motivo, lo standard di riferimento è considerato l'insieme dei valori ottenuti con il setup standard.
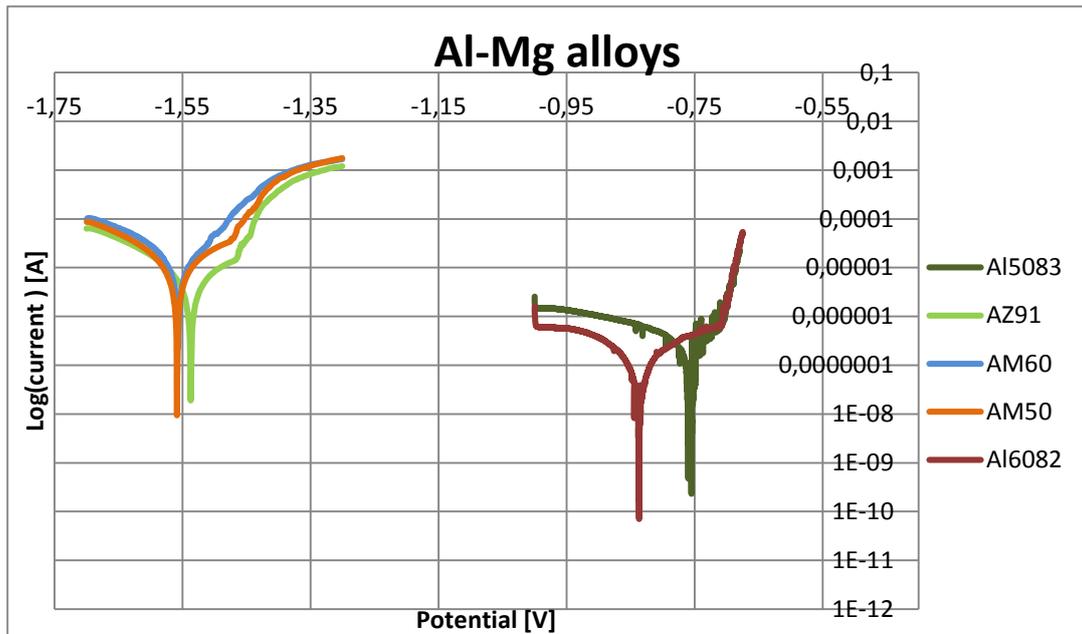
Tabella 1: Curve di polarizzazione per le varie leghe di alluminio e magnesio ottenute con il setup Rotating Disk Electrode.

I risultati delle curve di polarizzazione ottenuti dal setup standard mostrano che l'alluminio 6082 presenta un potenziale di corrosione (-0,69 V) meno negativo dell'alluminio 5083 perché contiene una quantità di magnesio inferiore e quindi la sua curva di polarizzazione è più lontana da quelle del magnesio; al contrario, per la più alta percentuale di magnesio nella lega 5083, il suo potenziale di corrosione risulta più negativo (-0,87 V). Per il magnesio, la lega AZ91 presenta un potenziale di corrosione (-1,43 V) leggermente meno negativo della lega AM50 (-1,48 V), dovuto alla maggior

percentuale di alluminio. Questo permette di concludere che la combinazione di alluminio 5083 e AZ91 presenta un gap nel potenziale di corrosione minore di quello della coppia 6082 e AM50 e quindi il comportamento a corrosione, una volta accoppiati, dovrebbe risultare migliore.
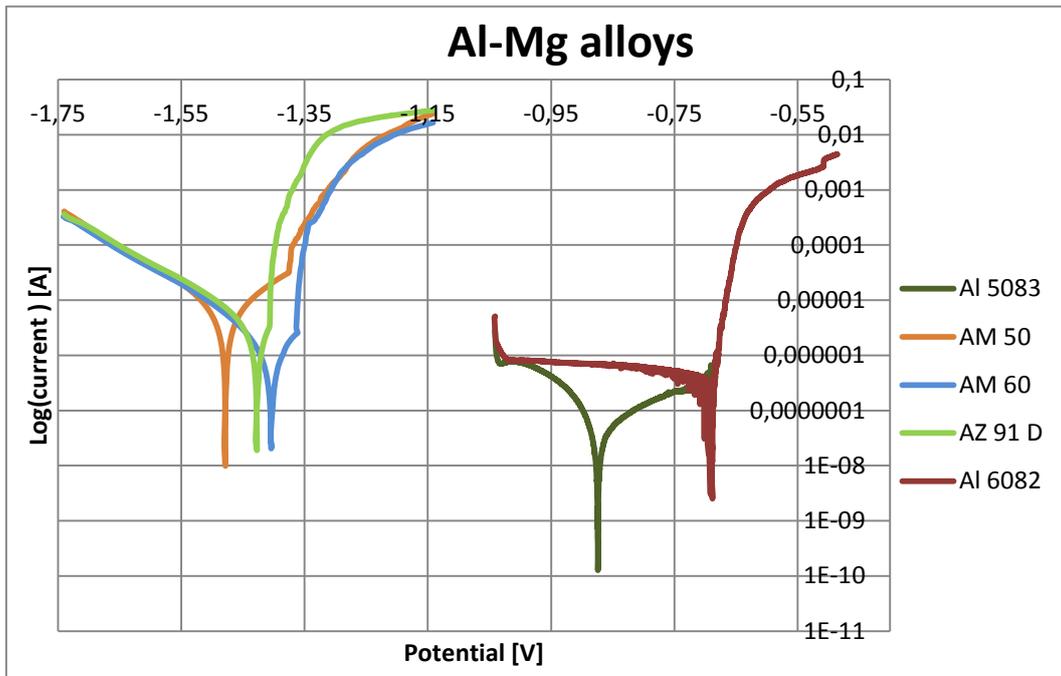
Tabella 2: Curve di polarizzazione per le varie leghe di alluminio e magnesio ottenute con il setup standard.

Passando ai risultati dei test con il setup della cella galvanica, la cosa più interessante da sottolineare è l'andamento della corrente galvanica per le due coppie durante le otto ore di misurazione. Appare chiaro che misurare la corrente per pochi minuti non è indicativo perché il tasso di corrosione è più elevato all'inizio per la coppia EN AW 5083 + AZ91 HP e cresce per un certo periodo di tempo ma per poi diminuire sensibilmente. Al contrario per la coppia EN AW 6082 + AM50 HP la corrente galvanica cresce più lentamente all'inizio per raggiungere un alto valore (in termini assoluti) alla fine del test, a dimostrare che la corrosione è maggiore in questo coppia e non nella precedente.
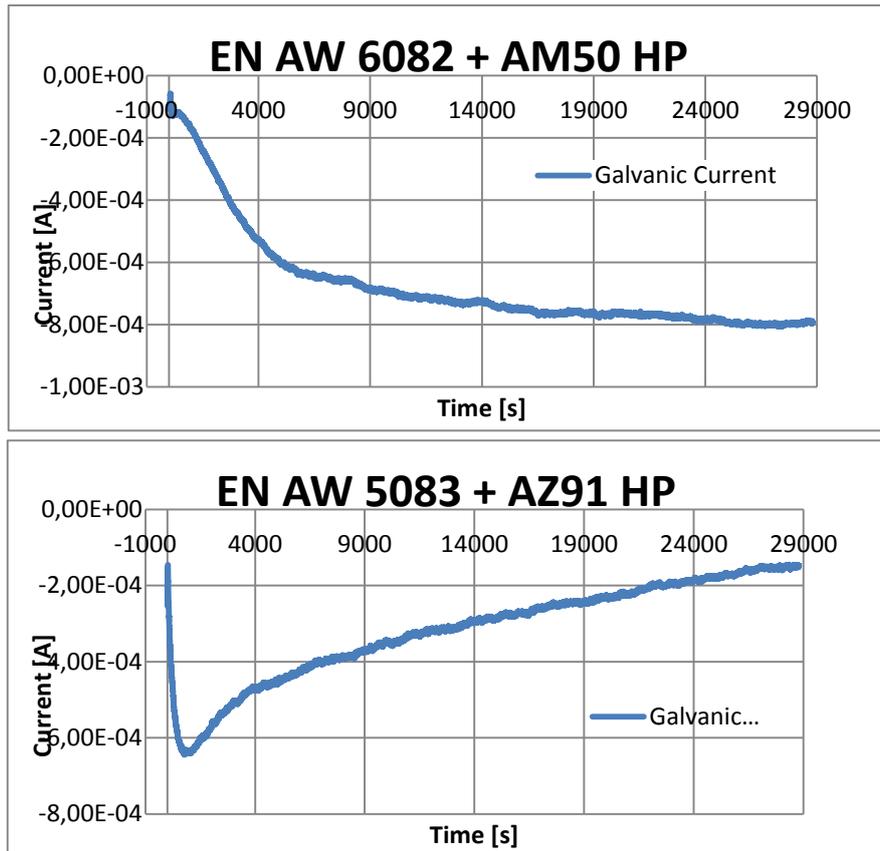
Tabella 3: Andamento della corrente nel test con uso della cella galvanica, (sopra) per la coppia EN AW 6082 + AM50 HP e (sotto) EN AW 5083 + AZ91 HP.

La misurazione dell'evoluzione dell'idrogeno nel successivo test ripresenta gli stessi andamenti nei risultati: la produzione d'idrogeno è inizialmente maggiore nella coppia EN AW 5083 + AZ91 HP ma poi cala notevolmente, mentre per l'altra coppia la produzione di idrogeno e quindi il tasso di corrosione inizia più lentamente per poi aumentare fino alla fine del test e mostrare un comportamento peggiore a corrosione.
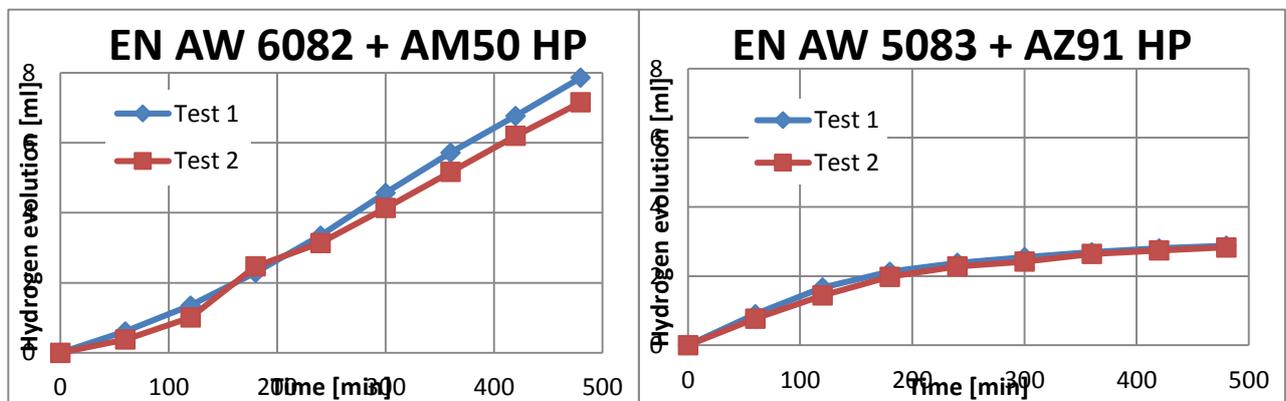
Tabella 4: Evoluzione dell'idrogeno, (sinistra) per la coppia EN AW 6082 + AM50 HP e (destra) EN AW 5083 + AZ91 HP.

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Osservando i provini alla fine di questi test, si nota che le leghe di alluminio presentano lo stesso tipo di corrosione ma l'alluminio 5083 si corrode meno dell'alluminio 6082 ovviamente perché l'alluminio 5083 presenta una percentuale più alta di magnesio. Entrambe le leghe di magnesio presentano tracce di corrosione puntiforme ma la lega AZ91 presenta segni leggermente meno evidenti della lega AM50.

Nell'ultimo test d'immersione il magnesio puro mostra segni di corrosione puntiforme subito dopo pochi minuti d'immersione nella soluzione che vanno aumentando visibilmente fino alla fino del test, mentre l'alluminio presenta corrosione filiforme, solo qualche traccia all'inizio e in larga parte dopo 100 minuti d'immersione. Anche in questo caso, come nei precedenti, entrambe le leghe si corrodono, non c'è protezione anodica per l'alluminio. È importante sottolineare che il modo di corrosione per i metalli puro è molto diverso da quello delle leghe, per la presenza di elementi aggiuntivi ma anche per la diversa microstruttura ottenuta dalla solidificazione. L'interfaccia metallica, al contrario dei due metalli, non si corrode e ciò può risultare utile per disaccoppiare i due materiali o ridurne la corrosione galvanica. Inoltre la coppia sottoposta a sei giorni di processo di diffusione mostra una corrosione maggiore perché lo spessore dello strato intermetallico è inferiore in quanto la diffusione ha avuto meno tempo per lavorare.

VII. Prospettive e conclusioni

Le coppie analizzate presentano sempre una severa corrosione galvanica quindi è necessario trovare una soluzione per proteggere le strutture ibride di alluminio e magnesio. Uno dei modi più efficace è ricoprire le intere strutture con dei rivestimenti, separando il substrato dall'ambiente ma le future ricerche si concentrano anche su rivestimenti da applicare agli inserti di alluminio per disaccoppiarli dal magnesio. La sfida più importante sarà trovare dei rivestimenti che resistano alla pressocolata, il metodo usato per creare questo tipo di strutture ibride.

In conclusione, le leghe leggere in alluminio e magnesio e le strutture ibride hanno un'importanza crescente nei futuri sviluppi in campo automotive ma presentano il grave problema della corrosione galvanica. I test eseguiti mostrano che nel caso di un

accoppiamento tra alluminio 6082 e magnesio AM50 HP, la corrosione è maggiore rispetto l'accoppiamento di alluminio 5083 e magnesio AZ91 HP ma è presente in entrambi i casi. Il lavoro eseguito dunque non porta a un'immediata soluzione del problema ma riporta un'analisi dettagliata del comportamento delle leghe studiate, utile per continuare lo studio sulle possibili tecniche di protezione utilizzabili.

Summary

This work has been executed to develop the analysis on the corrosion behavior of different aluminum and magnesium alloys, and, in particularly, the galvanic corrosion between the two, when they are coupled. The ultimate goal is to report the behavior of the metals investigated and to assert which coupled aluminum and magnesium alloys present the best resistance against the galvanic corrosion.

The work starts with an overview on the context of the study, i.e. the state of art on the hybrid light metal structure made by high pressure die casting, and then, the second chapter presents all the notions necessary to understand the galvanic corrosion like the polarization curves and the passivity behavior, considering also the testing process. Prior to the experimental part of the work, an overview on aluminum and magnesium is presented, respectively in chapter number three and four, to introduce the main features of the materials of interested and the propriety of corrosion resistance.

In the chapter five, there is presented the theoretical background and the setup for every test performed. The tests include two electrochemical techniques, used to obtain the polarization curves of different alloys, i.e. EN AW 5083 and EN AW 6082 for the aluminum alloys, and AZ91 HP, AM50 HP and AM60 HP for the magnesium alloys: the first technique uses the rotating disk electrode while the second one uses the standard three electrode setup. Other tests investigate the galvanic corrosion, coupling one aluminum alloy and one magnesium alloy. The first test uses the galvanic cell to measure the galvanic current between the couples; the second one measures the hydrogen evolution of aluminum and magnesium alloys in contact during an immersion test and the last one investigates couples of pure aluminum and magnesium connect together with the diffusion bonding. Chapter six present the results of the tests and chapter seven the discussion on these: at the end of all experiments, it is possible to assert that the couple EN AW 5083 + AZ91 HP has a better behavior against galvanic corrosion than the couple EN AW 6082 + AM50 HP.

Therefore uncoated system with coupled aluminum and magnesium presents always galvanic corrosion, consequently chapter eight deals with a discussion on different coatings and solution in future scenery of corrosion prevention.

Introduction

The use of light structural materials has become inevitable in the modern world by employing materials such as aluminum and magnesium, which have the lightest density of all common structural materials. Lightweight construction in the transport industry helps reduce weight and save fuel and, to optimize performance, a combination of materials is the most efficient method, because one material alone is often insufficient.

Magnesium is the lightest of all metals used as the basis for constructional alloys and it is this property which entices automobile manufactures to replace denser materials, steels, cast irons and copper base alloys but even aluminum alloys by magnesium based alloys. A wider use of magnesium base alloys necessitates several parallel programs like alloy development, process development improvement and design considerations because the use of magnesium for parts of automobile structures is still rather limited, while aluminum has already established a leading role in automotive applications.

The combination of aluminum alloys and magnesium alloys in a hybrid light metal structure is hence object of interesting in the last years. Hybrid structures have many vantages using in the car body design, most important the weight reduction and the integration of different parts. The state of art used as reference for the construction of the car body is the sheet steel and, in comparison to this, the best results in the weight reduction are now enable by the use of the carbon fiber-enhanced plastics (weight reduction of 60%). The hybrid Al-Mg structure made with the registered VarioStruct® by Imperia GmbH should permit a weight reduction around 45-55% in comparison the use of the steel.

Moreover aluminum and magnesium have almost the same density, so, compared to the structures made with steel and aluminum, there are vantages concerning the geometrical accuracy and it is possible to use scanning techniques contrast enhanced, useful for corrosion protection techniques. Furthermore aluminum and magnesium have almost the same thermal expansion coefficient and this is useful to reduce deformation and residual stress during the solidification process.

The high pressure die casting is the most cost-effective casting method for the mass production of light metal parts: components with a high complexity and precision can be fabricated which are especially used for a wide range of automotive parts but when a combination of materials is necessary to satisfied the condition requested, compound casting becomes the most promising way to produce the components. Compound casting simplifies joining processes by directly casting a metallic melt onto a solid metal substrate.

With high pressure die casting, the hybrid structure obtained combining aluminum sheets and magnesium casting permits the highest weight reduction but a severe problem is represented by the galvanic corrosion. This is a very common situation in the real life application of the hybrid light metal structures due to the high difference in the electrochemical potential of aluminum and magnesium (Al = -1,67 V, Mg = -2,37 V) and the possible contact with an electrolyte. The investigation on this kind of corrosion is the subject of this work.

Different tests are performed to study the corrosion behavior when some aluminum and magnesium alloys of interested are situated alone in an electrolyte, using electrochemical techniques; other tests are performed with coupled aluminum and magnesium alloys to analyze the galvanic corrosion and to understand which couple presents the best corrosion resistance. The materials investigated are for aluminum: EN AW 5083, an aluminum-magnesium alloy, and EN AW 6082, an aluminum-magnesium-silicon alloy, and for magnesium: AZ91 HP, AM50 HP and AM60 HP, all composed by a percentage of aluminum and all made by high pressure die casting. In particularly, the couples of interested are EN AW 5083 + AZ91 HP and EN AW 6082 + AM50 HP.

At the conclusion of the research, different tests show that the couple EN AW 5083 + AZ91 HP presents the best behavior against corrosion. This couple minimizes the bad effect of galvanic corrosion but next studies on this field should focus on methods to protect completely the hybrid Al-Mg structures against the inevitable corrosion. This could include the analysis of different coatings to isolate the entire structure from the environment or to avoid the contact between aluminum and magnesium, decoupling the two. The most critical issues will be find coatings that could survive during the HPDC.

CHAPTER 1

High pressure die casting hybrid light metal structure – state of art

1.1. High pressure die casting (HPDC)

Casting is a manufacturing process by which a liquid material is usually poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solidified part is known as casting which is ejected or broken out of the mold to complete the process. The modern casting process is subdivided in two main categories: expendable and non-expendable casting. It is further broken down by mold material, such sand or metal, and pouring method, such as gravity, vacuum, or low/high pressure.

The die casting is a method of molding materials under pressure and usually involves non-ferrous metals and alloys. The mold is coated with lubricant to help regulate the die´s temperature and to assist with component ejection. Molten material is then injected into the die under pressure, which remains continuous until the work-piece solidifies. A few of the major advantages provided by die casting include the close size and shape tolerances, a high component dimensional consistency and a reduced need for post-casting machining.

The filling speed and intensification pressure differentiates high-pressure die casting (HPDC) from die casting process. High pressure die casting (Figure 1.1) could be cold-chamber or hot-chamber: in the first one the pumping system is not in contact with the molten material and the metal is transferred with a melting pot into the shot sleeve, in the second one the pumping system is immersed in the melting material. In both cases, after the liquid material is transferred to the shot sleeve, the plunger slowly closes to shut-off the filling port. The plunger is then moved towards the die at controlled high speed in order to fill the die cavity and the pressure is maintained until the material solidifies.
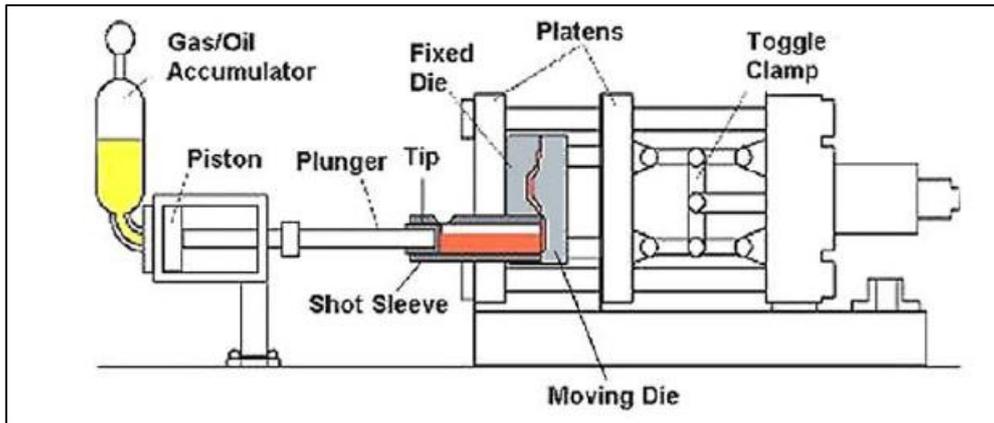
Fig. 1.1: Schematic drawing of a typical high pressure die casting machine.

Low melting points alloys are commonly cast by hot HPDC having a pumping system exposed to hot melt temperature. It is not practical to cast aluminum alloys in hot machines since the ferrous gooseneck experiences erosion by the melt resulting in casting with an unacceptably high Fe concentration and degradation of the metal injection system.

Magnesium alloys components are produced usually in cold chamber with special protective gases to prevent burning but also in hot chamber machines because they are less susceptible to Fe dissolution. Only magnesium AZ and AM are usually cast in hot chamber machines because has a low liquids temperature. In the cold chamber, magnesium alloys could be cast with up to 750°C of temperature, 25 kg of weight, 200 MPa of metal pressure and 30-120 s of cycle time. In the hot chamber the parameters are: temperature up to 650°C, weight up to 2 kg, metal pressure up to 40MPa and cycle time of 12-45 s. [1]

With the potential for highly automated operation, the HPDC process is capable of extremely high levels of productivity. The process cycle and the pressure cycle are
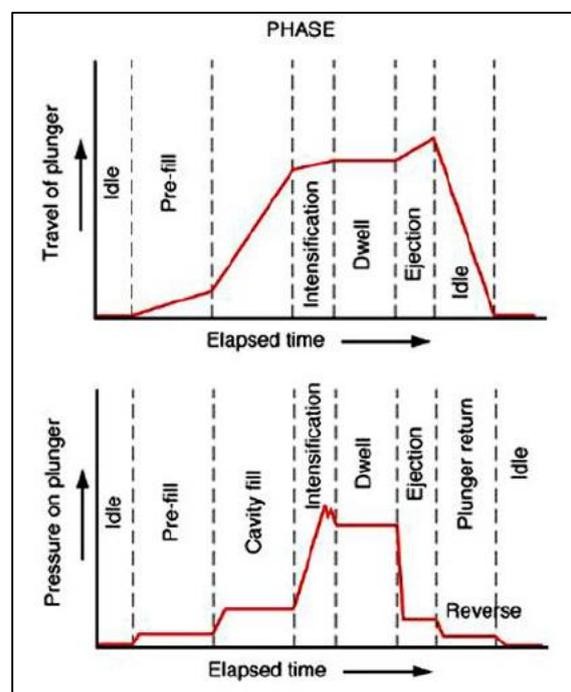
Fig. 1.2: Schematic plunger velocity-time and pressure-time curves for HPDC.

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shown in Figure 1.2: the pressure cycle in a modern HPDC machine is closely controlled in all stages. The filling times are typically on the order of 10-25 milliseconds for casting weighing no more than few grams to 30 milliseconds for casting weighing several kilograms. Once the die is filled, pressure, which may exceed 70 MPa, is maintained on the casting, using an accumulator, until the solidification is complete.

Two features of conventionally produced HPDC are the extreme turbulence experienced by the molten metal as it is forced at high speed into a die, and the very rapid rate at which it then solidifies. Because of these, casting usually contain internal pores in which gases such air, hydrogen or vapors formed by the decomposition of organic die wall lubricants are entrapped. Porosity may also result because of metal shrinkage during solidification and planar defects such as oxide skins and cold shuts may also be present. Whereas it is normal to accept some level of porosity in die-casting, the presence of internal gas-filled pores has the major disadvantages that HPDC components usually cannot be heat treated at high temperature. For HPDC AM- and AZ- series magnesium alloys, defect bands typically contain a high amount of porosity while aluminum-silicon alloys typically contain positive macro-segregation of AL-Si eutectic. [2]

During the HPDC process, the alloy experiences different deformation and solidification conditions. The alloy solidifies under different cooling rate ranges and, additionally, solidification occurs under high forced convention and elevated pressure. This leads to significantly different between as-cast microstructures observed in HPDC compared to the conventional casting, such as sand casting or gravity die casting. As macrostructure, die casting exhibit three regions internally: the surface skin that is dense and fine and gives die casting good fatigue life, so it should not be machined away unless absolutely necessary, moreover the skin contain less porosity and has better mechanical properties; next there are the interior body of casting and the core, the center of the part that is usually porous and it may not be present in high quality parts. The macrostructure and the microstructure influence the mechanical behavior of the casting products but also the corrosion behavior. [3]

The mechanical and also corrosion properties of high pressure die casting components are less predictable than those of components made from wrought material or other method of casting. This is caused by rather inhomogeneous material structure due to changing solidification conditions. The properties depend strongly on the manufacturing route and the variables involved; a geometrically complex casting exhibits a range of different microstructure and properties value. [4]

1.2. Compound casting for hybrid light metal structures

The compound casting of aluminum sheet and magnesium molten made by high pressure die casting is the context of interested in this work. Several researches are been reported until now on the investigation on the compound casting process of lightweight metals like the joint of magnesium molten with magnesium substrate, aluminum molten with aluminum insert or the creation of aluminum-magnesium compounds.

The main challenge for the high light metal structure is to join different alloys to obtain a structure with higher features. Compound casting simplifies joining processes by directly casting a metallic melt onto a solid metal substrate, forming a continuous metallic transition. To optimize performance, a combination of materials is the most efficient method, because one material alone is often insufficient but light metals are not easy to join: weak links arise at the joints, such as rivets, welds or brazing connections. A prerequisite is the formation of zones where the cast alloy's components diffuse into the solid material, partly via the formation of solid solutions and partly via the formation of intermetallic phases. [5] [6]

1.2.1 Magnesium-magnesium and aluminum-aluminum compound casting

Different tests [6] were made to analyze the process where a magnesium melt is cast onto a solid magnesium substrate. The natural oxide or hydroxide layer on magnesium alloys usually prevents metallurgical joining via casting but a pre-treatment could be applied to the substrate to replace the oxide layer with $Zn/MgZn_2$ coating. This procedure comprises a combined picking/redox-reaction and galvanization/heat-

treatment procedure, which drastically changes the substrate´s surface wetting properties. During casting it is observe the dissolution of the $Zn/MgZn_2$ coating into the bulk. The distribution of Zn around interface varies along with the position and width of the solidification intervals and thus with the heat which is transferred to the substrate by the droplet magnesium. The substrate fuses partially and the melt´s composition determines the mechanism of solidification and the distribution of Zn from the coating. The possibility of shrinkage cavity formation at the interface can be avoided choosing appropriate solidification intervals, which is definitely the case when using commercial wrought and cast alloys. This method of compound casting yields, in comparison to common techniques, a connection without a weak link and eliminates many disadvantages of conventional approaches, considering galvanic corrosion, welding depth or low process efficiency. By means of laboratory-scale compound casting experiments, the reproducible production of all-magnesium compounds was successfully established.

Also aluminum − aluminum compound casting were be investigated by many authors [5] [7]. When an aluminum melt is cast onto a solid aluminum substrate, difficult in joining aluminum is identify in its oxide layer, which results in insufficient wettability. Compounds with flawless and continuously metallic interfaces can be produced successfully by replacing the oxide layer with a zinc layer that inhibits repassivation and makes substrate´s surface wettable by metallic melts. The appropriate procedure for dealing with the oxide problem was developed by combining several aluminum surface pre-treatments, the most important step being the so-called zincate process. It replaces the Al_2O_3 layer with a metallic zinc film, via two parallel chemical reactions. The first is an etching procedure which removes the Al_2O_3 layer, the second is a redox reaction, where metallic Al oxidizes and dissolves and Zn anions are reduced and deposited as a dense metallic layer. Couples of various aluminum alloys were successfully produced by means of a laboratory-scale compound casting process. The combined coating of zincate treatment and electrolytically deposited zinc offers major advantages compare to other approaches to joining light metals, moreover, the zinc coating is durable, as it acts as corrosion protection, which makes the substrate material easily transportable and suitable for storage.

Other studies investigate not only compound casting but the development of aluminum - aluminum compounds during high pressure die casting [8]. An aluminum insert is mounted into a die casting mold and embedded into an aluminum casting alloy. Prior to that, the natural oxide layer is removed and replace by zinc coatings by combining zincate treatment and zinc galvanizing. During the casting process the zinc layer dissolves and a transition zone with elevated concentration and hardness forms between insert and casting alloy. The thickness of the initial Zn layer determines width and composition of the transition zone, but not the mechanical properties of the compound. The transition zone can be divided into three different zones defined by the zinc concentration: a diffusion zone into the insert, a Zn-rich interlayer and a diffusion zone into the cast matrix. At the end of the investigation, it is possible to assert that the fabrication of aluminum-aluminum compounds was successfully realized by high-pressure die casting.

1.2.2 Aluminum-magnesium compound casting

The most interested results are the tests on aluminum – magnesium compound casting. A variety of attempts have been dedicated to joining Al/Mg alloys using different fusion welding and solid-state joining methods such as tungsten inert gas welding, laser welding, friction-stir welding but the major problem is the formation of much more Al-Mg intermetallic compounds with a very high hardness and brittleness, which is deleterious for the mechanical properties. For this reason, some researchers focus on compound casting, trying to cast aluminum melt around magnesium insert and magnesium melt around aluminum insert [9]. After casting aluminum melt around magnesium insert, in almost all parts of the sample a relatively large gap has been formed at the interface and only some local and limited interactions in different parts of the interface have occurred. In casting magnesium melt around the aluminum insert, a relatively uniform interface has been formed; in this case, there is no macroscopic crack at the joint, but a few holes existed at the interface layer owing to gas and/or shrinkage porosities. As result, joining of aluminum and magnesium by the compound casting process is possible only via casting magnesium melt around the aluminum insert. The formation of different layers with different compositions between the aluminum insert

and the magnesium melt implies that diffusion is the dominant mechanism in the compound casting process, as is the case with the solid-state diffusion bonding. During this process, the heat of the melt causes the surface layer of the insert to be melted, and then concentration gradients cause the aluminum and magnesium melts to diffuse into each other.

Interfacial microstructure of Al/Mg light metals couples with the use of pure aluminum and pure magnesium was also studied [10]: the interface consists in three layers. Relatively uniform interface without visible defect has been formed along the interface. The layers adjacent to the Al and Mg base metals are rich in Al and Mg, respectively; in addition a concentration gradient of Al and Mg elements can be seen in the middle layer. The analysis shows that the layer adjacent to the Al base metal consists of about 60 % Al and 40 % Mg, this composition correspond to Al_3Mg_2 intermetallic compound. The layer adjacent to Mg base metal has a eutectic structure composed of about 27 % Al and 73 % Mg, combining with the Al/Mg binary phase diagram, this layer is estimated to consist of the $Al_{12}Mg_{17}$ intermetallic compound and Mg solid solution. Unlike the layers adjacent to the Al and Mg base metals, which almost have constant chemical compositions, the concentration of the Al and Mg elements for different areas of the middle layer are not constant and vary from about 49 % Al, 51 % Mg to 41 % Al, 59 % Mg at the left and right side of this layer, respectively. Considering the relatively wide range of the composition for the $Al_{12}Mg_{17}$ intermetallic compound in the Al/Mg phase diagram and the non-equilibrium condition for formation of the interface the compound casting, it seems that the middle layer is manly composed of the $Al_{12}Mg_{17}$ intermetallic compound.

Good results have been obtain [5] in casting Al/Mg compounds with the preparation of aluminum with the zincate treatment followed by electrolytic deposition of manganese layer. The manganese layer of several microns thickness is useful to protect the substrate from liquefaction by the magnesium melt, without sacrificing too much of wettability. A thin layer of IMPs forms during couple production which might affect mechanical integrity but, keeping this interface as thin as possible is a possible way to improve the compound's properties.
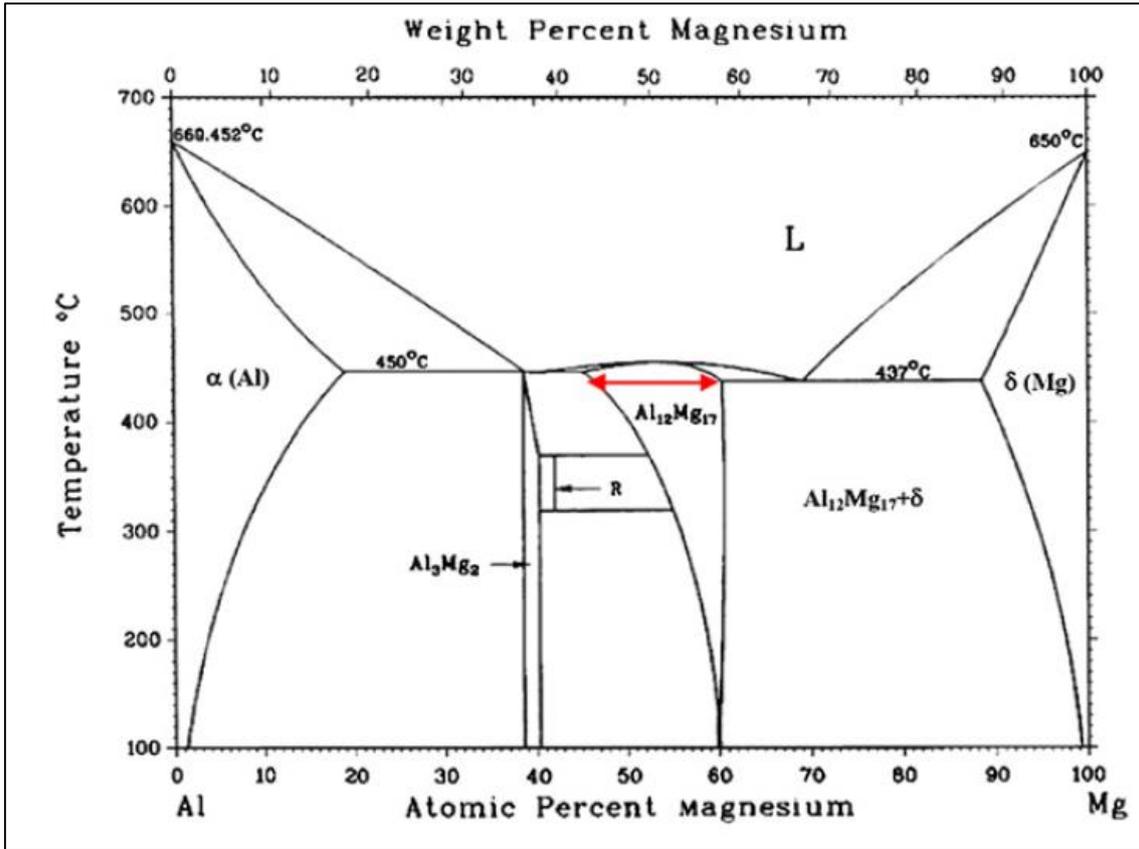
Fig. 1.3: Aluminum – magnesium binary phase diagram with Al_3Mg_2 and $Al_{12}Mg_{17}$.

However also other treatments are possible [11]: the test results show significantly improved welding and metallurgical bonding when a zincate + galvanizing surface treatment is applied to aluminum substrate. This surface treatment removes the intrinsic Al_2O_3 layer on the aluminum substrate and form a very thin metallic zinc layer. The low melting point of the zinc, compare to aluminum, promotes wetting and the formation of a metallurgical bond between the aluminum substrate and the overcast metal. The Al/Mg interfacial reactions and metallurgical bond are related to the temperature and the time of the total interaction. Excessive interaction leads to a reduction in strength due to the formation of excessive intermetallic compounds at the metal/substrate interface. Therefore, it is feasible to control the interfacial reactions by adjusting the pre-heat temperature and time of the substrate in the actual bi-metallic casting process.

Last studies [12] involve the compound casting of aluminum sheet and magnesium molten by high pressure die casting with the use of two types of hybrid structures: the Connection-Demonstrator, which has been designed to represent original-sized

structural car body and combined all types of hybrid-specific characteristics on a minimum package space, and the standard VarioStruct® registered by Imperia GmbH. They are made to analyze the behavior in the corrosion environment but also the characterization of the cast bounding surface before the corrosion test, useful to quantify the appearance of crevices that influence significantly the corrosion attack.

The as cast interface characterization was conducted in four dissimilar characteristic areas of the Connection-Demonstrator. The interface conditions between aluminum and magnesium alloys varied from defect-free form closure of crevice widths beyond 35 μm, depending on the geometry of the local areas, but some segments present also a metallic continuity with the intermetallic interface Al_3Mg_2 and $Al_{12}Mg_{17}$, with a coexistence of porosity in the neighborhood of the local metallic continuity. The results concerning the corrosion behavior of these hybrid structures are analyzed in the next chapter.

CHAPTER 2

Corrosion and galvanic corrosion

2.1. Introduction

Corrosion is the destructive attack of a material by reaction with the environment, usually it is a chemical reaction or electrochemical. Corrosion can occur often in metals but also in other materials like ceramics and polymers, although in this context, the term degradation is more common, but in both cases, corrosion degrades the useful properties of materials and structures. The demands for long-term performance of engineering structures over a wide size scale continue to increase thus the studies about corrosion and corrosion protection have an increasing importance.

Chemical reactions are those in which elements are added or removed from a chemical species and none of the species undergoes a change in its valence. Electrochemical reactions are chemical reaction in which not only may elements be added or removed from a chemical species but also at least one species undergoes a change in the number of valence electrons in processes called oxidation or reduction. The vast majority of engineering materials dissolve via electrochemical reactions because the dissolution of a metallic material requires an oxidation in order to render it soluble in liquid phase. [13]

Corrosion can be concentrated locally to form a pit or crack or it can extend across a wide area or less uniformly corroding the surface. One of the key factors in any situation is the environment and the definition of this variable can be quite complex. It is also important to realize that the environment that actually affects a metal corresponds to the local one at the surface of material. In the various types of environment, some examples are the natural water, the seawater, the atmosphere, the soil and the high temperature condition. [14]

2.2. Galvanic corrosion

The galvanic corrosion, also known as bimetallic corrosion, is a common mode of corrosion failure that is, for the most part, entirely preventable by proper corrosion design. It´s defined by ASTM International Committee as "accelerated corrosion of metal because of an electrical contact with a nobler metal or nonmetallic conductor in a corrosive environment". Galvanic corrosion involves the electrochemical interaction of at
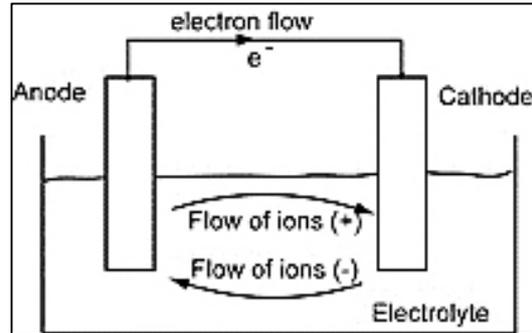
Fig. 2.1: Schematic diagram of four requirements for galvanic corrosion (anode, cathode, electrical contact and electrolyte).

least two different materials (metals or nonmetallic conductors) that accelerated the corrosion of at least one of them. The common factors are four: dissimilar metals, i.e. an anode (where oxidation of the metal occurs) and a cathode (where reduction of different species occurs), electrical contact and conductive electrolyte (Figure 2.1). If any of these factors is absent, galvanic corrosion cannot occur, so all successful corrosion control processes affect one or more of these requirements.

Galvanic corrosion accelerates the normal corrosion of metals in an electrolyte but even without galvanic corrosion, metals may suffer from uniform corrosion, crevice corrosion, pitting, or other forms of corrosion. [15]

2.3. Electrochemical theory

When a metal is immersed in a conductive solution, or an electrolyte, a series of reactions takes place that can cause corrosion. The corrosion reaction itself involves a change in the charge of the metal atoms from zero in the metal to a positive value for metal ions in the solution. For this positive change in charge, the reaction is called anodic reaction and can be written as:

$$M \rightarrow M^{n+} + ne^-$$

1.1

Where M = some metal atom or ion, and n is a number typically between 1 and 3 depending on the metal and electrolyte.

Since this reaction generates free electrons and since charge neutrality must be maintained, these electrons must be used up in one or more reactions where charge is reduced in order for corrosion to proceed. These are cathodic reactions and the most common ones found in aqueous environment are:

$$2H^+ + 2e^- \rightarrow H_2 (g) \ in \ acids \qquad\qquad 1.2$$

$$2H_2O + 4e^- + O_2 (dissolved) \rightarrow 4OH^- \ \ in \ netrual \ or \ alkaline \ electrolytes$$

Corrosion cannot proceed unless all of the electrons generated by the anodic reaction are used by a cathodic reaction. The balance between these two reactions leads to each metal, alloy, or nonmetallic conductor equilibrating at an electrochemical potential that is unique to that material and electrolyte, called the corrosion potential. For a given electrolyte, the corrosion potential of a number of materials can be listed together. Such a listing, where the materials are arranged according to ascending or descending corrosion potential, is called a galvanic series. If two materials with different corrosion potentials are immersed in that electrolyte and electrically coupled, there is a driving force for a current, called the galvanic current, to flow between them. It is this flow of current that increases corrosion of the material with the more negative potential, called the anode, while suppressing the corrosion of the more positive material, called the cathode. Metals with more negative corrosion potentials are said to be anodic compared to metals with more positive, or cathodic, potentials in galvanic series.

The most common galvanic series is the one show in Figure 2.2 for metals in sea water. In this case, the corrosion potentials are given as ranges, since seawater composition can vary and since corrosion potentials can be influenced by the presence of corrosion products on the surface of the corroding metal. Some metals show two bands of corrosion potentials, one in white and other in black. These are metals that can exist in two different states in seawater, a passive state during which they are not corroding and an active state when they are corroding. Galvanic series are useful to predict which in a pair of electrically connected materials in an electrolyte, called galvanic coupled, will tend to have its corrosion rate accelerated by the electrical contact. [15]
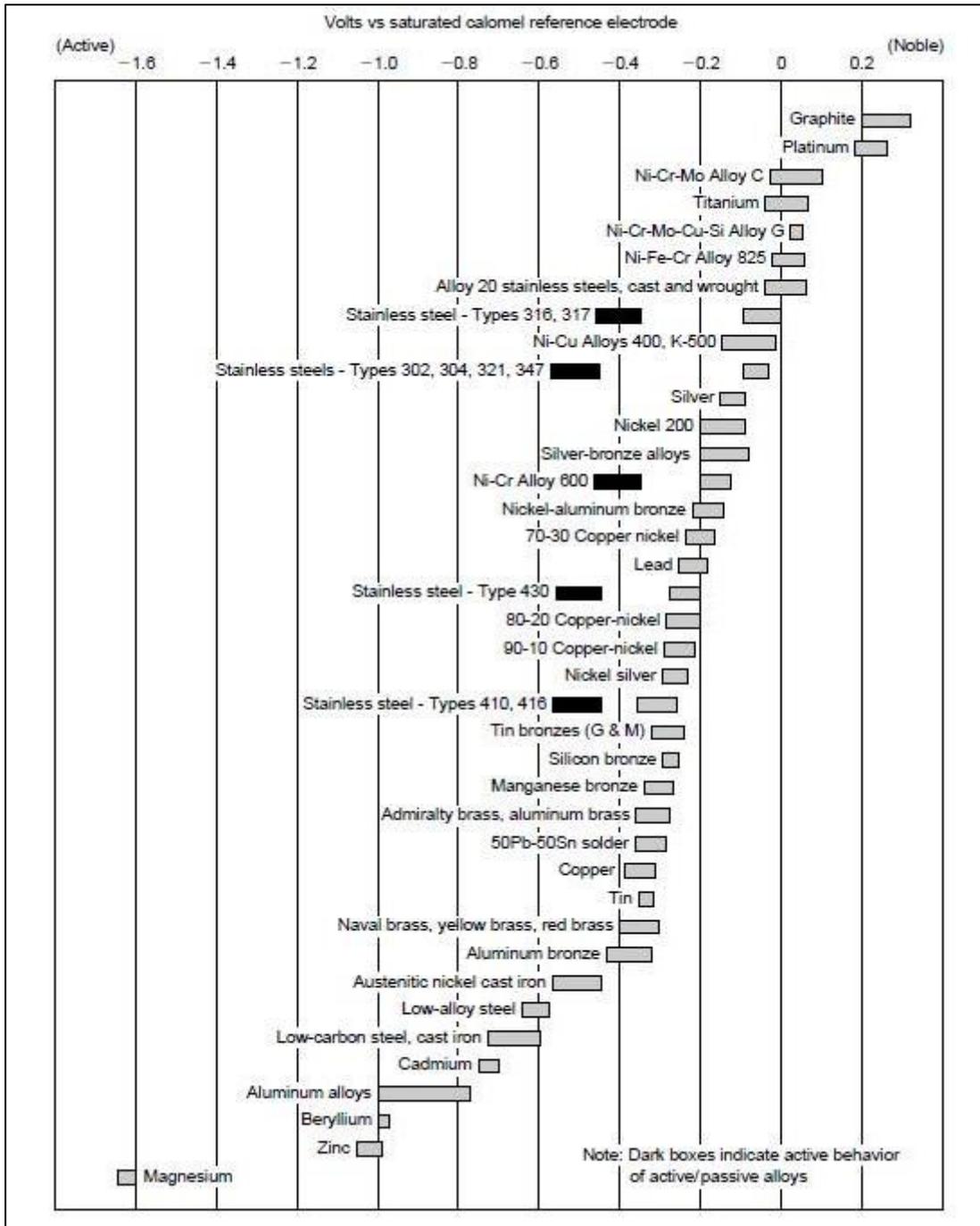
Fig. 2.2: Galvanic series for metals and alloys in seawater. Flowing seawater at 2.4 to 4.0 m/s, immersion for 5 to 15 days at 5 to 30° C.

The kinetics of electrochemical reactions at a metals-solution can best be studied when the electrode of interest is of an electrochemical system or cell. Electrochemical cells are two-terminal devices that can be classified as either driving or driven according to their function. A driving electrochemical cell is a power producer, converting chemical energy into electrical power and in some cases this power can be used externally to the

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cell. A driven electrochemical cell is a power consumer. When used to power an electrical device, a battery is a driving system and when a battery is being recharged, it becomes a driven system. Corrosion systems in the absence of external influence are short-circuited, driving systems: the positive electrode is the cathode and the negative electrode is the anode. [13]

2.3.1. Faraday´s law of electrolytes

Important rules related to electrochemical reactions was introduced by Michael Faraday that was also able to demonstrate that electrochemical reactions follow all normal chemical stoichiometric relations. The two rules are:

- Faraday´s first law: the mass, m, of an element discharged at the electrode is directly proportional to the amount of electrical charge, Q, passed through the electrode.

- Faraday´s second law: if the same amount of electrical charge, Q, is passed through several electrodes, the mass, m, of an element discharged at each will be directly proportional to both the atomic mass of the element and the number of moles of electrons, z, required to discharged one mole of the element from whatever material is being discharged at the electrode. Another way of stating this law is that the masses of the substances reacting at the electrodes are in direct ratio to their equivalent masses.

These empirical laws of electrolytes are critical to corrosion as they allow electrical quantities to be related to mass changes and material loss rates. These laws are the basis for the calculations concerning the power of electrochemical corrosion measurements to predict corrosion rates.

It is possible to write Faraday´s laws as a single equation that relates the charge density, q, to the mass loss per unit area and, taking the time derivate of the equation, it allows the mass loss rate to be related to the dissolution current density:

$$\dot{m} = \frac{i(AM)}{nF\rho} \qquad\qquad 1.3$$

Where i = corrosion current density [mA/cm²],

AM = atomic mass [g],

ρ = density [g/cm³],

n = number of electrons lost per atom oxidized,

F = 96485 C.

In many cases, a penetration rate, in units of length/time, is more useful in design. The inclusion of corrosion allowances in a structure requires an assumption of uniform penetration rate. [13]

2.3.2. Reference electrode

Measurements of voltages in electrochemical can be more complicated that measure of voltage within electrical circuits. In electrical circuits there are the positive terminal of voltmeter connected to the point in the circuit of interest and the negative terminal connected to the point known as the ground. In electrochemical measurements, it is necessary to introduce the equivalent of the ground because it is impossible to measure the potential across an electrochemical interface without introducing another electrochemical interface. If the additional interface is at thermodynamic equilibrium, the practical problem of measure is resolved: by maintaining a reaction in equilibrium at the interface, the potential across it is constant, thus any changes in the measurement of the potential between the two interfaces can be attributed to the electrode of interest, called the working electrode (WE).

Many years ago, the hydrogen reaction was selected as the reaction to which a value of zero is ascribed. The standard for all reference electrodes is the hydrogen electrode in which a catalytic but corrosion-free surface is exposed to a pH 0 solution saturated with hydrogen gas at room temperature. Its value is zero as the reaction is at equilibrium in a 1 M solution of the ion of interest with the other reactant at unit activity. It is sometimes called the standard hydrogen electrode (SHE) or the normal hydrogen electrode (NHE).

The perfect reference electrode (RE) is one for which the value depends only on the concentration of one species, is in thermodynamic equilibrium, does not contaminate the solution of interest, is cheap to acquire and easy to maintain. Many more practical than hydrogen RE have been developed and are commercially available. In order to maintain the RE at equilibrium, most of they have a glass or polymeric body that separates the inner or fill solution from the test environment. The ionic communication with the test solution needed is controlled often through a porous frit (Figure 2.3). The most commonly RE used in aqueous solutions are the saturated calomel electrode (SCE), the Ag/AgCl electrode and the Hg/Hg2SO4 electrode. [13]
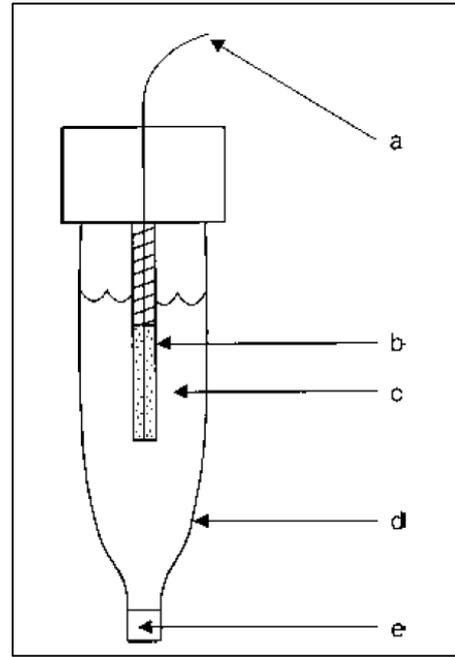
Fig. 2.3: Components of typical commercial reference electrode: a) electrical connection, b) metal – metal salt electrode, c) filling solution that maintains electrode interface equilibrium, d) glass or polymeric electrode body, e) porous frit.

The RE used in the corrosion tests performed in this work are the saturated calomel electrode and the Ag/AgCl electrode [16]: the satured calomel electrode consists of pure mercury covering a platinum wire which passed through a sealed glass tube. The mercury is covered with mercurous chloride and immersed in satured potassium chloride. The temperature coefficient is $-6{,}6 * 10^{-4}$ V/°C and the reference reactio is:

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^- \qquad E° = 0{,}268 V_{SHE} \qquad 1.4$$

The silver/silver chloride reference electrode consists of a silver wire, the surface of which has been chlorized, typically in diluite hydrocloric acid. The temperature coefficient is $-4{,}3 * 10^{-4}$ V/°C and the reference reaction is:

$$AgCl + e^- \rightarrow Ag + Cl^- \qquad E° = 0{,}222 V_{SHE} \qquad 1.5$$

2.4. Polarization curves and Evans diagram

When two dissimilar materials with dissimilar corrosion potentials are coupled in an electrolyte, they will each be forced to a common potential somewhere between the two individual corrosion potentials. Materials far apart in potential will not necessarily result in higher galvanic corrosion rates than materials close together in potential. The magnitude of current flow and the increase in corrosion rate due to this coupling are determined by the tendency of each of the materials in the couples to deliver current when its potential is forced to change, called polarization. If a material delivers little current for a large change in potential, it is said to have a large polarization resistance, while if it can delivers a large current for a small enforced potential change, it is said to have a small polarization resistance and this is illustrated by plotting the current produced as a function of applied potential, called polarization curves. Example of a real polarization curves are shown in Figure 2.4. When the anode has low polarization resistance and the cathode has high resistance, the couple is said to be under cathodic control. When the reverse is the case, the couple is said to be under anodic control, and when the polarization resistances of the anode and the cathode reactions are similar the couple is said to be under mixed control.

When two materials are coupled in an electrolyte, the galvanic current flowing between them is determined by the superposition of the cathodic polarization curve of the anodic material and the anodic polarization curves of the cathodic material (Figure 2.5). The magnitude of the galvanic current flowing in a galvanic couple gives a qualitative fell for the amount of increased corrosion of the
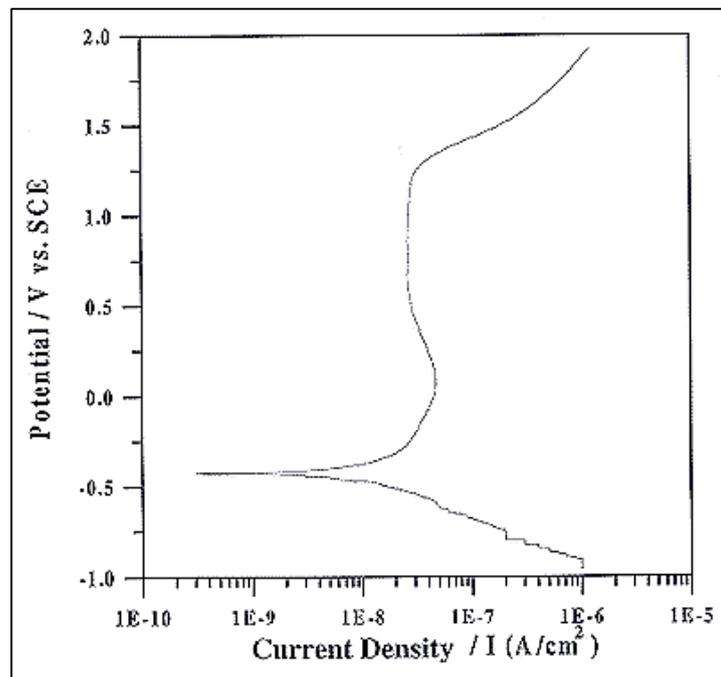
Fig. 2.4: Example of a real polarization curve.

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anode, but it is not a good quantitative measure. To understand why is so, it is necessary to look at the magnitude of the anodic and cathodic reactions that are occurring on each metal in the couple, both before the metals are electrically connected and afterwards. To understand the corrosion rates in a galvanic couple, it is necessary to look at a plot of individual reaction rates as a function of potential, called an Evans diagram, for each of the material in the couple before they are coupled (Figure 2.6).

The rate of the anodic reaction increases as the potential becomes more positive, while the rate of the cathodic reaction increases as the potential becomes more negative. The net current flowing to or from the metal is the difference between these two currents, or zero at the points where the two curves cross. Applying a current will force a potential shift to occur.

For two materials in electrical contact, the sum of all anodic reactions must be equal the sum of all cathodic reactions. Where the anodic sum crosses the cathodic sum determines the potential of the galvanic coupled, called the coupled potential. Once this potential in known, the rates of all reactions on both materials are read from the Evans diagram for each reaction at that coupled potential. This coupled potential can also be obtained from polarization curves. This is the application of mixed potential theory that can be used to predict a corrosion rate. The galvanic current from the polarization curves is the actual measurable current that flows between the two materials, but is not necessarily directly related to the corrosion rate of the anode.

In practice, it is difficult to determinate the exact position of all reaction curves on all materials, particularly in complex environments. For this reason, it is more common to determine corrosion rates for galvanic corrosion by first determining the coupled potential using polarization curves, and then testing the anode material by holding it at that potential and measuring the actual corrosion rate experienced. The impossibility of a direct measurement of corrosion rate using electrochemical testing would seem to be discouraging. Application of mixed potential theory allows determination of the corrosion rate using a method known as Tafel extrapolation. [13] [15]
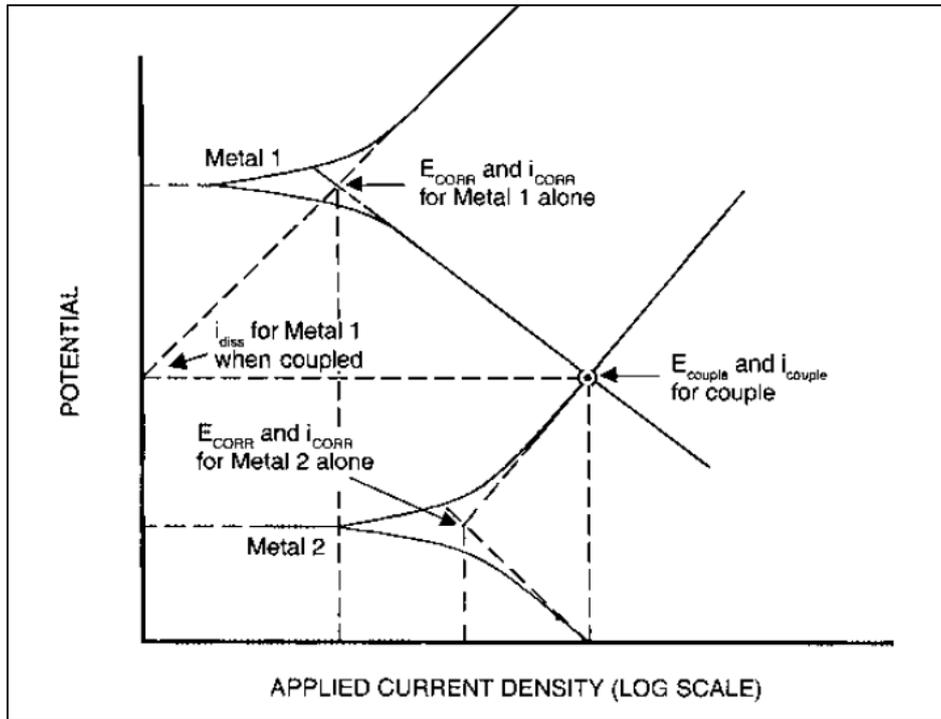
Fig. 2.5: Polarization curves of metals 1 and 2 that are analyzed for their behavior in a galvanic couple.
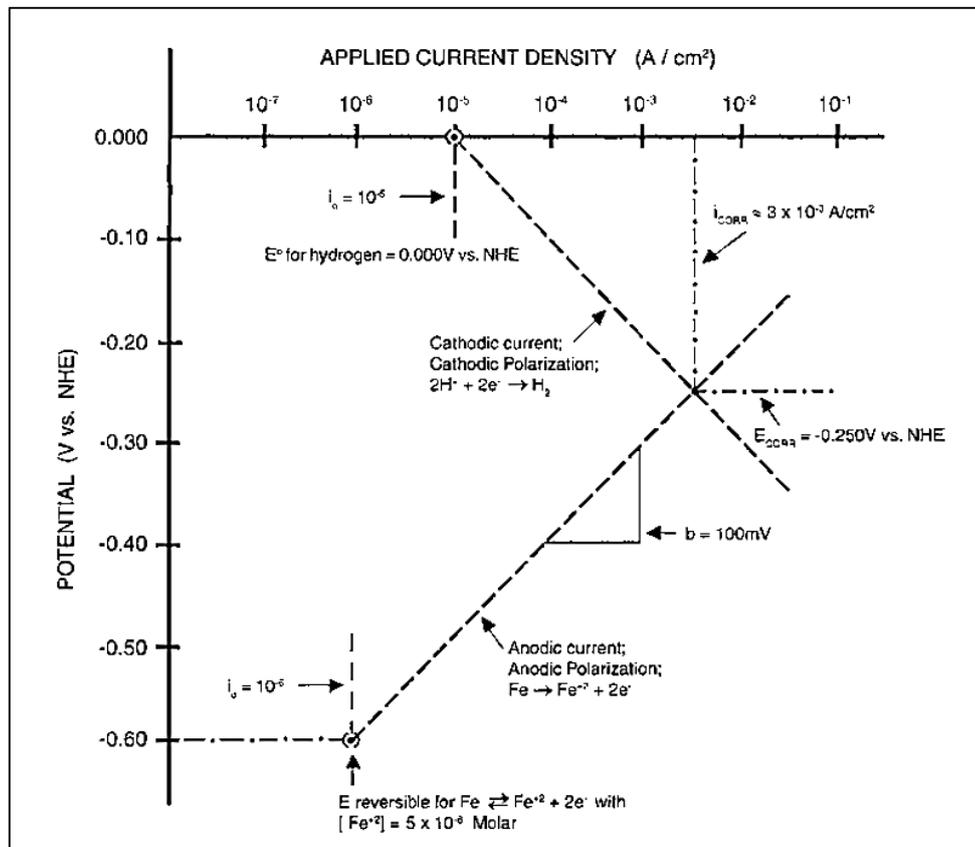
Fig. 2.6: Evans diagram for Fe in acid showing use of conservation of charge to determine E_{corr} and corrosion rate (i_{corr}).

Polarization does not always take the form of straight lines on Evans diagrams but real polarization curves are affected by the formation of corrosion products and the ability of reactants and reaction products to move to and from the surface where the reactions take place. This leads to various polarization curve shapes, including some curves back on themselves. Galvanic reactions with materials having these types of curves can lead to some unusual corrosion consequences, including having several different stable corrosion potential for a given galvanic couple.

The difference between the Evans diagram and the polarization curve is that the polarization curve data display applied current densities, whereas the Evans diagram displays the reaction rates in terms of current densities. The applied current density is the difference between the total anodic and the total cathodic current densities (reaction rates) at a given potential. At the corrosion potential, the anodic and cathodic rates are exactly equal; thus the applied current density is zero. No external device is needed to supply or remove electrons from the reactions; all of the electrons generated by oxidation reactions are consumed by reduction reactions on the same metal surface. [13]

2.4.1. Tafel extrapolation

The Evans lines are keys to the method of Tafel extrapolation that permits to obtain the Tafel slope, i.e. the slop of the Evans lines. At potentials well away from the corrosion potential, the applied current density affects the kinetics of only one of the reactions. Extrapolating the linear portions of the polarization curves found at potentials well away from corrosion potential leads to an intersection at corrosion potential. This intersection corresponds to current corrosion, the corrosion rate. Assuming uniform dissolution across the surface, Faraday's laws can be used to convert it to penetration rate for engineering design.

The logarithmic nature of the current density axis amplifies errors in extrapolation. A poor selection of the slope to be used can change the corrosion current density calculated by a factor of 5 to 10. Two rules should be applied when using Tafel extrapolation. For an accurate extrapolation, at least one of the branches of the polarization curve should exhibit Tafel (i.e., linear on semi-logarithmic scale) over at

least one decade of current density. In addition, the extrapolation should start at least 50 to 100 mV away from the corrosion potential. These two rules improve the accuracy of manual extrapolations.

Commercial corrosion electrochemistry software applies nonlinear least squares fitting to fit the entire polarization curve, which can improve accuracy but not all computation algorithms are created equally robust against noise and other realities of corrosion measurements. In addition, the use of Tafel extrapolation invokes the implicit assumption that the dissolution is uniformly spread over the entire specimen surface and it is not always true like in case of pitting corrosion. Using Tafel extrapolation on these data would lead to highly erroneous conclusions. Moreover the interpretation of the data can be a tremendous challenger.

Finally, even the most skilled interpretation of electrochemical data is akin to the best photograph in that it contains only a portion of the information available. Correlation of electrochemical measurements to as many varied measurements as possible is good practice. Whereas electrochemical measurements may be the most rapid, they are also the most susceptible to variations in conditions. Corrosion rate estimations based on Tafel extrapolation should be compared to weight loss measurements whenever possible. Often decisions need to be made regarding material selection in a narrow time window that precludes such information; in these cases, post-selection weight loss measurements in the actual environment are invaluable checks on the applicability of the electrochemically derived corrosion rates. [13]

2.4.2. Exposed surface areas

Either current density or total current can be used on the horizontal axis in the chart with polarization curves, if the exposed surface areas of the anode and the cathode metals are the same, otherwise, the effect of different exposed surface areas of the anode and cathode materials can be examined by realizing that the total current is just the current density multiplied by the exposed surface area. Larger exposed areas will shift the polarization curves to the right for that material. [15]

The most direct example of the importance of differentiating between current density, i, and current, I, is the application of the conservation of charge to corrosion. The conservation of charge means that in an isolated system, all electrons that are liberated in oxidation reactions must be consumed in reduction reaction. In terms of charge, the total cathodic charge must equal the total anodic charge:

$$\sum_i Q_a = \sum_j Q_c \qquad 1.6$$

Taking the time derivative converts the law to a rate expression:

$$\sum_i I_a = \sum_j I_c \qquad 1.7$$

For each reaction, the current density is the current for that reaction divided by the area over which it occurs:

$$i_i = \frac{I_i}{A_i} \qquad 1.8$$

Thus combining these expressions demonstrates that only in the cases in which the areas on which the anodic and cathodic reactions occur are equal can the anodic and cathodic current densities be equal:

$$\sum_i i_a A_a = \sum_j i_c A_c \qquad 1.9$$

The faster (as defined by current density) reaction cannot produce current any faster the slower can consume it. This principle is used in several ways including sacrificial anodes and corrosion inhibitors. [13]

This lead also with the conclusion that to minimize galvanic corrosion small cathode-anode area ratios are required, or conversely the larger this ratio, the larger is the galvanic corrosion. This is sometimes called catchment area principle. For this reason, it is best to paint the no-corroding cathode, not the corroding anode, to control galvanic corrosion. [15]

2.4.3. IR drop

Galvanic corrosion can also be affected by electrical or ionic resistances between the two coupled materials. Electrical resistance can come about if one of the materials is a poor electrical conductor or if the contact between them is not made properly. Ionic resistance occurs because electrolytes are not perfect conductors, so that high electrolyte resistivity coupled with a large distance between the anode and cathode can lead to significant resistance between the anode and the cathode. The total circuit resistance is the product of the galvanic current and various resistances, called IR drop.

IR drop leads to the anodic and cathodic materials being at different potentials, with the associated lowering of corrosion rate of the anode from value if there were no resistance. Low galvanic currents lead to low IR drop, so this effect is more pronounced on large structures. Also, larger distance between anode and cathode lead to larger IR drop, and therefore lower galvanic corrosion rates. For this reason, in galvanic couples that are large or where electrolyte resistance is high, galvanic corrosion rates are highest on the anode closest to the cathode and drop off as distance between anode and cathode increases, although if conductivity is high or distances are small this drop-off effect may not be observed. [15]

2.5. Passivity

The passivity is the origin of the utility of all corrosion resistant alloys. While passivity can be defined in a number of ways, two have become generally accepted: a metal is passive if it substantially resists corrosion in an environment where there is a large thermodynamic driving force for its oxidation (also known as thick film passivity), or a metal is passive if, on increasing its potential to more positive values, the rate of dissolution decreases, exhibiting low rates at high potentials (also known as thin film passivity).

Examples of material–solution combinations that fall within the first definition are Mg or Al in water. These materials can be considered to have very high (near infinite) anodic Tafel slopes in these solutions. Thus large increases in potential do not cause significant increases in dissolution rate. On the other hand, metal–solution combinations

such as nickel, molybdenum, or chromium in sulfuric acid would be classified as passive according to the second criterion. For these materials, the Tafel slope can be thought of as having a strong potential dependence.

Thick film passivity can be due either to oxide formation or salt film precipitation. Salt film precipitation can in some cases be either a precursor for a thin passive film or provide adequate protection alone. While thick film passivity has been documented and understood for many years, the difficulties in studying thin film passivity were daunting. It took many years to determine that indeed a film was responsible for the effect, as these films are so thin that they are invisible to the eyes. Two main types of theories were developed in order to explain the phenomena observed: theories based upon the idea of adsorption reducing the corrosion rate, and theories based upon the formation of a new phase, an oxide of the base metal, on the surface. In all cases, an increased barrier to dissolution results upon the increase in potential. This increased kinetic barrier upon anodic polarization contrasts with the exponentially decreased barrier which develops during anodic polarization of an active material.

Independent of the mechanism of passivity, its electrochemical manifestations can be best understood on the basis of mixed potential theory (Figure 2.7). If there are no strong oxidizing agents in the solution, the corrosion potential is E_{corr}, and the metal corrodes uniformly in a film-free condition. As the potential is raised in this active region, either by the application of an external current or by the introduction of oxidizing species into the environment, the dissolution rate of the metal increases until a potential of E_{pp} is
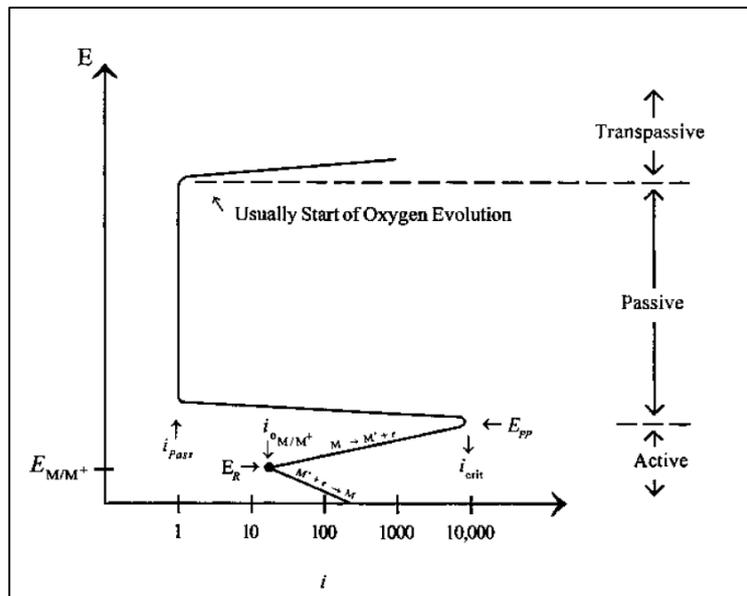
Fig. 2.7: Typical anodic dissolution behavior of active-passive metal. E_{pp}= primary passivation potential, i_{crit} = critical anodic current density, i_{pass} = passive current density.

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reached. Above this passivation potential, a dramatic decrease in the dissolution rate occurs. Further increases in potential usually have little effect on the passive current density, i_{pass}. In some cases, the difference between the critical anodic current density for passivation, i_{crit}, and i_{pass} can be over four orders of magnitude. These current densities are directly related to the dissolution rate of the material. In solutions without aggressive species such as Cl^-, further increases in potential will eventually lead to an increase in the current due to a combination of oxygen evolution and trans-passive dissolution of the passivation film for most metals. For the valve metals (aluminum, tantalum, lead, titanium), certain solutions will allow a thick, insulating oxide film to grow on which oxygen evolution does not occur. Under these conditions, anodization occurs.

The corrosion potential is determined by the intersection of the sum of the anodic Evans lines and the sum of the cathodic Evans lines. For active–passive materials, the only new wrinkle is the increased complexity of the anodic line. Since the anodic line is not single-valued with respect to current density, three distinct cases can be considered. Thus the nature and kinetics of the cathodic reactions are critical in determining the corrosion state and rate of dissolution of an active–passive material.

The presence of galvanic couples can affect passivity in three ways (two of which are bad): 1. increasing the potential of the active–passive material so that passivity can occur for conditions under which it otherwise would not, 2. increasing the potential of the active–passive material to the point that localized corrosion can occur, and 3. decreasing the potential of the previously spontaneously passive material so that passivity cannot be maintained and active dissolution occurs on the (previously) passive metal. In case 1 the cathodic material must be able to deliver a cathodic current density higher than the i_{crit} of the active–passive material. In case 2, the cathodic reaction raises the corrosion potential above E_t, leading to trans-passive corrosion. If an aggressive species such as chloride ion is present, the dissolution can become non-uniform. Case 3 is an example of a sacrificial anode that is causing, rather than solving, problems. While the idea of cathodic protection by galvanic coupling might be appealing, in the schematic shown this would lead to rapid uniform dissolution of the cathode (active–passive) material. Thus galvanic couples involving active–passive materials must be considered carefully. [13]

2.6. Recognizing and predicting galvanic corrosion

There is no absolutely certain method of determining the corrosion seen on a structure in actually galvanic corrosion, since the action of galvanic corrosion is usually to accelerate the type of corrosion normally experienced by anode material. There are clues, however, that can help to make the determination: if two materials with different corrosion potentials are present in the system and they are electrically connected in a common electrolyte, this is a strong clue that the corrosion that is observed is galvanically accelerated. This is particularly true if the anodic material has a small surface area compared to the cathodic material and the two different materials are closer together.

There is one good indicator for galvanic corrosion, if the anodic material corrodes the fastest near the cathodic material, and if the amount of corrosion lessens as distance increases from the cathode, galvanic corrosion is the likely cause. [15]

When designed a structure it is important to take into account galvanic corrosion either by preventing or by predicting where it will occur and how much metal will be lost over time so that structures lifetime can be determinate and maintenance activities can be planned accordingly. The methods used to predict galvanic corrosion include:

- Experience with similar materials and geometries in similar environments;
- Use of exposure data in similar environments when the exact geometry cannot be found;
- Use of laboratory data: laboratory test can generate data on corrosion potentials, polarization behavior and galvanic current for specific geometries. Information regarding how to measure and generate a galvanic series in a specific environment is given in a standard guide from ASTM International. There are many ways to generate polarization curves but a good place to start is by generating either a potentiodynamic scan or a series of potentiostatic tests. Once corrosion potentials are known for the materials of interest in the environment of interest, classification of the material as anode or a cathode can be made. Superposition of a cathodic polarization curve of the anode material with the anodic polarization curve of the cathodic material can generate information on the potential of couple. Using potentiostatic corrosion rate date at this potential, the corrosion rate of the anode can be determined.

- Use of computer modeling, specifically boundary element modeling;

- Use of physical scale modeling of complex structures;

- Numerical calculations such as Wagner number that is the ratio of the polarization resistance of the material of interest to the resistivity of the environment, expressed as the slope of a polarization curve.

The issue of accuracy and precision are often controversial in discussions of corrosion electrochemistry. Analytical electrochemists can achieve high accuracy and precision through the strict control of variables such as temperature, solution composition, surface condition and mass transport. Unfortunately, in practice, close control of such important parameters is often impossible. In addition, corrosion systems are generally variable in time in practice, further complicating reproducibility. [13] [15]

2.7. Testing

In general, when conducting test for galvanic corrosion, the closer the test comes to the actual situation, the more accurate will be the results so the environment, the material tested and the geometry must be accurately modeled. Tests also must be conducted over sufficient duration to ensure that the results can accurately predict the corrosion evolution. Beyond the basic properties of the metal related to chemical composition structure and surface finish, an investigation needs to consider the requirements for the metal in terms of achieving a necessary level of corrosion resistance. Other fundamental characteristics of metallic material also have to be considered in planning a testing program. These characteristic are determined by the production history of the material and the final forming, machining, welding and heat-treating steps:

- Forming can affect the structure of metal profoundly. It can create internal stresses that may lead to such detrimental manifestations as stress cracking or structural changes and cause stress-induced inter-granular corrosion in aluminum alloys.

- Machining affects the surface structures of the metal and its profile. Machining processes can chemically change the surface of the metal by absorption or inclusion of components from coolants, grinding compounds and blasting media,

in addition, local high temperatures often occur during machining operations, resulting in substantially changed chemical or microstructural properties.

- Welding can change the metal structures and have significant effects on the corrosion behavior of the metal. Galvanic corrosion can arise between the weld metal, the heat-affected zone, and the parent plate. The heat-affected zone of the base metal sometimes receives a damaging heat treatment and the heating and cooling cause residual stresses in the structure.

- Heat treatment can change the structure of metal with the precipitation of alloying elements. [14]

For laboratory corrosion testing, polarization methods are often used. These techniques can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility to corrosion of specific materials in designed environments. Developing polarization curve can be done in a variety of ways.

Potentiodynamic polarization curves are generating by holding a specimen at a given potential and gradually sweeping the potential in one direction while measuring the current required. If the starting potential is the corrosion potential, then an anodic polarization curve is generated by sweeping in the positive direction, while a cathodic polarization curve is generated by sweeping in the negative direction. Sometimes scans are started at a cathodic potential and swept in a positive direction, generating both anodic and a cathodic branches of the polarization curve in a single scan. The speed of the potential scan is important, with slower usually giving better results. [15]

An important variant of potentiodynamic polarization is the cyclic polarization test. This test is often used to evaluate pitting susceptibility: the potential is swept in a single cycle and the sized of hysteresis is examined along with differences between the values of the starting open-circuit corrosion potential and the return passivation potential. The existence of the hysteresis is usually indicative of pitting, while the size of the loop is often related to the amount of pitting.

Another variant of potentiodynamic polarization is cyclic voltammetry, which involves sweeping the potential in a positive direction until a predetermined value of current or potential is reached, then immediately reversing the scan toward more negative values

until the original value of potential is reached. In some cases, this scan is done repeatedly to determine changes in the current-potential curve produced with scanning. [14]

Polarization curves can also be generated potentiostatically by taking a series of specimens and holding each at different constant potential while measuring current as a function of time. This better approximates the potential behavior of a galvanic couple than a potentiodynamic scan but the technique is very labor and time intensive. [15]

The main complications or obstacles in performing polarization measurements can be summarized in the following categories:

- Effect of scan rate: the rate at which the potential is scanned may have a significant effect on the amount of current produced at all values of potential. It is an experimental parameter over which the user has control. If not chosen properly, the scan rate can alter the scan and cause a misinterpretation of the features. The problem is best understood by picturing the surface as a simple resistor in parallel with a capacitor. In such a model, the capacitor would represent the double-layer capacitance and the resistor the polarization resistance, which is inversely proportional to the corrosion rate. The goal is for the polarization scan rate to be slow enough so that this capacitance remains fully charged and the current-voltage relationship reflects only the interfacial corrosion process at every potential. If this is not achieved, some of the current being generated would reflect charging of the surface capacitance in addition to the corrosion process, with the result being that the measured current would be greater than the current actually generated by the corrosion reactions. When this happens, the polarization measurement does not represent the corrosion process, often leading to an erroneous prediction. A relatively valid method would be to use the lower breakpoint frequency of the impedance spectrum as the starting point. The method is based on the premise that the scan rate (voltage rate of change) is analogous to a frequency at every applied potential. That frequency must be low enough so that the impedance magnitude is independent of frequency. Then the polarization or charge transfer resistance is being measured with no interference from the capacitance. The frequency below which there is no capacitive contribution is about an order of magnitude lower than the

breakpoint frequency. The assumption is that this lower frequency is analogous to a scan rate.

- Effect of solution resistance: the distance between the Luggin probe (of the salt bridge to the reference electrode) and the working electrode is purposely minimized in most measurements to limit the effect of the solution resistance. In solutions that have extremely high resistivity, this can be an extremely significant effect.

- Changing surface condition: since corrosion reactions take place at the surface of materials, when the surface is changed as a result of processing conditions, active corrosion, or other reasons, the potential is usually also changed. This can have a strong effect on the polarization curves.

- Determination of pitting potential: in analyzing polarization curves, the appearance of a hysteresis (or loop) between the forward and reverse scans is often thought to denote the presence of localized corrosion (pitting or crevice corrosion). This observation is particularly valid when the corrosion potential is higher or nobler than the pitting potential. [14]

IR drop is not taking into account by the above testing. It can be measured during an exposure of galvanic couples either by using reference electrode or Luggin-Haber capillary and moving it near the various surfaces, or by rapid interruption of galvanic current if this current travels through an external wire followed by immediate measurement of potential.

Once corrosion current is known, corrosion rate can be calculated using Faraday´s law. If the cathode corrosion potentials are more than 120mV apart, the current that can be used in Faraday´s law calculations is the galvanic current. If not, Evans diagrams must be used to determine reaction currents that can put into Faraday´s law to get corrosion rates of anode and cathode materials. An easier method for obtaining corrosion rates is to determine specimen mass of anode metal before and after an exposure in a galvanic couple or at a potential indicative of the couple potential. This corrosion rate should be compared to that of a freely corroding specimen of the anode metal to determine the amount of acceleration due to the presence of the couple. [15]

2.7.1. Influence of mass transport

The information required to predict electrochemical reaction rates (experimentally determined by Evans diagrams, etc.) depends upon whether the reaction is controlled by the rate of charge transfer or by mass transport. Charge transfer controlled processes are usually not affected by solution velocity or agitation but on the other hand, mass transport controlled processes are strongly influenced by the solution velocity and agitation. The influence of fluid velocity on corrosion rates and the rates of electrochemical reaction is complex. To understand these effects requires an understanding of mixed potential theory in combination with hydrodynamic concepts.

For this purpose, he rotating disk electrode (RDE) is an important system because the axial followed by radial flow across the disk brings fresh solution to all points across the disk. The surface is therefore uniformly accessible to reacting species. The RDE operates under laminar flow for Re<$1.7x10^5$ and flow is turbulent above $3.5x10^5$, transitional in between. This testing system is described in detail in the Chapter 5. [14]

2.8. Corrosion behavior of hybrid metal structures – state of art

As explain in the introduction, the combination of aluminum and magnesium in the hybrid structure helps to reduce the weight but the main problem is relating to the corrosion protection, because, due to the high difference in the electrochemical potentials of the two elements of interesting for this work (i.e. aluminum and magnesium alloys), hybrid Al-Mg structures could act as a galvanic couple when they are in electrolytic and electronic contact.

In the research conducted by D. Joop, S. Heuple, C. Schnatterer at all. [12], hybrid parts in shape of Connection-Demonstrators, structured to represent original-size structural car body component, and Standard-Profiles, were manufactured to be analyzed in a near-neutral pH solution. In the near-neutral condition investigated (6<pH<8) magnesium suffers anodic dissolution, accompanied by hydrogen evolution, while aluminum-surfaces reach a stable passivity. The Standard-Profile has been registered as VarioStruct® by Imperia GmbH and used mainly for the material combination steel-sheets and aluminum casting, but this research tested it with the combination aluminum-

sheets and magnesium casting. Connection-Demonstrator I is made with EN AW 5083 + AZ91 HP while Connection-Demonstrator II is made combining EN AW 6082 + AM50 HP.

Connection-Demonstrators were used to perform immersion test in 0.1 M NaCl aqueous solution for 500 minutes. Both material combinations showed visually hydrogen formation during the test and after 10 hours, macroscopic corrosion could be observed on the surface of both alloys in both couples. Mg alloys AZ91 as well as AM50 sustained severe deterioration with penetration depths up to ~140 μm. For both material combinations, the corrosion attack is predominant in the Mg alloy. The Al sheets revealed rather homogeneous damages with penetration depths of ~20 μm.

In case of EN AW 5083 + AZ91 HP, the hydrogen-evolution was characterized by two distinct regions. During the first ~200 minutes, the hydrogen-evolution rate was comparatively high but then the hydrogen evolution decreased considerably to show a linear corrosion rate. The AM50 HP + EN AW 6082 samples revealed only a marginal hydrogen evolution during the first ~100 minutes but the corrosion behavior after ~200 minutes can be described again as linear. The combination EN AW 5083 + AZ91 HP showed superior corrosion properties in 0.1M NaCl solution in comparison to EN AW 6082 + AM50 HP. The predominant factor for the corrosion properties of these galvanic couplings is supposed to be the difference of standard potentials. The high amount of Al in AZ91 HP (~9 wt.%) and the high amount of Mg in EN AW 5083 (~ 4,5 wt.%) affect an approach of the standard potentials of both materials, resulting in less galvanic activity.

CHAPTER 3

Overview of Aluminum

3.1. Physical and mechanical properties

Aluminum is the third most plentiful element known, only oxygen and silicon exist in greater quantities. The element aluminum (Al) has the atomic number 13 and, like copper, silver and gold, crystallizes with face-centered-cubic (FCC) arrangement of atoms, common to most of the ductile metals.

Lightness is the outstanding and best known characteristic of aluminum. The metal has an atomic weight of 26,98, approximately one-third the weight of other commonly used metals, with exception of titanium and magnesium, and a density of 2,70 g/cm³.The addition of other metals in the amounts commonly used in aluminum alloys does not appreciably change the density. Low weight combined with the high strength possible with special alloys has placed aluminum as the major material for aircraft construction and automotive. Weight is important for all application involving motion; saving weight also saves energy, reduces vibration forces, improves the performance of reciprocating and moving parts, reduces tiredness when using manually operated equipment, offers lower shipping, handling and erection costs.

The coefficient of thermal expansion is non-linear over the range from minus 200 to plus 600°C but for practical purpose is assumed to be constant between the temperature ranges from 20 to 100°C. The coefficient of thermal expansion of alloys is affected by the nature of their constituents: the presence of silicon and copper reduces expansion while magnesium increases it. Another form of dimensional change important in the production of castings is the contraction of the metal during solidification; this is dependent upon alloy and is between 1 and 2%.

The melting point of aluminum is sensitive to purity and for 99,99% pure aluminum at atmospheric pressure it is 660°C but this reduces to 635°C for 99,5% commercial pure aluminum. The additional alloying elements reduce this still further down to 500°C for some aluminum-magnesium alloys under certain conditions. [14] [17]

3.2. Production

The scientific researching for the low cost production of aluminum was taken place by Héroult and Hall and they believed that the answer to economic production lay in an electrolytic method. They discovered that aluminum oxide (Al_2O_3), known as alumina, would be dissolved by an electric current passed through a solution of cryolite and the process could deposit the aluminum as metal. Cryolite is a white sodium-aluminum-fluoride material component today synthetically produced and, held at 1030°C, the molten cryolite dissolves up to 20% of alumina readily. The electrolytic cell holding the molten cryolite is a tank lined with carbon which serves as one electrode. Large carbon blocks inserted from the top of the bath act as the anode, or other electrode, and a heavy electrical current passed between these two sets of electrodes through the solution. This current break down the alumina into aluminum and oxygen, the molten metallic aluminum collects at the bottom of the cell and is drained off every few days as sufficient metal accumulates. The oxygen combines with carbon at the anodes and is given off as carbon dioxide gas. This method, call Hall-Héroult process, became the first industrially method of making the metal aluminum from alumina and is the one still use today.

Alumina is produced in a totally separate first stage process from Bauxite ore. This (Bayer) chemical process starts by immersing crushed bauxite into a caustic soda solution which dissolves the alumina to form sodium aluminate liquor. After filtering, the impurities are left behind as a "red mud" and the liquid is treated to precipitate the aluminum content out of the solution which is now in the form of aluminum hydroxide. This material is then separated from the liquor and changed to alumina by heating in kilns at 1000°C. Approximately 4 kilograms of bauxite is required to produce 2 kilograms of alumina and 1 kilograms of aluminum.

Aluminum is relatively unique in being highly economic to recycle. Metal can be reclaimed and refined for further use at an energy cost of only 5 per cent of that required to produce the same quantity of aluminum from its ore. There has been a healthy secondary metal industry for many years and as refining techniques improve the use that can be made of reclaimed aluminum will increase from its present usage in Europe of 40% of all metal currently processed. [14] [17]

3.3. Alloys

The properties of a particular aluminum product depend on the alloy chosen. Knowledge of these alloys is the key to the effective use of aluminum. Most countries have agreed to adopt the 4 digit classification for wrought alloy composition designation. The European reference for the alloys will be identified with the preface EN and AW which indicated European Normative Aluminum Wrought alloys. The first of the four digits in the designation indicates the alloy group in terms of the major alloying elements:

1XXX	Aluminum of 99.00% minimum purity and higher	NHT
2XXX	Copper	HT
3XXX	Manganese	NHT
4XXX	Silicon	NHT
5XXX	Magnesium	NHT
6XXX	Magnesium and silicon	HT
7XXX	Zinc	HT
8XXX	Other elements	HT

Table 3.1: Four digit classification of aluminum alloys. HT indicates heat treatable alloys and NHT indicates non heat treatable alloys.

For the group 1XXX, the last two of the four digits indicate the minimum percentage of aluminum. For examples, 1070 indicates aluminum purity of 99,70 %. The second digit indicates modifications in impurity limits or alloying elements, if it is zero indicates unalloyed aluminum having natural impurity limits while integer 1-9 indicated special control of one or more individual impurities or alloying elements.

From 2XXX to 8XXX groups, the last two of the four digits have no special significance but serve only to identify the different alloys in the group. The second digits indicates alloys modification, if it is zero it indicates the original alloy. The following list presents an overview of the different alloys:

- Unalloyed aluminum: commercial pure aluminum is soft, ductile and of little structural value. It is widely produced in sheet form and has an excellent corrosion resistance, so it is ideal for use in the foods and chemical industries.

- Aluminum-copper alloys: these alloys require heat treatment to achieve optimum mechanical properties, which can exceed that of mild steel. Generally, these alloys have limited cold formability, except in the annealed condition, and less corrosion resistance than other alloys; they are therefore generally anodized for protection from aggressive environments. They are also more difficult to weld. Alloys in this family are particularly useful for aircraft and military applications.

- Aluminum-manganese alloy: the addition of approximately 1% manganese increase the strength by approximately 10-15% compared with aluminum 1200, without any major loss in ductility. This non-heat treatable alloy generally finds a wide application where greater strength than aluminum 1200 is required without any major loss in corrosion.

- Aluminum-silicon alloys: silicon can be added to aluminum alloys in quantities sufficient to cause a substantial lowering of the melting point. For this reason this alloy system is used entirely for welding wire and brazing filler alloys, where melting points lower than the parent metal are required.

- Aluminum-magnesium alloy: this series of alloys exhibits the best combination of high strength with resistance to corrosion, also good weldability but when the magnesium level exceed 3% there is a tendency for stress corrosion resistance to be reduced, dependent on the temper used and temperature of operation.

- Aluminum-magnesium-silicon alloys: this group uses a combination of magnesium and silicon to render it heat-treatable. These alloys find their greatest strength combined with good corrosion resistance, ease of formability and excellent ability to be anodized.

- Aluminum-zinc-magnesium and aluminum-zinc-magnesium-copper alloys: this group exhibits the highest strength as far as aluminum is concerned and in many cases they are superior to that of high tensile steels. This group of alloys is, however, relatively difficult to fabricate and requires a very high degree of technology to produce. [14] [17]

3.4. Process development

After the addition of the alloying elements, the molten aluminum is ready to be used to create semi-finished product that includes plates for rolling, billets for extrusion, or also ingots used in the casting technologies.

The rolling of aluminum uses the plates as raw material. It could be hot rolling or cold: hot rolling is a process that occurs above the recrystallization temperature of the material and it is used mainly to produce sheet metal; typical uses includes truck frames, automotive wheels, railcar components, metal buildings, doors, and others. The cold rolling occurs with the metal below its recrystallization temperature and commonly cold-rolled products include sheets, strips, bars and rods.

Extrusion is the process used to create objects of a fixed cross-sectional profile. The material is pushed or pulled through a die of the desired cross-section. The two main advantages are the ability to create very complex section, to work materials that are brittle and it also forms parts with an excellent surface finish. Aluminum is very indicated for this kind of treatment.

The casting process is subdivided into two main categories: the expendable casting that involves the use of temporary, non-reusable molds, and the non-expendable casting in which the mold do not need to be reformed after the cycle. Aluminum is possible to cast in both condition: some example for casting process with expandable casting are the sand casting, investment casting and the lost foam casting, for the non-expendable casting is possible to use techniques like die casting, low pressure die casting, high pressure die casting, vacuum die casting and squeeze casting. [18]

3.5. Corrosion resistance

Aluminum has a higher resistance to corrosion than many other metals owing to the protection conferred by the thin but tenacious film of oxide. This oxide layer is always present on the surface of aluminum in oxygen atmospheres. The formation of the oxide is so rapid in the presence of oxygen that special measures have to be taken in thermal joining processes to prevent the oxide instantly forming while the process is being carried out. This oxide film is stable in aqueous media when pH is between 4.0 and 8.5

and it is naturally self-renewing, accidental abrasion or other mechanical damage of surface is rapidly repaired. The acidity or alkalinity of the environment significantly affects the corrosion behavior of aluminum alloys: when aluminum is exposed to alkaline conditions, corrosion may occur, and when the oxide film is perforated locally, accelerated attack occurs because aluminum is attacked more rapidly than its oxide under alkaline conditions and the result is pitting. In acidic conditions, the oxide is more rapidly attacked than aluminum, and more general attack should result.

Aluminum is, however, a very reactive chemical element and its successful resistance to corrosion depends on the completeness with which the protective film of aluminum oxide prevents this underlying activity coming into play. The film of oxide can be enhanced electrolyticly by a process called anodizing, in which the aluminum articles are suspended in a vat similar to that used for electroplating but containing chromic, phosphoric or sulphuric acid solutions. The anodic film also possesses the property of absorbing dyes thus enabling the metal to be tinted with attractive and enduring colors, thereby combining decoration with protection.

Nearly all engineering metals are cathodic to aluminum and its alloys, aluminum presents an electrochemical potential of -1,67 V relative to standard hydrogen electrode at 25°C; therefore aluminum becomes sacrificial in the presence of an electrolyte. Exceptions to this situation are magnesium, cadmium and zinc which are anodic to aluminum.

As a general rule, aluminum alloys, particularly the 2XXX series, are less corrosion resistant than the commercial purity metal. Some aluminum alloys, for example, are susceptible to inter-granular corrosion as a result of low-temperature aging reactions and the subsequent precipitation in the grain boundaries. Susceptibility to inter-granular attack in these alloys shows up as exfoliation and stress-corrosion cracking.

The additions of alloying elements to aluminum change the electrochemical potential of the alloy, which affects corrosion resistance even when the elements are in solid solution. Zinc and magnesium tend to shift the potential markedly in the anodic direction, whereas silicon has a minor anodic effect while copper additions cause marked cathodic shifts. This results in local anodic and cathodic sites in the metal that

affect the type and rate of corrosion. Very high-purity aluminum, 99.99% or purer, is highly resistant to pitting corrosion and any alloying addition will reduce this resistance. The 5XXX Al-Mg alloys and the 3XXX Al-Mn alloys resist pitting corrosion almost as well. The pure metal and the 3XXX, 5XXX and 6XXX series alloys are resistant to the more damaging forms of localized corrosion and exfoliation. [14] [19]

3.5.1. Corrosion in aqueous solution

Thermodynamic principles to explain and predict the passivity phenomenon and the corrosion behavior of aluminum in the aqueous solution are summarized by Pourbaix-type analysis. This result is plot in a diagram with potential versus the pH based on the electrochemical reaction of the species involves, visible in Figure 3.1. Aluminum is nominally passive in the pH of ~4 to 9 due to the presence of a Al_2O_3 film while in environment that deviate from near neutral range, the continuity of this film can be disrupted, facilitating the relatively rapid dissolution of the alloy: in acid range, aluminum is oxidized by forming Al^{3+}, in alkaline range AlO^{2-} occurs. The E-pH diagram gives an impression that corrosion prediction is a straightforward process, however in actual engineering applications, there are several variables that weren't considered by Pourbaix. These include the presence of alloying elements in most engineering metals, the presence of substances in the electrolyte such as chloride, the operating temperature of the alloy, the mode of corrosion, and the rate of reaction.
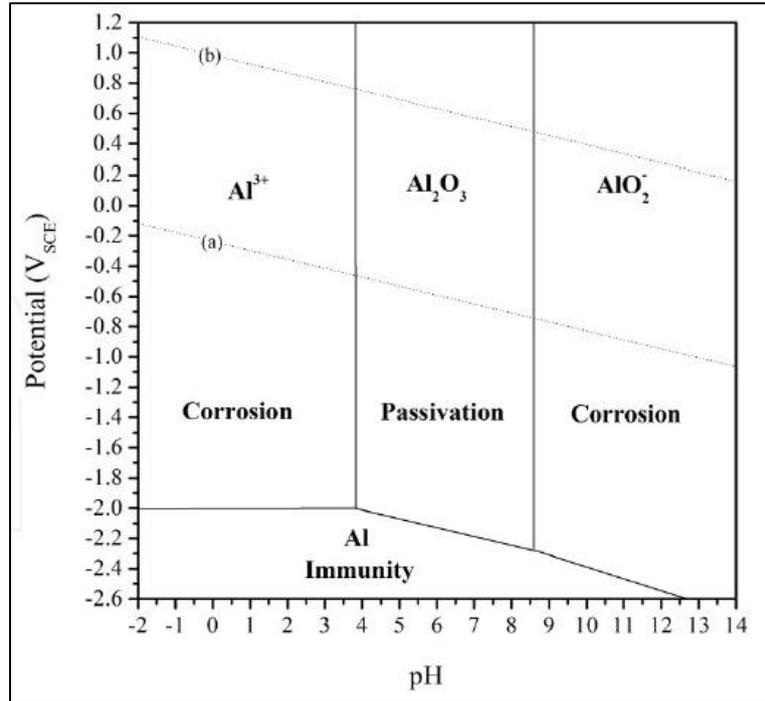
Fig. 3.1: Pourbaix diagram for pure aluminum in aqueous solution at 25°C. The line (a) and (b) correspond to water stability.

The alloying elements added to pure aluminum introduce heterogeneity into the microstructure which is the main cause of localized corrosion that initiates in form of pitting. Each alloying elements has a different effect on the corrosion of aluminum, in particular, for our interested, magnesium, founded in 5xxx and 6xxx, does not have a significant effect on pitting corrosion when present in solid solution, it decreases the rate of the cathodic reaction increasing corrosion resistance. In contrast, excess of magnesium or long term exposure to elevate temperature will cause the precipitation of Al_8Mg_2 or Al_3Mg_2, these phases are founded typically along grain boundaries and are known to be anodic to aluminum matrix, therefore prone to localized corrosion.

The addition of silicon in conjunction with magnesium, typically in 6xxx aluminum alloys, allows Mg_2Si particles to precipitate. This particles renders the alloy prone to localized corrosion, they are also anodic to the matrix and undergo selective dissolution. Excess amount of silicon increases the cathodic corrosion rate and may lead to inter-granular corrosion and stress corrosion cracking.

In order to understand the corrosion performance, not only alloying elements but also the microstructure is important to know. For homogeneous alloys, such as pure aluminum or

5xxx series alloys, corrosion susceptibility is low due to lack of pre-existing microstructural attack sites. The main concern however is regarding heterogeneous alloys, particularly the higher strength Al alloys such as the 2xxx, 7xxx and heat-treatable 6xxx series, where microstructural heterogeneity is a necessity. The most common features of a microstructure are the intermetallic particles which are classified into precipitates (forming from nucleation and growth, nominally 1nm to 300nm in diameter), constituent particles (from insoluble or impurity elements, unable to redissolve, nominally a few microns, to a few tens of microns, in size) and dispersions (nominally << 1 micron in size). Each of these features consists of different electrochemical characteristics and act as the sites which dictate the severity of corrosion attack. [20]

3.6. Aluminum alloys of interest

The aluminum alloys selected for the following tests are EN AW 5083, aluminum-magnesium alloy, and EN AW 6082, aluminum-magnesium-silicon alloy.

The aluminum 5083 is composed nominally by 4,5% of magnesium, 0,7% of manganese and some little percentage of other elements. It is known for exceptional performance in extreme environments and high resistant to attack by both seawater and industrial chemical environments. It has the highest strength of the non-heat treatable alloys but is not recommended for use in temperature in excess of 65°C. Alloy 5083 is typically used in shipbuilding, rail cars, vehicle bodies, pressure vessels. [21]

The aluminum 6082 is composed by 1% silicon, 0,6-1,2% magnesium, and other alloying elements like manganese. It is a medium strength alloy with excellent corrosion resistance and it is known as structural alloy. The typical applications are: highly stressed applications, trusses, bridges and transport. [22]

CHAPTER 4

Overview of Magnesium

4.1. Physical and mechanical properties

Magnesium is a widely distributed element in nature. There are over 80 minerals that have more than 20% Mg within their crystal structure, but dolomite ($CaMg(CO_3)_2$) and magnesite ($Mg(CO_3)$) are the most commonly used Mg metal ores. [23]

Magnesium (Mg) has the atomic number 12 and it is the ninth most abundant element in the universe and only occurs naturally in combination with other elements. Its density is 1.74 g/cm³ so two-thirds the density of aluminum and the lowest of all metallic constructional materials. The melting point for pure magnesium is 650°C.

The advantages of magnesium are many: it has a high specific strength, good castability (suitable for high pressure die casting), good weldability at high speed and also can be turned/milled at high speed. The strength of magnesium alloys is reduced at elevated temperatures, temperature as low as 93°C produce considerable reduction in the yield strength.

One of the reasons for the limited use of magnesium has been some poor properties exacerbated by a lack of development work; the disadvantages are: low elastic modulus, limited cold workability and toughness, limited high strength at elevated temperatures, high degree of shrinkage on solidification, high chemical reactivity and limited corrosion resistance in some applications.

It is not possible to use conventional alloying technique to improve some of the properties because the solubility of alloying elements in magnesium is limited so fiber and particle reinforcement must be used. The reinforcement materials are usually Al_2O_3, SiC o carbon. [24]

4.2. Production

Known Mg extraction methods belong to either thermal reduction or electrolytic categories. Thermal reduction methods (silico-thermic, alumino-thermic and carbo-thermic) operate at high temperatures. The silico-thermic process relies on the use of ferrosilicon to reduce magnesium oxide to a molten slag at temperatures between 1200ºC-1600ºC. A reduced gas pressure above the slag produces magnesium vapor and this vapor is condensed at a location removed from the main furnace or in the low temperature zone of the converter. The crowns of condensed magnesium are then re-melted, refined and casted. The Pidgeon, Magnetherm and Bolzano processes were all successfully used in the past. The Pidgeon process is the simplest, oldest, least energy efficient, and most labor intensive production process; however, it requires the lowest capital investment. This process is widely used in China, which dominates world magnesium production and effectively controls the price of magnesium metal. The main advantage of the thermal reduction methods is that, under the right conditions, high purity metal (99.95% Mg) is produced. Dolomite and magnesite, are the key ore minerals in the production of Mg metal by thermal reduction methods.

Plants using Mg electro-winning methods are less labor and energy-intensive than thermal reduction processes, but they require higher capital investments. There are a large number of technically proven, electrolysis-based processes; however, commercial magnesium electrolysis is conducted most commonly in a chloride melt of mixed alkali metals at temperatures below 700°C. The feed to the electrolysis process is either anhydrous magnesium chloride, $KMgCl_3$ produced from the dehydration of carnallite or partially dehydrated magnesium chloride. The later feed can be derived from a variety of raw materials including dolomite, magnesite, bishofite, serpentine group minerals, sea water or brines. Although pure anhydrous magnesium chloride is probably the preferred feed material, the production of magnesium chloride with low levels of magnesium oxide is difficult due to its hygroscopic nature. Plants based on the electrolytic approach have difficulty achieving metal purity over 99.8 %.

In theory, considering all the key parameters such as energy efficiency, labor requirements, environmental impacts and economy of scale, electrolysis should be preferred over the high temperature processes when targeted production exceeds 10,000

tons per year. In practice, this is not the case as labor costs, access to inexpensive Mg raw materials and abundant, low-cost energy are controlled in part by geography and political factors. Furthermore, environmental standards vary between countries, and the costs required to adhere to strict western standards are high. It is difficult for a western Mg-producer to successfully compete with the current low cost Mg exports from China and to provide an acceptable return on investment for its shareholders. [23]

4.3. Alloys

The property profiles demanded by automobile and other large-scale potential users of magnesium have revealed the need for alloy development.

Magnesium alloys name are often given by two letters following by two numbers. Letters tell main alloying elements and numbers indicate the respective nominal composition of main alloying elements. The designation system for magnesium alloys is not as well standardized as in the case of steels or aluminum alloys. The letters for the alloying elements are: A = aluminum, B = bismuth, D = cadmium, E = rare earths, F = iron, H = thorium, J = strontium, K = zirconium, L = lithium, M = manganese, N = nickel, P = lead, Q = silver, R = chromium, S = silicon, T = tin, V = gadolinium, W = yttrium, X = calcium, Y = antimony, Z = zinc.

Aluminum, zinc, zirconium and thorium promote precipitation hardening, manganese improves corrosion resistance and tin improves castability. Aluminum is the most common alloying element. Most common cast alloys are: AZ63, AZ81, AZ91, AM50, AM60, ZK51, ZK61, ZE41, and ZC63. The most common wrought alloys are: AZ31, AZ61, AZ80, ZK60, and HK31.

The vast majority of magnesium applications are covered by AZ91, a die-casting alloy. This alloy has insufficient creep resistance for many desirable applications at temperature above 130°C. A binary of 6% Al provides the optimum combination of strength and ductility. The lack of large-scale applications of magnesium alloys in the past has resulted in limited research and development, consequently, there are few optimized casting alloys available and ever fewer wrought alloys. [24]

4.4. Process development

The main categories of process used for magnesium are the casting techniques even if magnesium could be also extruded or wrought. In the casting techniques, although pressure die casting (hot chamber or cold chamber) dominates the techniques currently used, magnesium can be produced by virtually all other gravity and pressure casting methods like sand casting, permanent and semi-permanent mold and investment casting. The choice of a particular method depends upon many factors, e.g. the number of castings required, the properties required, dimensions and shape of the part and the castability of the alloy. Nevertheless, there is a need to develop conventional techniques further and also develop new techniques even if, at present, the use of pressure die cast alloys is increasing rapidly.

Magnesium needs particularly attention during the melting or the processing because the metal and its alloys are explosive hazards, they are flammable in their pure form when molten, in powder or in ribbon form. Burning or molten magnesium metal reacts violently with water and its metal forms will burn easily in air, both cases for the presence of oxygen; however in order to start the reaction of burning, the magnesium needs a source of energy. The reaction between magnesium and oxygen is:

$$2Mg_{(s,l)} + O_{2\ (g)} \rightarrow 2MgO_{(s)} + energy \qquad 4.1$$
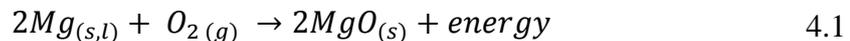
Due to this behavior, magnesium needs extra security procedures. [24] [25]

4.5. Corrosion resistance

The main reasons for the reluctance to use magnesium mass-produced vehicles or to use magnesium in other fields are related to its limitation in high temperature performance and corrosion resistance. Pure magnesium alloy reacts in the presence of oxygen and water producing magnesium hydroxide. Unlike other similar metals, like aluminum, the passivation film on magnesium could be very instable in many environments, including neutral or acid ranges of pH. Additionally, magnesium has an electrochemical potential of -2,37 at 25°C versus the standard hydrogen electrode, so it is anodic to most

engineering metals; make it very prone to severe galvanic corrosion when coupled with dissimilar metals.

Over the years, there have been significant advances in alloy development and as a result, new improved magnesium alloys have become commercially available. This has been possible due to additions of aluminum, zinc, manganese, for better corrosion resistance as well as additions of
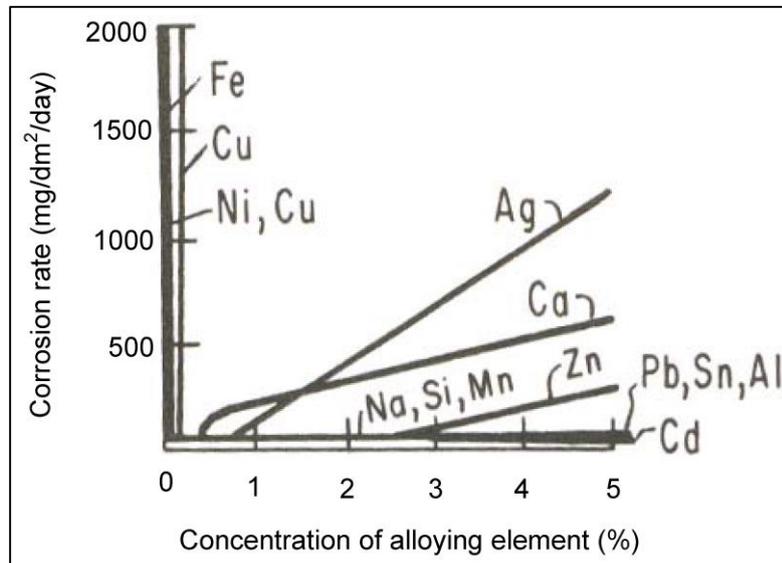
Fig. 4.1: Corrosion rate in function of the concentration of alloying element. Little percentage of Fe, Cu and Ni rapidly increase the corrosion of magnesium.

zirconium, rare earths, thorium, and silver for better elevated temperature mechanical properties, all in combination with the reduction of harmful impurities such as iron, nickel, copper during the alloy making process (Figure 4.1). Very little percentage of these impurity elements increase enormously the corrosion rate of the magnesium alloys.

In recent years, the demand for lighter, more fuel-efficient vehicles, has spurred increased interest by automakers to consider the use of magnesium in more critical components such as engine blocks, engine cradles and transmission housings. This has led to the formation of special interests industrial consortiums to develop solutions to the technical and economic challenges facing wide applications of magnesium and its alloys. General corrosion rates of modern high-grade magnesium alloys, especially when adequately coated, are acceptable in most applications. Galvanic corrosion, however, remains a challenge in many situations. Therefore, design considerations need to be made in order to avoid galvanic contact with other dissimilar metals. This is particularly important in components exposed to exterior environments such as road

salts and slurries which can easily damage conventional organic coatings, creating sites for rapid electrochemical dissolution of magnesium. [26]

There are two important features to underline in the corrosion process of magnesium: magnesium has a partially film covers on the surface but the film is not as good as the one of aluminum and the dissolution of magnesium is intimately associated with the hydrogen evolution ($Mg + 2H_2O = Mg^{2+} + 2OH^- + H_2$), therefore the corrosion rate could be estimated through the measurements on the hydrogen evolution.

These features have some important implications on the corrosion mechanism. The partially protective film is potential dependent: there is complete film coverage over the whole surface and a low rate of corrosion for potential below the pitting potential, at pitting potential there are some film-free areas and the surface area free of surface film increases with increasing potential. Furthermore, as the potential increases above pitting potential, the speed of the chemical reaction is increased. The existence of a partially film means that the common form of corrosion is localized corrosion.

The reaction of corrosion of magnesium in water tends to increase the local pH at cathodic sites. This tendency is particularly strong in a thin surface water layer as is often associated with atmospheric corrosion, in which is relatively common to have a high local pH value, which tends to facilitate precipitation of a corrosion-product film.; this behavior of magnesium is called alkalization. [27]

4.5.1. Corrosion in aqueous solution

According to the Pourbaix diagram in Figure 4.2, passivation on magnesium is possible in the basic environment as a result of the formation of a $Mg(OH)_2$ layer on the metal surface. Since the films that form on unalloyed magnesium are slightly solution in water, they do not provide long-term protection. In the neutral or acid ranges, the magnesium hydroxide is not stable and the material corrodes; moreover the immunity region of the diagram is below the region of water stability and, as result, magnesium dissolution is accompanied by hydrogen evolution.

0.8
0.4
0
−0.4
−0.8
−1.2
−1.6
−2
−2.4
−2.8

$2H_2O = O_2 + 4H^+ + 4e^-$

$H_2 = 2H^+ + 2e^-$

Potential (E), V

Corrosion

Passivation

Immunity

−2 0 2 4 6 8 10 12 14 16

pH
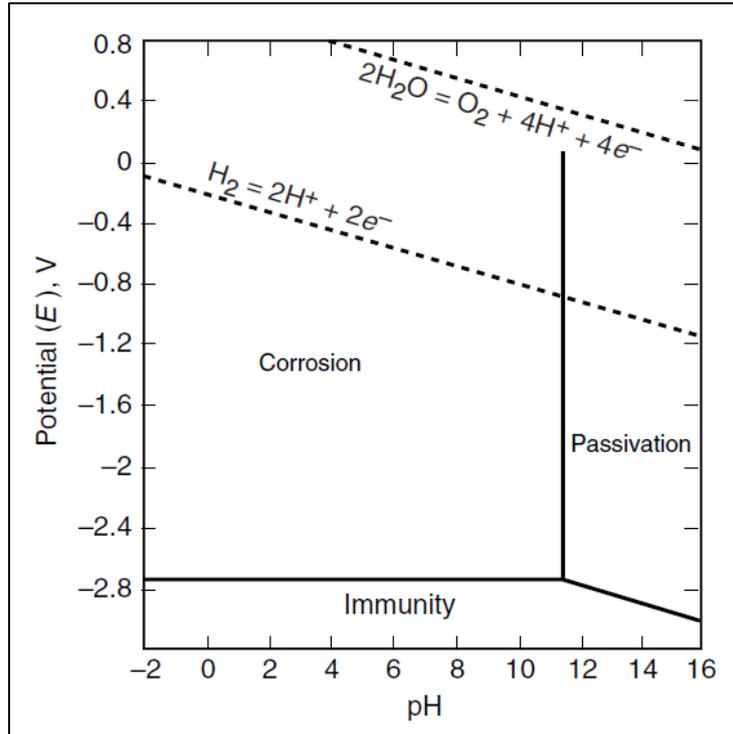
Fig. 4.2: Pourbaix diagram for pure magnesium in aqueous solution at 25°C. The line (a) and (b) correspond to water stability.

4.6. Magnesium alloys of interest

The magnesium alloys tested are AZ91 HP, the most common alloys, AM50 HP and AM60 HP.

Magnesium AZ91 HP is composed nominally by 9% of aluminum, 1% of zinc and percentages of others elements. It is the most popular commercially available magnesium alloy and it shows superior castability, good mechanical properties and good corrosion resistance for the high purity versions of the alloy. Typical applications include transmission casings, valve covers, pumps, brackets. Mg-Al-Zn based alloys are, in general, utilized for applications at ambient or slightly elevated temperatures primarily in automotive and electronic industry. [28]

The composition of magnesium AM50 HP is 5% of aluminum, 0,28-0,50% of manganese and some other alloying elements. It allows high-energy absorption and

elongation at high strength and has good castability. Typically it is used in automotive industry for steering wheels, dashboards and seat frames.

Magnesium AM60 HP is composed by 6% of aluminum, 0,21-0,35% of manganese and other elements. It is one of the most popular magnesium alloys with great potential for applications in automotive industry, like AM50.

CHAPTER 5

Experimental methods

5.1. Electrochemical technique - Rotating disk electrode (RDE)

First of all, electrochemical techniques are used to perform two kinds of test: one with the use of rotating disk electrode and one with the standard three electrode setup (Chapter 5.2).

The information required to predict electrochemical reaction rates depends upon the rate of charge transfer or the mass transport. Cathodic and anodic processes are made up of different kinds of heterogeneous chemical reactions that usually involve the transfer of electrons across the interface between a solid and an adjacent solution phase. Obviously, the continuous conversion of reactant to product requires the supply of reactant to the electrode surface and the removal of product. In addition, mass transport usually becomes the dominant consideration when dilute solutions are dealt with. When emphasizing the importance of mass transport processes, the supply and removal of reactant and product contribute to three different processes. Three forms of mass transport can be important in electrochemistry:

1. diffusion, defined as the movement of a species due to a concentration gradient;
2. convection, in which the movement is due to external mechanical energy, for example, electrode rotation;
3. migration due to a potential gradient, only the charged species are affected by this effect.

In laboratory experiments, it is very interesting to work under experimental conditions in which the mass transport regime is totally defined and well known, and describable by a set of solvable mathematical equations.

The rotating disk electrode (RDE) is a device that creates a totally defined solution flow pattern in which the mass transport of the species is almost completely due to

convection. This property allows the RDE to be used to calculate parameters related to mass transport, such as the diffusion coefficient of the various electro-active species.

Fig. 5.1: Representation of the reactant concentration in function of the distance from the electrode surface.

An RDE is a polished disc surrounded by an insulating sheath of substantially larger diameter. The structure is rotated about an axis perpendicular to the surface of the disc electrode. The rotating structure acts as a pump, pulling the solution upward and then throwing it outward. The electrolyte can be divided into two zones (Figure 5.1):

1. A first region close to the surface of the electrode where it is assumed that there is a totally stagnant layer and thereby diffusion is the only mode of mass transport.
2. A second zone outside the first region where a strong convection occurs, and all species concentrations are constant. [29]

The rotating disk electrode setup used in the tests performed is the RDE710 Gamry Instruments shown in Figure 5.2; it is composed by a control unit, a voltametric cell and a motor unit. The glass voltametric cell (or electrochemical cell) is controlled in temperature through the use of water, heated or cooled, flowing in the double bottom of the cell and it contains the electrolyte of interested.

The rotating electrode consists in two parts: a shaft, that can be fixed in the motor unit, and a tip in which the specimen made by the material of interest to be analyze, i.e. the working electrode (WE), is added (Figure 5.3). The specimen has a cylindrical shape, obtained with the machining of the material, and the circular surface exposed to the electrolyte is typically polished; the other sides are insulated by a Teflon film and an insulating shroud. After the rotating electrode disk has been fixed at the motor unit, it can be moved down in the electrolyte and, with the control unit, it is possible to manually adjusted the rotation rate from 50 to 2000 RPM.

80

The setup needs also a reference electrode and a counter electrode, in addition to the working electrode. For these tests, the reference electrode used (RE) is a saturated calomel electrode (SCE), in contact with the solution, while the counter electrode (CE) is a platinum wire, directly immersed in the electrolytic solution. Voltammetric curves are recording using a potentiostat Gamry Reference 600.
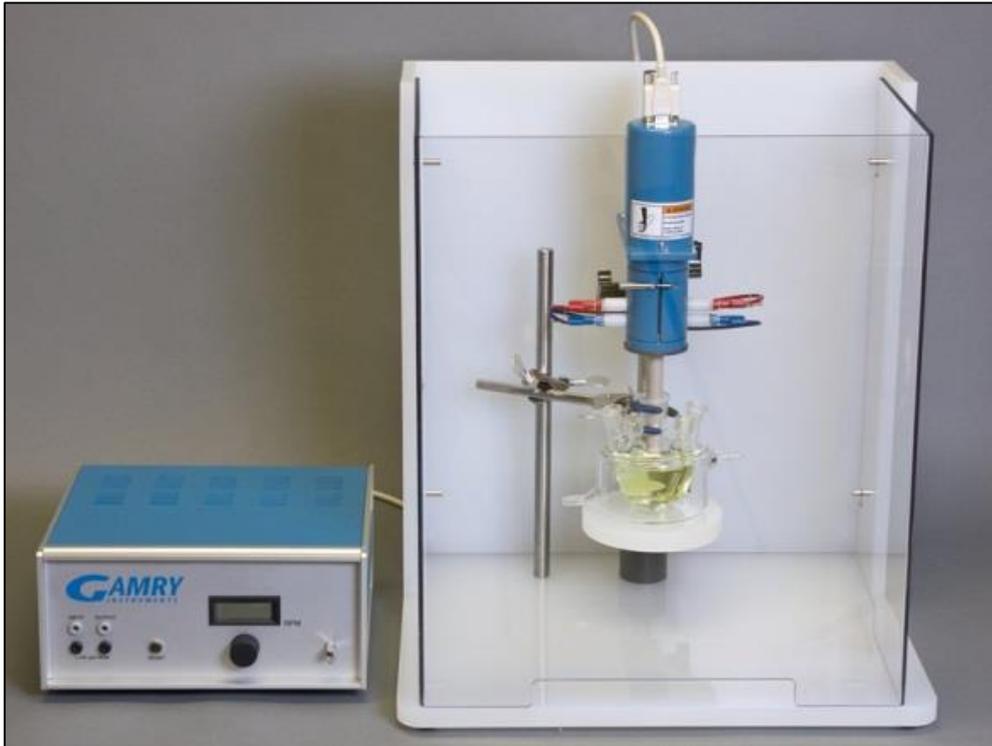
Fig. 5.2: Control unit and electrochemical (or voltametric) cell with motor unit of Gamry rotating electrode.

All the experiments are carried out with 400 rpm rotation speed of the working electrode and the electrolytic is a 0.1 molar sodium chloride aqueous solution (NaCl) at the temperature of 20°C. For each test, the pH of the solution is measured at the beginning and at the end and, before the measurements of data of interest, argon is used as flushing gas in the electrolyte for 15 minutes to remove dissolved gasses (i.e. oxygen) from the liquid. Moreover, prior to use, the metallic surface of the specimens is polished with abrasive paper of 1000 grit and then of 2500 grit and washed with bi-distilled water. The active area of the specimen exposed at the electrolyte is 19,63 mm².

The specific test that is performed with RDE is the potentiodynamic test, with DC polarization technique. The ultimate goal is to obtain the anodic and cathodic polarization curves for each material, i.e. plotting the current (in logarithmic scale) in function of the

Fig. 5.3: Working electrode with the circular active area exposed.

applied potential, after a measurement of the open circuit potential (OCD) that described the equilibrium potential assumed by the metal in absence of electrical connections, plotted as potential in function of time. Three replications of the experiments under the same condition are performed to control the statistic possibility of reproducibility of the tests. At the beginning of each test, it is necessary to set up the start and the final potential of the measurements, the scan rate, than could sensitive influence the reliability of the results and the time for measuring the open circuit potential.

DC electrochemistry, and in particular, the potentiodynamic scan, allows considerable information on electrode processes to be acquired, not only the polarization curves, but also the corrosion rate and the pitting susceptibility. [30]

5.2. Electrochemical technique – Standard three electrode setup

This corrosion test uses the electrochemical technique, as the rotating disk electrode, but it is the standard method to obtain the polarization curves. The theoretical concept is the same of the RDE test even if, in this case, there is no rotation of the working electrode. The WE is fixed in the voltammetric cell, consequently the solution does not present a convention shuffling.

The setup used for this test is shown in Figure 5.4. The glass voltammetric cell (or electrochemical cell), in which the electrolytic is situated, is controlled in temperature: it is possible to select the desire temperature for the electrolyte and maintains it constant during the time.

The specimen (the working electrode) has an active area exposed at the electrolyte of 1 cm². It is created by cutting the material from the original shape, typically from a foundry casting, and then cold mounted in epoxy to expose at the electrolyte only the area of interested. The sample is gritted using increasingly grit paper, from 180 grit, trough 320, 500, 1000 and to 2500 for aluminum, the

Fig. 5.4: Standard set up for three electrode corrosion tests. There are the three electrodes (working electrode, counter electrode and reference electrode) immerse in the electrolyte solution and connect to the potentiostat.

same grit sizes but until 4000 for magnesium. At the end, both aluminum and magnesium are polished with adequate processes and the samples are cleaned with ethanol.

In the last step of sample preparation, the material embedded in the epoxy is connected to a copper wire that passed through the epoxy and a glass tube, to be protected against contact with the electrolytic solution. If the material is too thin to make a good contact with the wire, a piece of copper, connected to the material and immersed in the epoxy, is used to help the electric connection (Figure 5.5).

The reference electrode (RE) is an Ag/AgCl electrode, in contact with the solution through a Luggin capillary very close to the working electrode surface, while the counter electrode (CE) is a platinum wire, directly immersed in the solution. However, all results are reported versus saturated calomel electrode to facilitate the comparison with the RDE results.

Fig. 5.5: An example of two samples used for the corrosion test: material embedded in the epoxy and connected to the wire.

All the experiments are carried out with the same conditions of RDE tests, i.e. the electrolytic is a 0.1 molar sodium chloride solution (NaCl) at the temperature of 20°C. For each test, the pH of the solution is measured at the beginning and at the end and, before the measurements of open circuit potential and polarization curves, argon is used as flushing gas in the electrolyte for 15 minutes. The voltammetric curves are then recording using a Gamry potentiostat.

Two replicate experiments are performed for each selected alloy under the same condition; the start and finish potential of the measurements, the scan rate and the initial delay time for the open circuit potential, are set up at the beginning of the test.

The test performed is potentiodynamic test with DC technique, the same with the RDE setup, in order to compare the results, and also the aluminum and magnesium alloys tested are the same.

5.3. Galvanic corrosion - Galvanic cell setup

After the use of electrochemical technique, other experiments are performed using aluminum and magnesium in a galvanic couple. This setup for the corrosion test permits to create a galvanic cell and it is used to obtain useful parameters to determinate the galvanic current between the two metals of interest.

The setup used is the following: the glass voltammetric cell is very similar to the one used for standard polarization scan and the specimens (the working electrodes) have the same shape and the same preparation of the samples used in the standard setup for the polarization scan (Figure 5.5). The difference is that in this following experiment, the specimens used are two, one made with aluminum alloy and one with magnesium, to create a galvanic couple. They are immersed in the solution inside the voltammetric cell, it is 0.1 molar sodium chloride (NaCl) at the temperature of 20°C +/- 1°, the same condition of the previous tests.

The reference electrodes are two silver/sliver chloride electrodes, in contact with the electrolytic through Luggin capillaries that are closed to the specimens' surface. The two electrodes are connect with a circuit that has a known resistance (0,5 Ω) and a
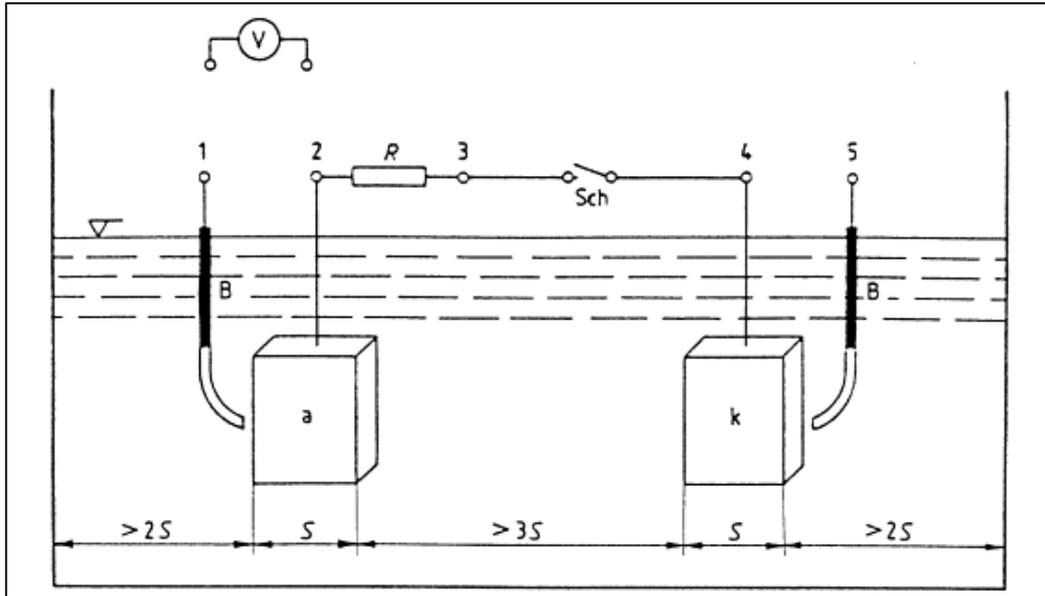
Fig. 5.6: Circuit for the galvanic corrosion test with point of interested indicated: a = anode, k = cathode (working electrodes), R = resistance, B = Lugging capillary with reference electrode.

switch. The circuit created is show in Figure 5.6 where different points are indicated. Opening or closing the circuit through the switch, it is possible to measure different potentials with a voltmeter. Connecting the terminals of the voltmeter in the point 1, at one reference electrode, and 2, at the correspondent working electrode, maintaining the circuit open, it is possible to measure the open circuit potential of the anode, $U_{R,a}$, while, when the circuit is close, it is possible to measure the potential of the anode, U_a. The same parameters are measured for the other working electrode, the cathode, connecting terminals in the point 4 and 5 ($U_{R,c}$, U_c). Connecting the terminals at point 2 and 3 with the circuit closed, it is possible to measure the potential between the two working electrode and the resulting measure is the galvanic corrosion potential $U = I_e * R$, where I_e is the galvanic current and R is the known resistance.

Important relations are:

$$I_e = \frac{U_{R,c} - U_{R,a}}{R_a + R_c + R_M} \qquad \qquad 5.1$$

$$R_a = \frac{U_a - U_{R,a}}{I_e} \qquad \qquad R_c = \frac{U_c - U_{R,c}}{-I_e}$$

In which R_a is the resistance of the anode and R_c of the cathode.

The anode is the material that has the more negative potential, when it is not coupled, $(U_{R,a})$ and the cathode has the less negative potential $(U_{R,c})$, so the anode will corrode. Testing aluminum and magnesium, magnesium becomes the anode and corrodes preferentially. The potentials U_a and U_c are measured when the circuit is closed so when the galvanic coupled exists and their values are positioned between the potentials of anode and cathode when they are not coupled $(U_{R,a}, U_{R,c})$.

Two experiments are made for each couple just to verify that the results are reproducible. Measuring the potential U between the two materials is difficult with the voltmeter because the values are too small, therefore a potentiostat is used to measure directly the galvanic current I_e. The potentiostat is used as a Zero Resistance Ammeter (ZRA): it maintains the samples at the same potential and measures the current flow between the samples.

The couples tested with the galvanic cell are aluminum 5083 + magnesium AZ91 and aluminum 6082 + magnesium AM50, the couples tested also with the following immersion test, but also the combination aluminum 5083 + magnesium AM50 and aluminum 6083 + magnesium AZ91 are tested to have a better vision of the situation. The galvanic current is measured for every couple with the potentiostat for 90 seconds but only for the couples aluminum 5083 + magnesium AZ91 and aluminum 6082 + magnesium AM50 for 8 hours long, to compare the change of the current with the hydrogen evolution measured in the immersion test, as explained later.

5.4. Galvanic corrosion - Immersion test: coupled aluminum and magnesium alloys in contact

This test, based on the hydrogen evolution, is performed because, due to the negative difference effect of magnesium, significant errors can be introduced into corrosion rate measurements when using traditional electrochemical techniques. Also the classical weight-loss method only provides final corrosion information and moreover errors may easily be introduced into the final result during the removal of corrosion products and in the calculation of the corrosion rate.

Normal methods of measuring the corrosion rate of magnesium alloys mainly include measuring weight-loss (after salt spray or immersion) and estimating the corrosion current density (by means of Tafel extrapolation on polarization curves). These methods have been successful in some cases, but their disadvantages are also significant.

The weight-loss rate method has been regarded as the most basic and reliable method but the weight-loss rate is actually an average result of a corroding specimen over a certain period of time and how the corrosion rate changes in this period is unknown. Moreover, to accurately measure the weight-loss caused by corrosion, all of the corrosion products stuck on the specimen surface should be completely removed without removing any un-corroded metal.

The corrosion current density obtained by electrochemical techniques, as done in the previous tests, has been widely and successfully used in corrosion studies of other metals. The advantage of this method over the weight-loss method is its ease of obtaining instantaneous corrosion rates. However, the corrosion of magnesium alloys is a special electrochemical dissolution process, which is always accompanied by a special electrochemical phenomenon, the negative difference effect. It has an abnormal polarization behavior because the hydrogen evolution rate increases during anodic polarization.

It is well known that the overall corrosion reaction of magnesium in aqueous solutions at its corrosion potential can be expressed as follows:

$$Mg + 2H_2O = Mg^{2+} + 2OH^- + H_2 \qquad 5.2$$
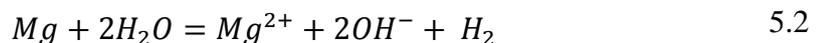
This means that the dissolution of one magnesium atom generates one hydrogen gas molecule. In other words, the evolution of one mole of hydrogen gas corresponds to the dissolution of one mole of magnesium. Therefore, in theory, measuring the volume of hydrogen evolved is equivalent to measuring the weight-loss of magnesium dissolved, and the measured hydrogen evolution rate is equal to the weight-loss rate if both have been converted into the same units. The corrosion products do not affect the relationship between the hydrogen evolution and magnesium dissolution so the hydrogen evolution rate directly reflects the corrosion rate of magnesium. Therefore, theoretically the corrosion rate of magnesium measured by hydrogen evolution should be very reliable.

For magnesium alloys, the corrosion mechanism is more complicated than for pure magnesium. Since most alloys have a multi-phase microstructure, all the microstructural constituents can affect the corrosion rates of the alloys. However, no matter how complicated the interaction among those microstructural constituents in an alloy, the matrix α phase always corrodes preferentially. The other constituents usually act as cathodes to the α phase or act as corrosion barriers that are inert to the corrosion process. The α matrix is a magnesium based solid solution and it has been shown that the α phase of AZ alloys has the same corrosion reaction mechanism as pure magnesium. This indicates that the overall corrosion rate can be expressed by an equation similar to reaction. Not only the elemental Mg is involved in the corrosion of the α matrix, but also other alloying elements in the solid solution as solutes would be dissolved during corrosion. Therefore, simply using reaction to estimate the corrosion rate of a magnesium alloy could result in an error. How significant the error depends on the amount of the other alloying elements involved in the corrosion of the α matrix but the error in practice would be expected to be much lower than the theoretical error. In conclusion, the hydrogen evolution rate should be a reliable indication of the corrosion of a magnesium alloy [34].

The test performed here uses samples with an aluminum alloy coupled to a magnesium alloy, immersed in the solution for 8 hours to measure the hydrogen evolution.

The setup for hydrogen evolution collection is easy to create. Figure 5.7 shows it schematically: the specimen is put in a beaker containing the test solution, in these tests the solution is again 0.1 M NaCl in aqueous solution and the
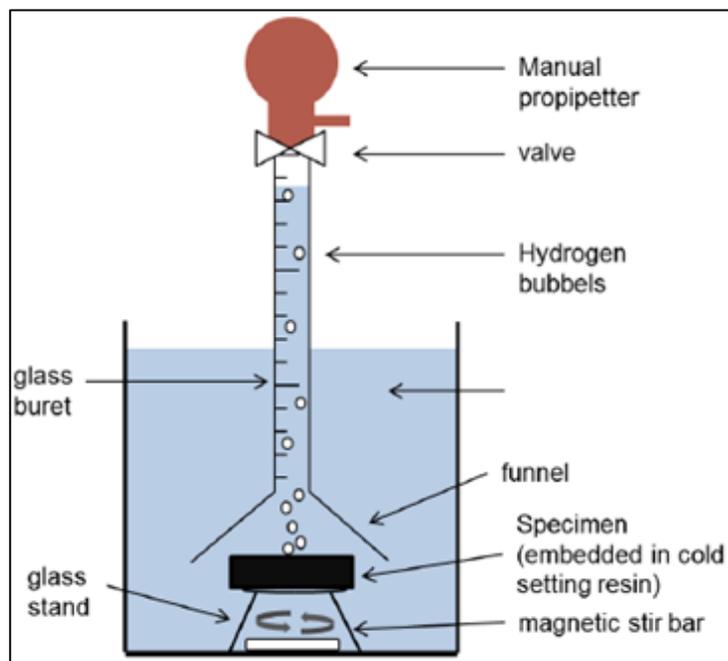
Fig. 5.7: Setup for the immersion test with hydrogen evolution collection.

volume is 1500 ml. A funnel is placed over the specimen to ensure the collection of all hydrogen from the specimen surface and a burette is mounted over the funnel, initially full of the test solution. The hydrogen collects by the funnel goes into the burette and gradually displaces the test solution in the burette. In this way the volume of the hydrogen is easy to measure by reading the position of the test solution level in the burette. Under the sample, a magnetic stir bar is placed to permit the recirculation of the solution in the beaker.

The samples are created using magnesium alloys, which size is 1 cm x 1 cm, in contact by one side with aluminum alloys, with the same size. The materials are connected on the part not exposed to the solution by a piece of copper to have better electrical connection. After the creation of this connection, the couples are embedded in the green epoxy and the grit from

Fig. 5.8: Crevice between 1 cm x 1 cm square of magnesium AM50 HP and 1 cm x 1 cm square of aluminum EN AW 6083 – optical microscope 25x.

180 to 2500 grit. At the end the surface of the samples are washed with ethanol.

The samples created are four: two with the couple EN AW 5083 + AZ91 HP and two with EN AW 6082 + AM50 HP. Some images of the crevice on the border of contact between the two materials are taken with a light optical microscope to identify the extension of the crevice. An image of the crevice between aluminum 6083 and magnesium AM50 is reported in Figure 5.8 with 25x and in Figure 5.9 with 200x whit the sizes of the crevice indicated. Creating samples that present always the same distance between the two material coupled is hard to do: the average space between EN AW 6082 + AM50 HP is 12 μm for the first sample and 35 μm for the second one, for the couple EN AW 5083 + AZ91 HP, it is 92 μm for the first sample and 30 μm for the second one. Also the influence on corrosion of the size of the crevice between the two coupled metals could be investigated but this is not the ultimate scope of this test.

The goal of the test is to measure the hydrogen evolution. The hydrogen evolution collection is registered every 60 minutes for 450 minutes, and also the pH of the solution is registered in the same intervals of time. After the tests, the samples are washed with bid-distilled water and then analyzed at the optical microscope to individuate the entity of the corrosion on the surface.

Fig. 5.9: Crevice between AM50 HP (on the left) and EN AW 6083 (on the right), sample number 2 – optical microscope 200x.

5.5. Galvanic corrosion - Immersion test: diffusion bonded pure aluminum and magnesium couples

The test described below is again an immersion test but pure aluminum metal and pure magnesium are used, connected together by diffusion bonding process under pressure in a compound bonding to study the intermetallic structure created in between and its corrosion properties. The intermetallic interface is composed by three layers as explain in chapter 1.2.

The samples used in the experiment are shown in Figure 5.10: a sheet of pure commercially aluminum and a sheet of pure commercially magnesium are connected together applying pressure for different periods of times. One compound is created pressing the two sheets for 6 days under 400° C degrees and one with the same condition but during 7 days. After this, an intermetalic interface is created between pure aluminum and pure magnesium. After this, the compound material is embedded in the green epoxy resin to create the samples, then grid until 1200 grit and washed with ethanol.

Each sample is put in a Becker with 200 ml of 0.1 M sodium chloride solution and leave there to react with the solution. At different intervals of time, the sample is take off from the solution, washes with bi-distilled water and then analyzed with the optical microscope to see where and how the corrosion process proceeds. The analysis takes place after 10 minutes of immersion, 20 minutes, 40 minutes and 100 minutes.

In Figure 5.11, the thickness of the intermetallic layer for the two samples is reported: for the aluminum + magnesium after 6 days, the layer is around 549 μm and for aluminum + magnesium after 7 days is ca. 593 μm because the diffusion has more time to work so the diffusion layer results more extensive. The three different layers created with the diffusion bonding are not visible with the optical microscope.
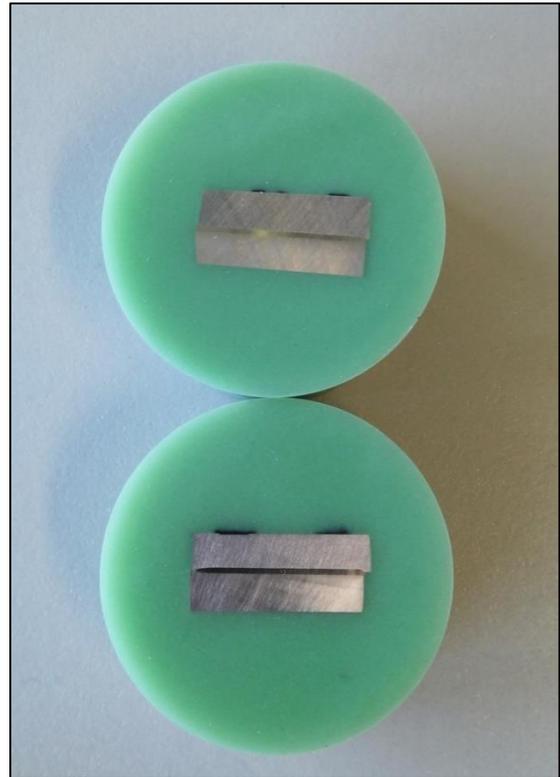
Fig. 5.10: Samples before the immersion tests: pure aluminum and magnesium sheets and the intermetallic interface in the between created by diffusion bonding.
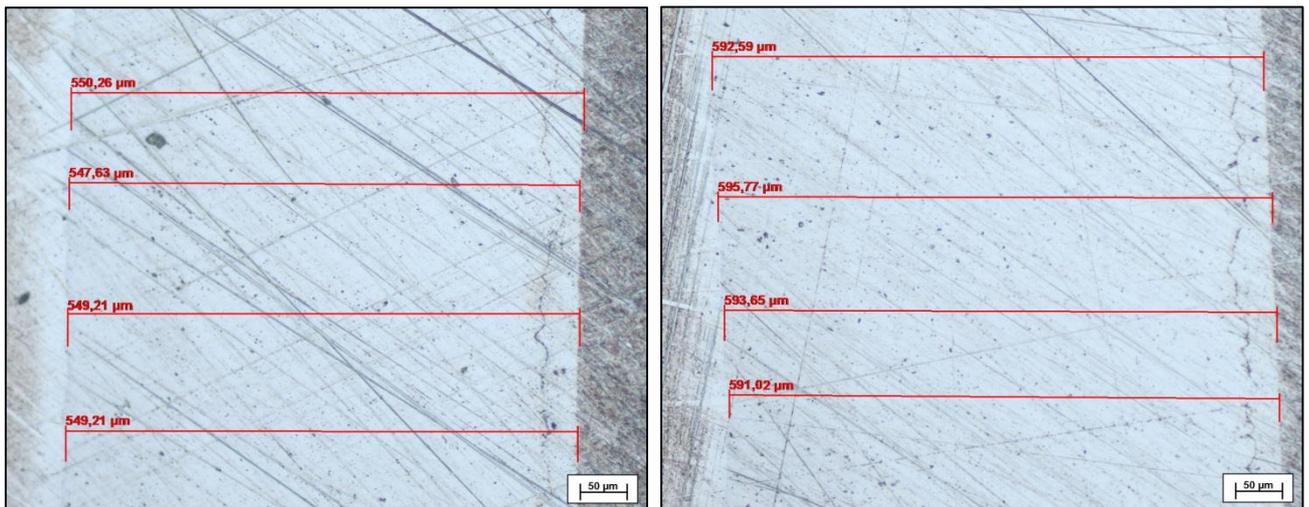
Fig. 5.11: Samples before the immersion tests. Thickness of the intermetallic interface in sample aluminum + magnesium 6 days (left) and aluminum + magnesium 7 days (right) – optical microscope, 200x.

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CHAPTER 6

Results of the experimental tests

6.1. Rotating disk electrode

The goal of the test with the rotating disk electrode is to measure the polarization curves of different alloys to obtain the corrosion potential.

6.1.1. Aluminum alloys

The aluminum alloys tested are EN AW 5083 and EN AW 6082. The scan rate used in the potentiodynamic tests for aluminum is 0,1 mV/s, the initial delay time for the OPC is set at 1800 s and the start and the finish potential chosen are respectively -1 V and 0 V because the corrosion potential is situated for the material in this range. The pH of the original solution varies in a range around neutral condition between 6 and 8, and it increases of some decimal points after the tests. At the end of the tests, the surface of both alloys shows only some visible signs of corrosion.

EN AW 5083 (AlMg4,5Mn0,7)

In Table 6.1 there are reported both the OCP curves for the three performance of the experiment and the polarization curves. In the OCP, the potential measured starts around -1,10 V and increase very regularly asymptotically to -0,75 V. The potential curves show scattered charts, mostly in the anodic part and it could depends on the passivation and repassivation behavior of the metal. The corrosion potential is between -0,71 and -0,77 V but the experiments do not show a very good reproducibly, due to not really predictable behavior of the passivation layer. The anodic curves show also pitting corrosion with a rapidly increase of the current, starting at pitting potential approximately at -0,70 V.

This material is tested also with a OCP of 3600 s to understand if the different duration of the OPC could give better results for the polarization curves but they present again scattered trend and the corrosion potential is situated in a range between -0,72 and

-0,80 V for the three experiments. It is possible to argue that for aluminum 5083, there is not a sensible difference in using different duration of time for OCP measurements; the results are not precise, in both cases tested, because they reflect the passivation and repassivation behavior of the material.

EN AW 6082 (AlSi1MgMn)

The OCP curves are visible in Table 6.2: the potential starts at different values but end around -0,90 V after 1800 s. All the polarization curves show the same trend, with a little scattering and the corrosion potential is situated in a range from -0,78 to -0,88 V. The pitting corrosion begin at -0,70 V in the anodic part of the curves.

6.1.2. Magnesium alloys

The magnesium alloys tested are AZ91 HP, AM50 HP and AM60 HP. The scan rate used in the potentiodynamic tests for magnesium is 0,8 mV/s, the initial delay time for the OPC is 1800 s, as for aluminum alloys, and the start and the finish potential are chose respectively at -1,7 V and -1,3 V because the corrosion potential is situated in this range. The pH of the solution before the tests is around neutral condition, i.e. 7 pH +/-1, and at the end it increases by some decimals points but more than the gain in the pH condition of solution in the aluminum tests, because of the alkalization due to magnesium alloys. All the specimens show evidently sights of corrosion and pitting corrosion on the surface at the end of the experiment; pitting corrosion is also visible in the polarization curves of each magnesium alloys.

AZ91 (MgAl9Zn1)

This material for the tests is equipped by the Gießerei Institut (GI) and it is made by high pressure die casting. There are reported, only for this magnesium alloy, both the OCP curves for the three performance of the experiment and the polarization curves (Table 6.3). In the OCP, the potential starts round -1,6 V and increases regularly; the polarization curves show very good reproducibility of experiment with a corrosion potential of approximately -1,54 V and a flexion in the anodic part at pitting potential around -1,45 V.

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AM50 (MgAl5Mn)

The material tested is made by high pressure die casting and obtain from two different suppliers, the Gießerei Institut (GI) and another supplier (SUP1). There are reported on Table 6.4 the polarization curves obtain in the three tests of AM50 supplied from GI. They show quite good reproducibility, the corrosion potential is between -1,54 and -1,59 V and the pitting potential is in the range from -1,47 to -1,50 V. The same material made by the other supplier (SUP 1), presents a corrosion potential between -1,54 and -1,58 V in the three tests and the pitting corrosion starts at the same potential of the material supplied by GI. As expected, the material from the two different suppliers shows almost the same behavior and results in the experiments.

AM60 (MgAl6Mn)

The material for the tests is equipped by a different supplier (SUP2) and made by high pressure die casting. Table 6.5 shows the three results for AM60: the corrosion potential is around -1,55 V and the tests show very good reproducibility. The material show pitting corrosion in the range of potential between -1,47 and -1,51 V.
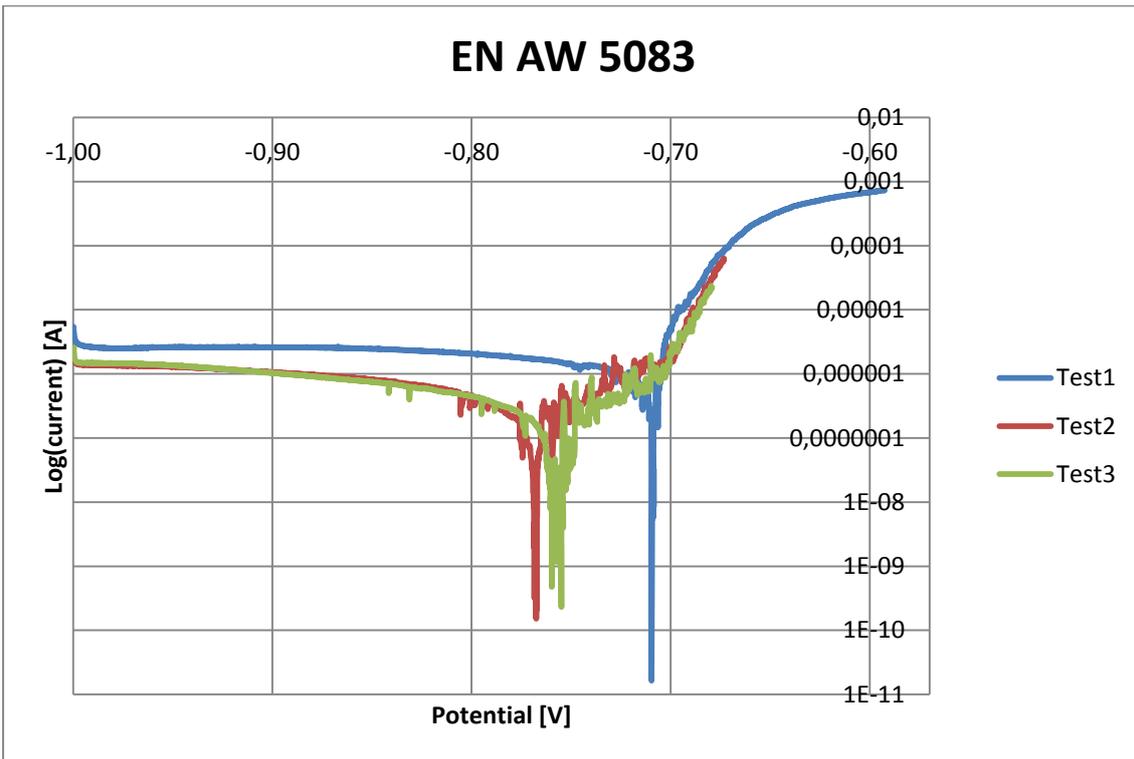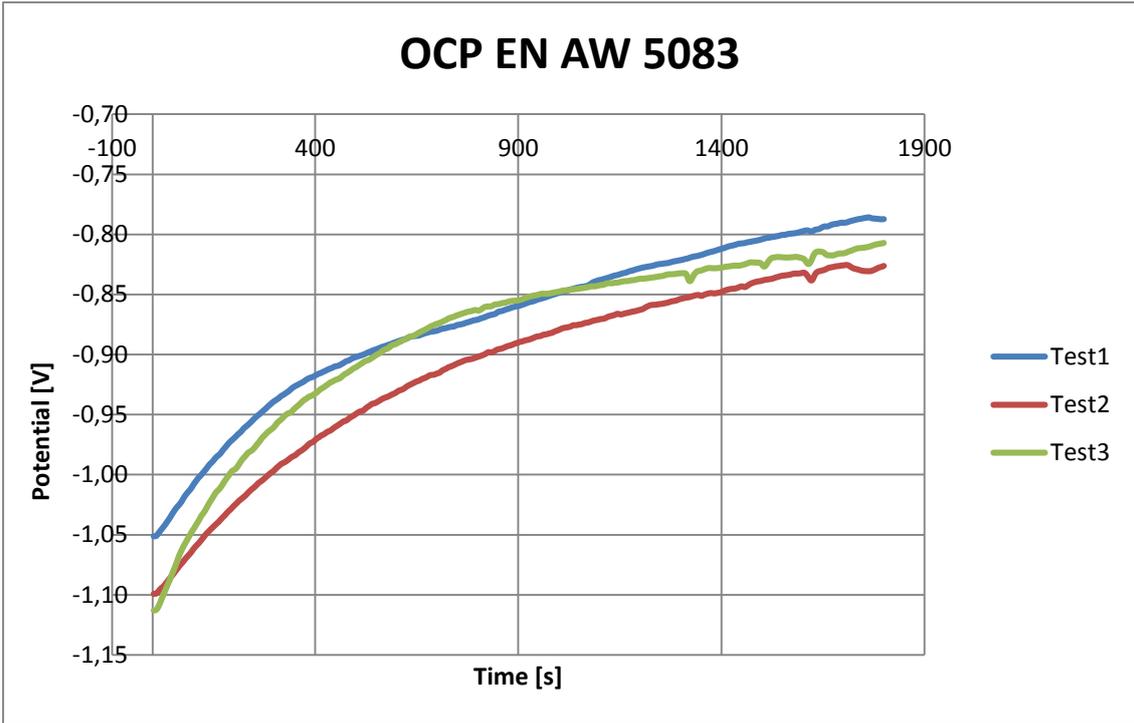
Table 6.1: Results of the three experiments on aluminum EN AW 5083: OCP curves (above) and polarization curves (below). The experiments do not show very good reproducibility in the polarization curve but the passivation and repassivation behavior is clear visible.
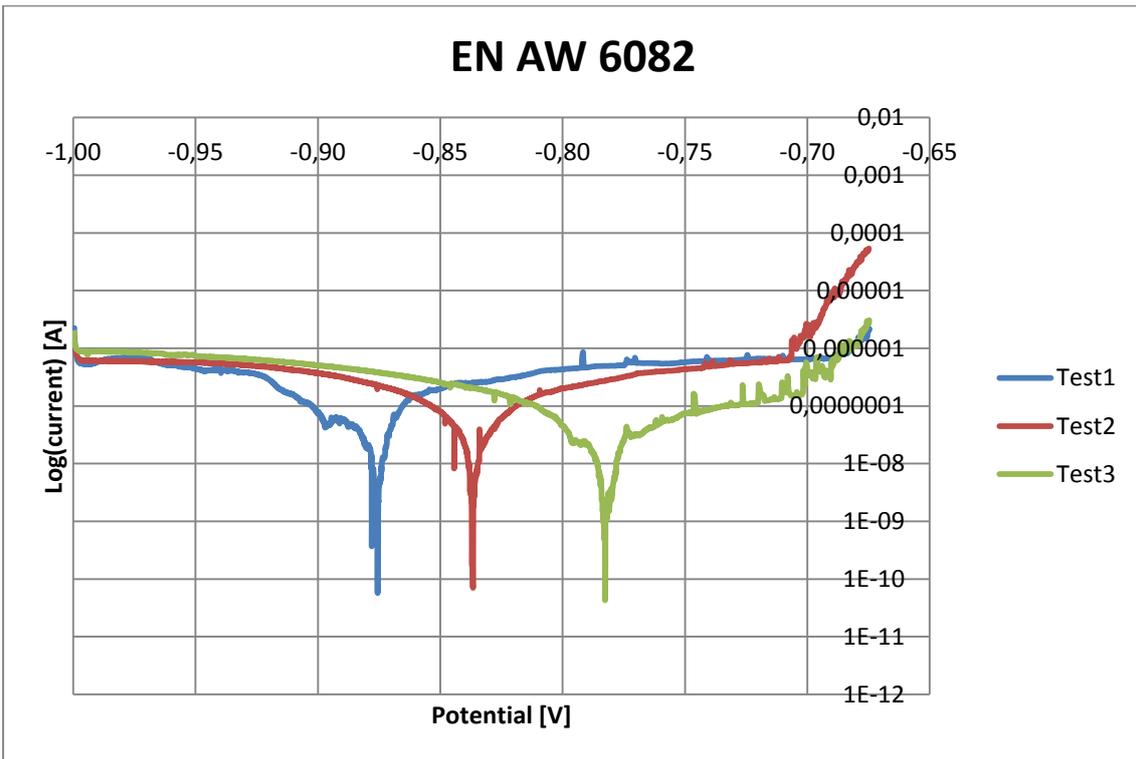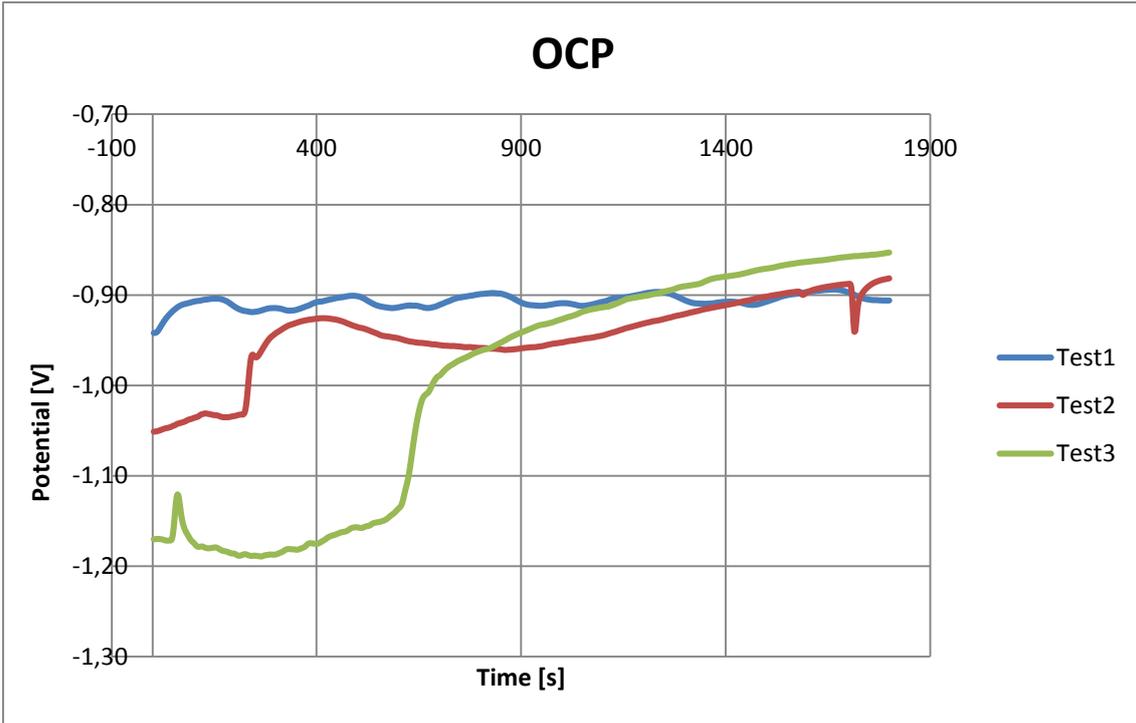
Table 6.2: Results of the three experiments on aluminum EN AW 6082: OCP curves (above) and polarization curves (below). The experiments do not show very good reproducibility in the polarization curve.
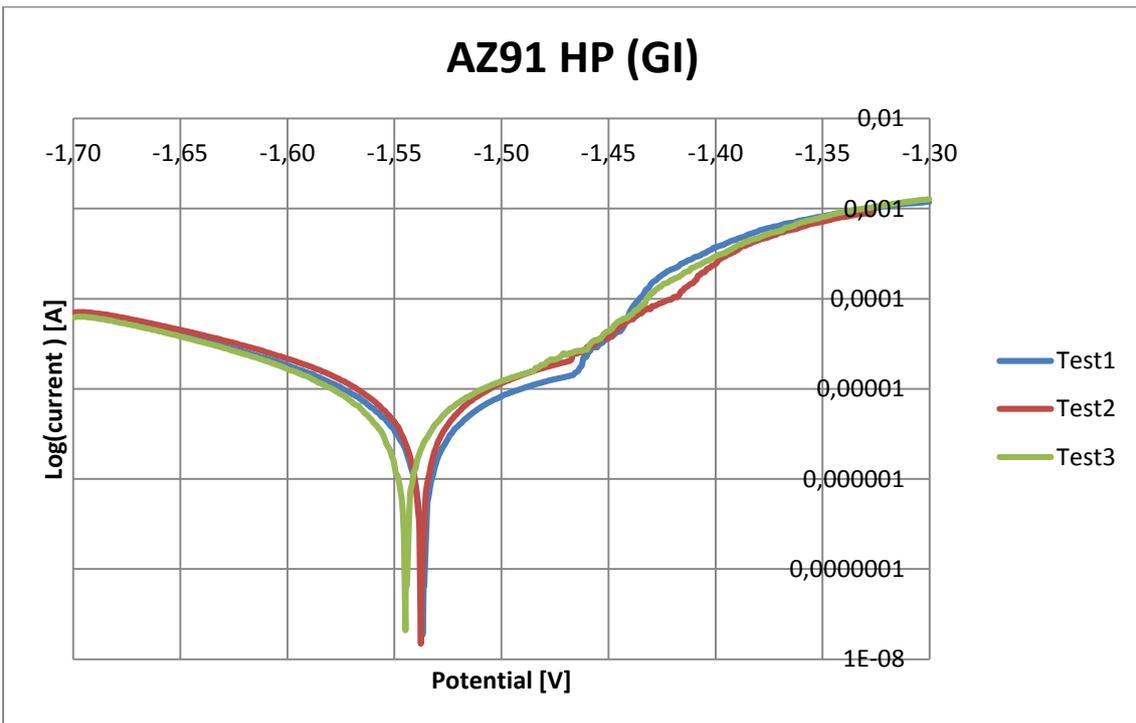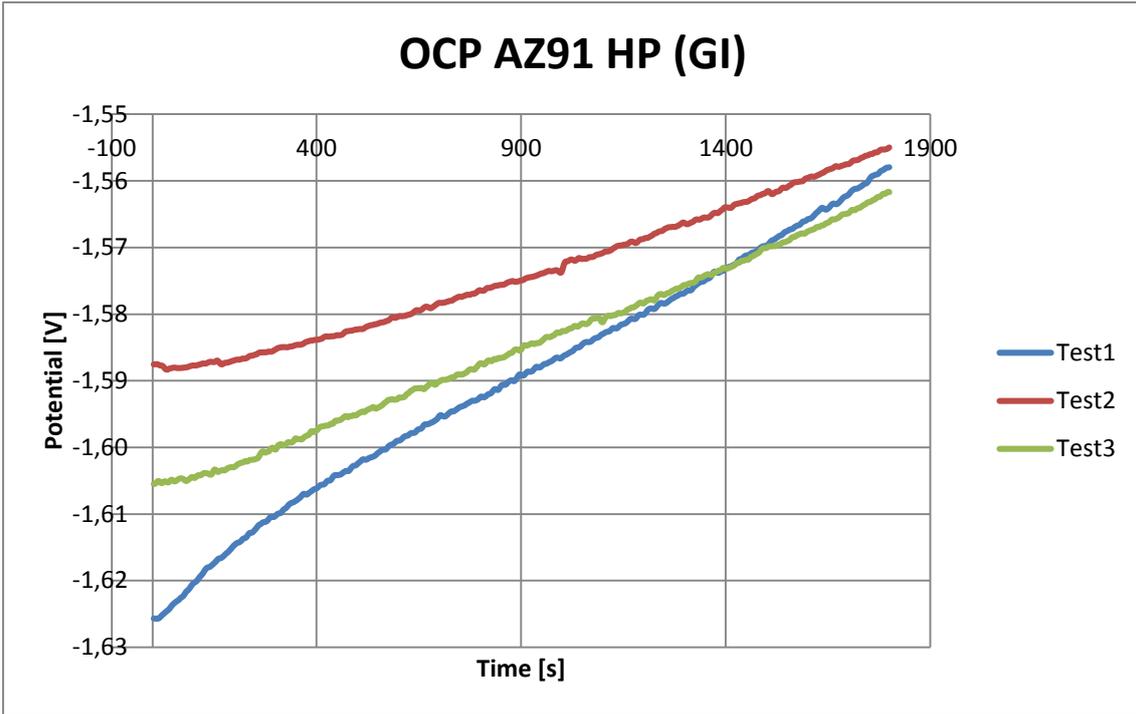
Table 6.3: Results of the three experiments on magnesium AZ91 HP equipped by Gießerei Institut: OCP curves (above) and polarization curves (below). The experiments show very good reproducibility.
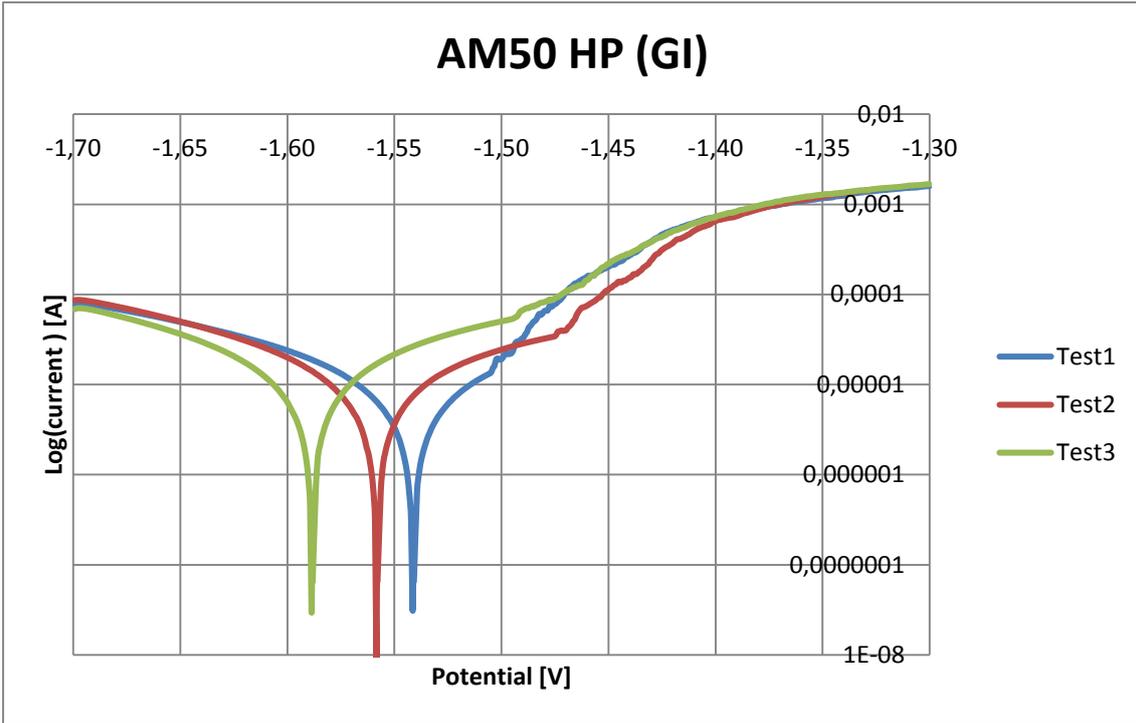
Table 6.4: Results of the three polarization curves on magnesium AM50 HP equipped by Gießerei Institut.
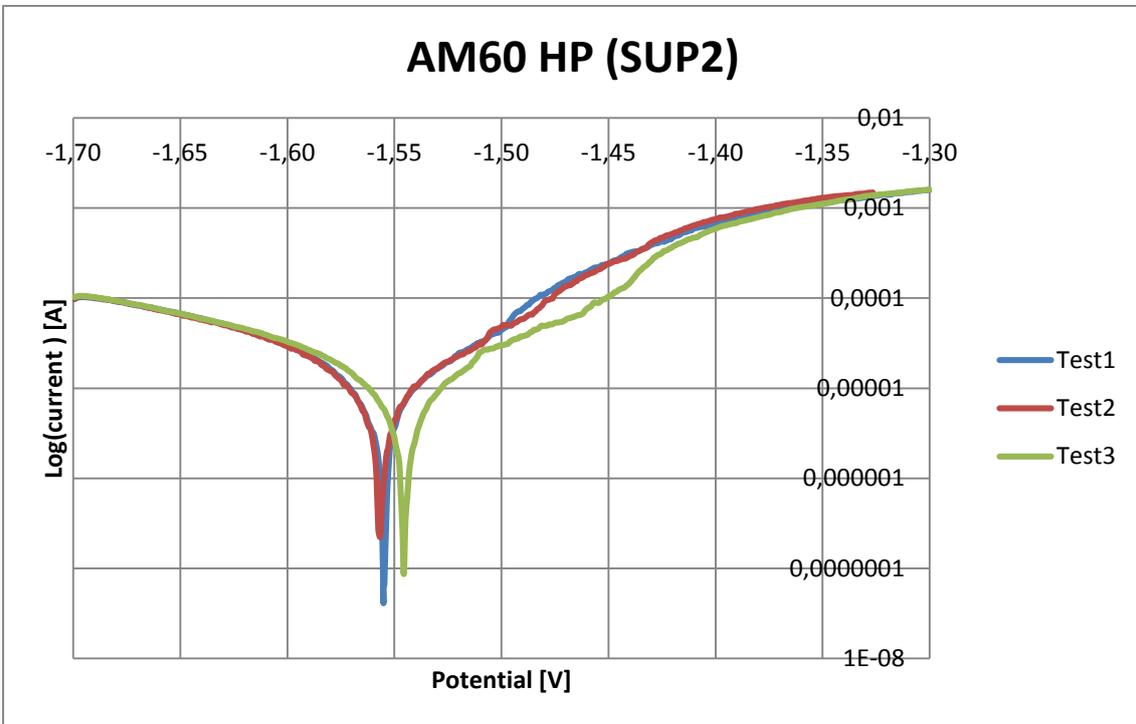
Table 6.5: Results of the three polarization curves on magnesium AM60 HP equipped by the supplier 2. The experiments show very good reproducibility.

6.2. Standard three electrode setup

This test is performed to obtain again the polarization curves but the setup is different from the previous test with the rotating disk electrode.

6.2.1. Aluminum alloys

The conditions of the setup in this test are the same of the rotating disk electrode. The initial delay time for the OPC is 1800 s, the start and the finish potential chosen are respectively -1 V and 0 V and the scan rate is 0.1 mV/s. The pH of the solution is around neutral condition at the beginning of the test and only some decimal points higher at the end of the tests. The surface of both aluminum alloys does not show evidently visible sign of corrosion after the conclusion of the test.

EN AW 5083 (AlMg4,5Mn0,7)

Table 6.6 shows the results of the tests for aluminum 5083. The reproducibility of the experiment is very good and the corrosion potential is at -0,87 V. The material does not seem to have a significant pitting corrosion, there is some scattering at the end of the anodic curve, starting at -0,72 V. The OCP starts in the rage of -0,60 / -0,80 V and increase not always regularly.

EN AW 6082 (AlSi1MgMn)

Table 6.7 shows the results for the aluminum 6082. The corrosion potential is around -0,69 V but there are visible scattering nearby, mostly in the cathodic part of the curves, therefore the corrosion potential is not perfectly definable for each polarization curves. The current shows a rapid increase in the anodic part of the curve, starting suddenly after the corrosion potential.

6.2.2. Magnesium alloys

The scan rate used in the potentiodynamic tests for magnesium is 0,8 mV/s, the initial delay time for the OPC is set at 1800 s and the start and the finish potential are respectively -1,7 V and -1,1 V. The pH of the solution before the tests is around neutral condition, i.e. 7 pH +/- 1 but at the end it increases until 8 / 9.5 pH due to the alkalization effect. The increase in pH value of the solution could influence the electrochemical behavior of cathodes and hence the galvanic corrosion.

The samples show also the formation of bubbles on the material surface during the tests for the reaction of the magnesium with oxygen in the water that releases hydrogen:

$$Mg + 2H_2O = Mg^{2+} + 2OH^- + H_2 \qquad\qquad 6.1$$
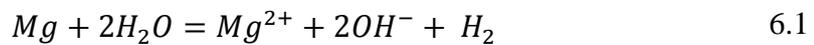
The surface of the material in each sample presents evidently signs of pitting corrosion at the end of the tests, such as for the RDE tests, and the curves present also a variation in the trend of the anodic part when the pitting corrosion starts.

AZ91 (MgAl9Zn1)

The material is made with high pressure die casting and it is AZ91 D, different from AZ91 tested with RDE because it presents too much porosity to be tested with the standard setup. In AZ91 D, the percentage of the impurity element are fewer than the other (e.g. AZ91 A, AZ91 B, AZ91 C): 0,10% max of Si, 0,005% max of Fe, 0,030% of Cu and 0,002% max of Ni.

The OCP starts at around -1,54 V and increases regularly until a point where scattering starts. The corrosion potential is at -1,43 V and the pitting corrosion begins at -1,41 V, like shows in Table 6.8 in the test number 1. Test number 2 presents a different corrosion potential, the cathodic curve suddenly change at -1,46 V with a vertical decrease but the anodic curve shows the same trend of the anodic part of test 1. This could depend on the little sign of porosity presents on the surface of the sample number 2.

AM50 (MgAl5Mn)

The AM50 alloy tested is furnished by SUP 1. In Table 6.9 there are reported the polarization curves: the corrosion potential is between -1,48 and -1,51 V and the pitting corrosion start around -1,40 V with a rapid increase of the current. The curves are clearly defined without sign of scattering.

AM60 (MgAl6Mn)

The magnesium AM60 is furnished by SUP 2. As shows in Table 6.10, the corrosion potential varies between -1,40 and -1,48 V in the two tests and the pitting potential is around -1,38 V. The tests do not show very good reproducibility of the results, exactly as the results obtain in the RDE tests.
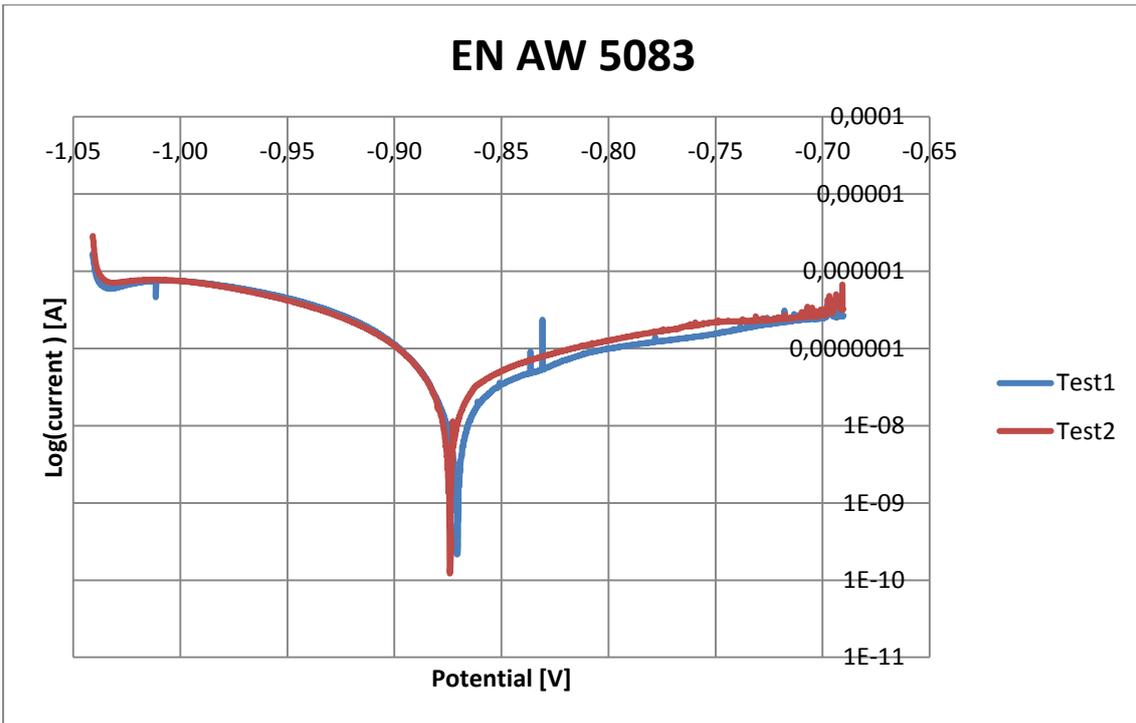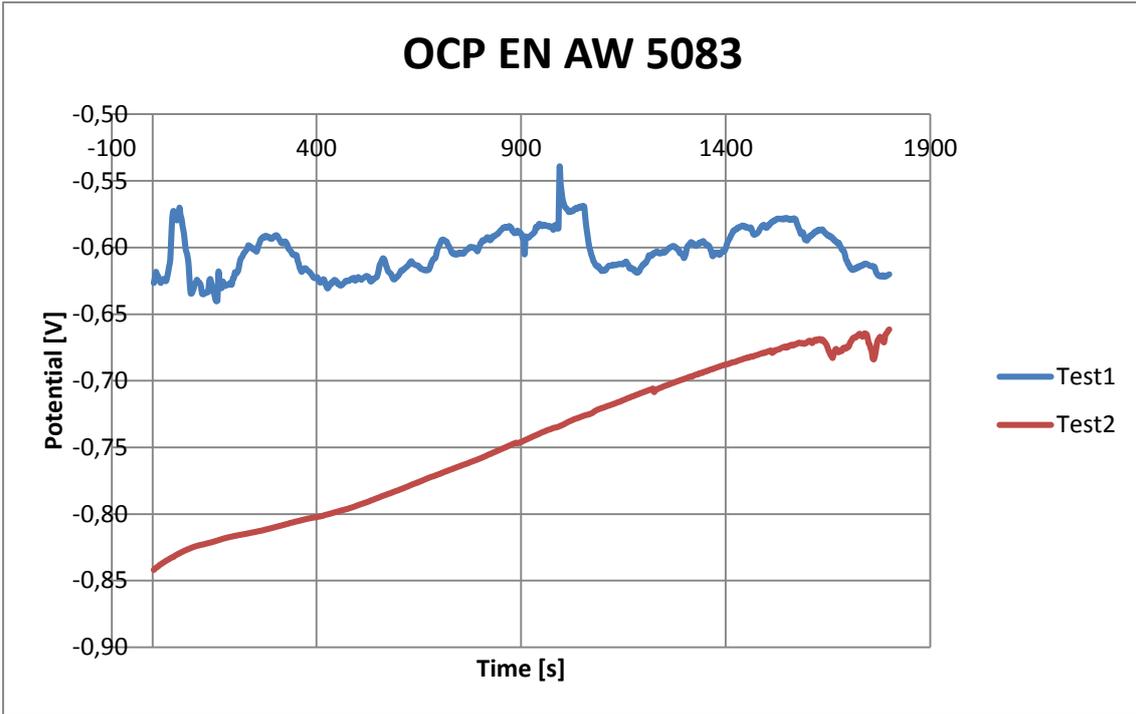
Table 6.6: Results of the two experiments on aluminum EN AW 5083: OCP curves (above) and polarization curves (below). The experiments show very good reproducibility in the polarization curves.
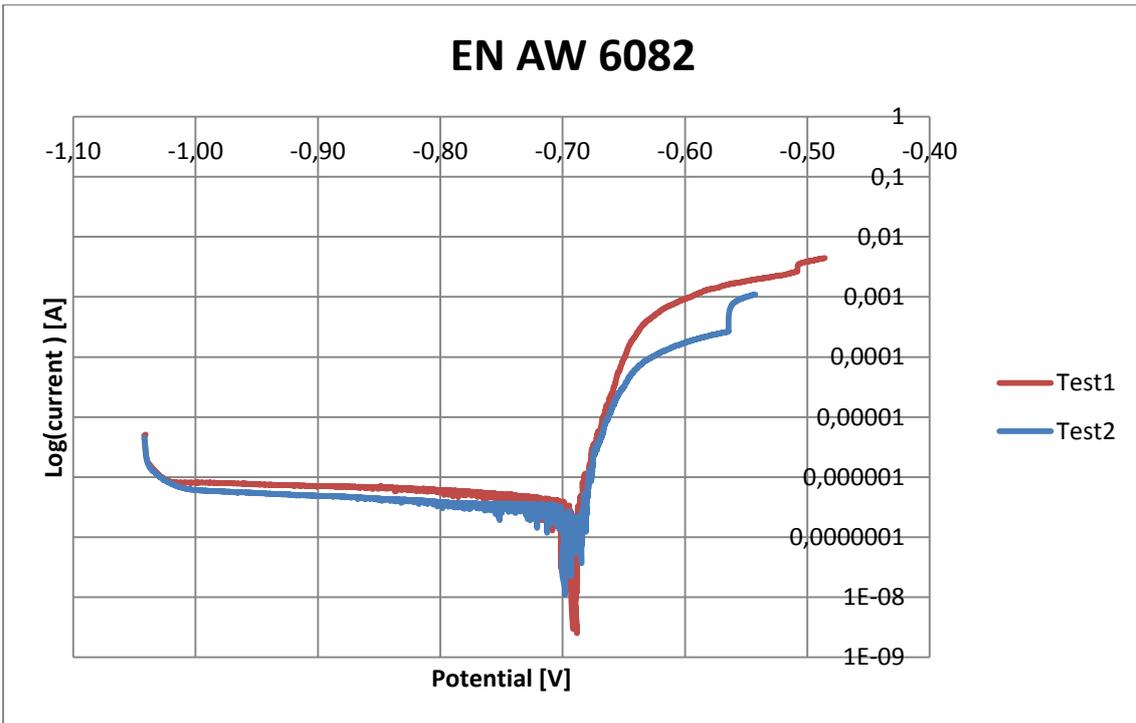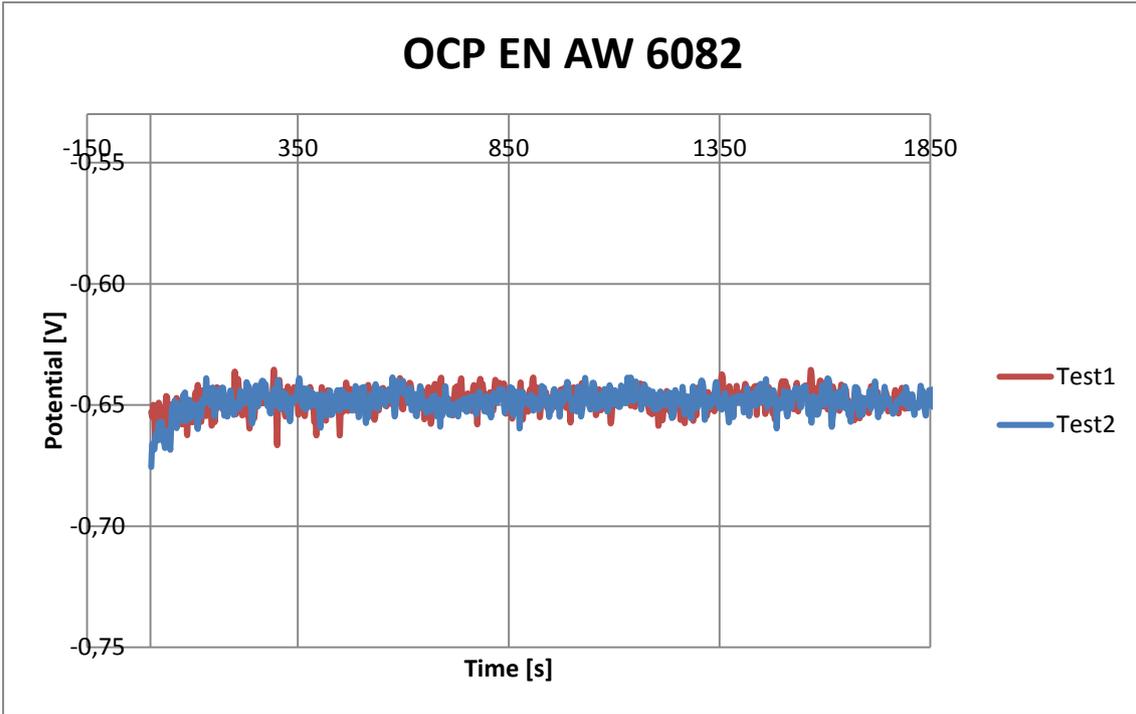
Table 6.7: Results of the two experiments on aluminum EN AW 6082: OCP curves (above) and polarization curves (below). The experiments show very good reproducibility in the polarization curves.
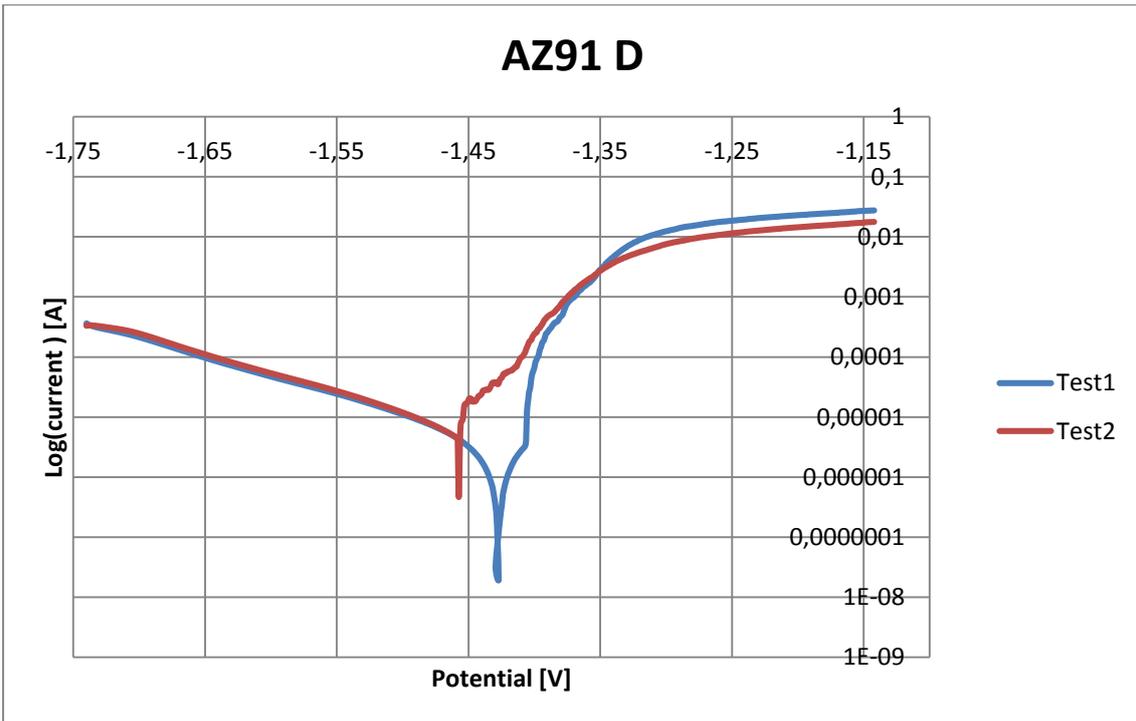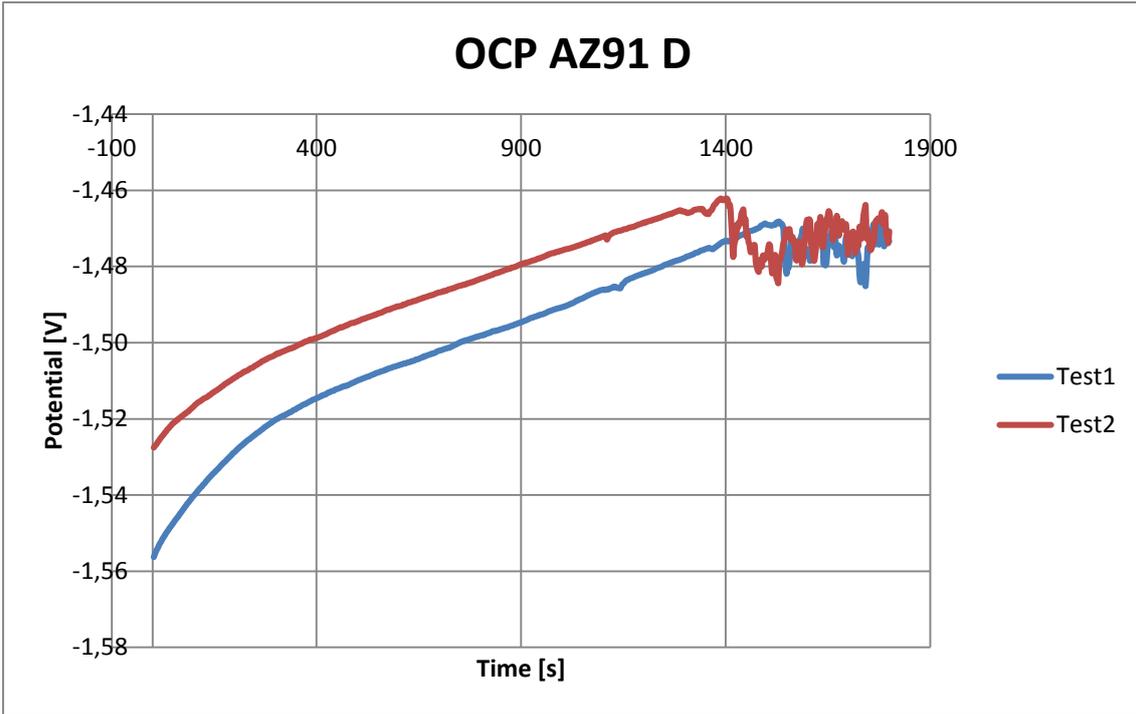
Table 6.8: Results of the two experiments on magnesium AZ91 D: OCP curves (above) and polarization curves (below). The sample for the test number 2 presents porosity on the surface.
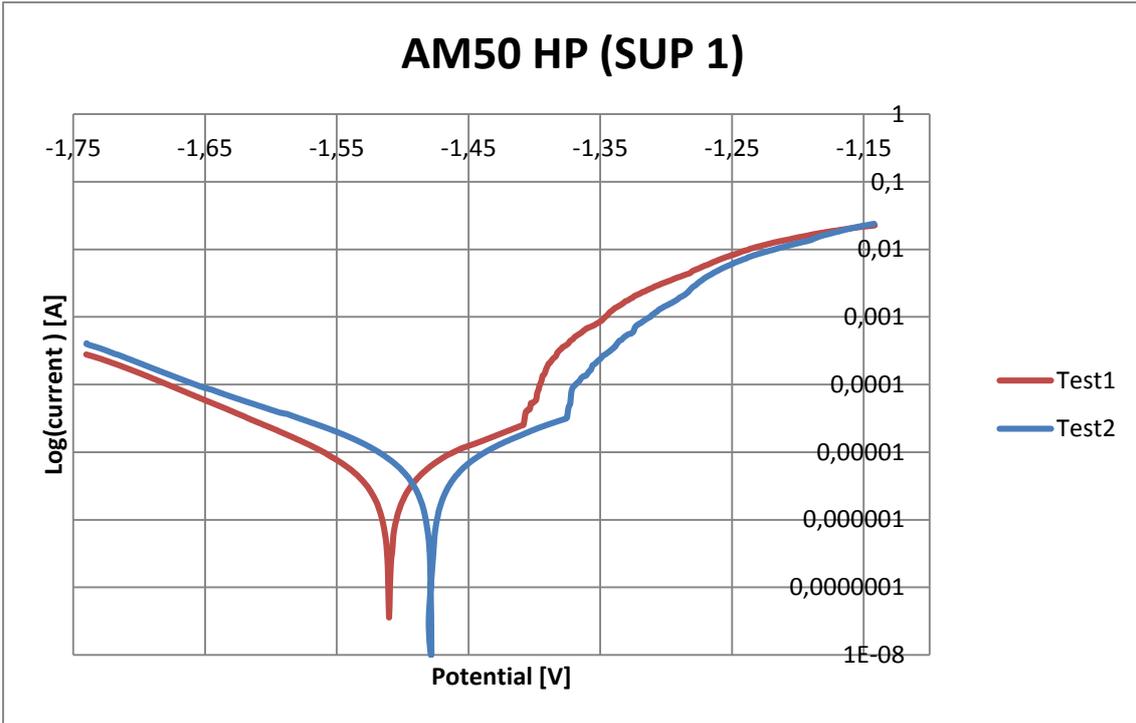
Table 6.9: Results of the two polarization curve on magnesium AM50, supplied by SUP 1.
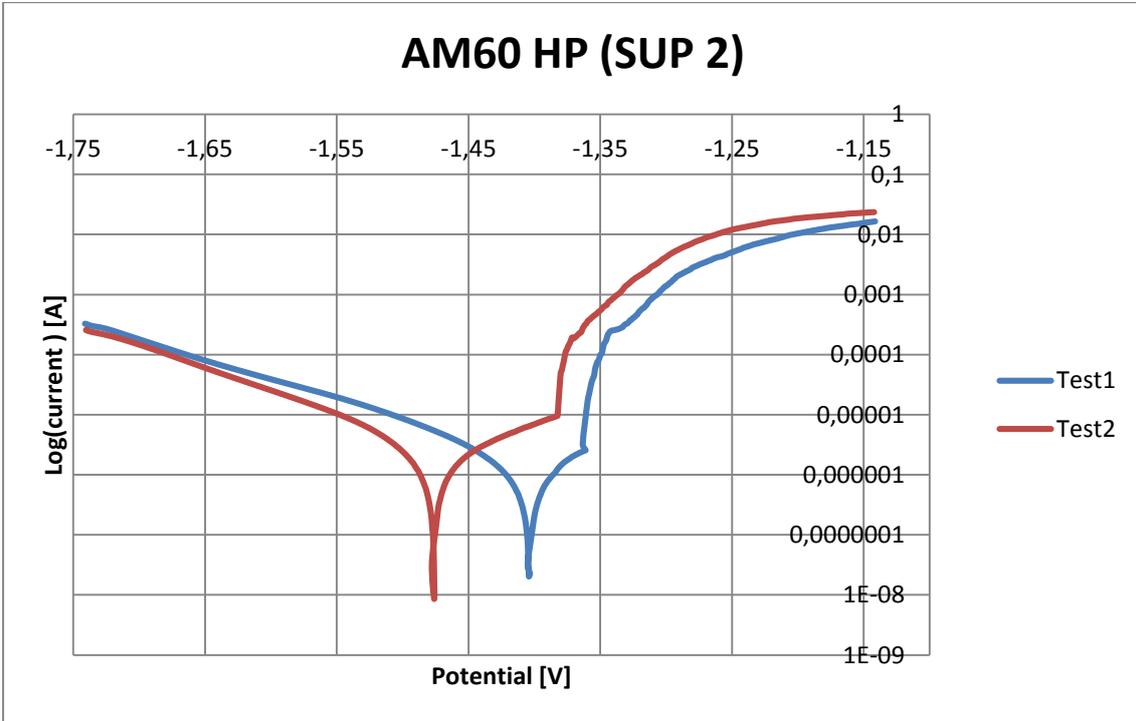
Table 6.10: Results of the two polarization curve on magnesium AM60, supplied by SUP 2.

6.3. Galvanic cell setup

Galvanic couples are investigated in this test. The values of the potential measured with the voltmeter, as explained in the experimental setup, are reported for each couple.

EN AW 5083 + AZ91 D HP:

$U_{R,c}$ = -0,65 V , U_c = -1,43 , $U_{R,a}$ = -1,51 V , U_a = -1,41 V , U = 0,1 mV.

EN AW 6082 + AM50 HP:

$U_{R,c}$ = -0,65 V , U_c = -1,50 , $U_{R,a}$ = -1,55 V , U_a = -1,47 V , U = 0,0 mV.

EN AW 5083 + AM50 HP:

$U_{R,c}$ = -0,69 V , U_c = -1,48 , $U_{R,a}$ = -1,55 V , U_a = -1,47 V , U = 0,1 mV.

EN AW 6082 + AZ91 HP:

$U_{R,c}$ = -0,65 V , U_c = -1,46 , $U_{R,a}$ = -1,56 V , U_a = -1,46 V , U = 0,0 mV.

As it is clear from the results, the potentials U measured in the couples with aluminum 6082 are too small to allow calculating the galvanic current, also in the case of aluminum 5083, the values are not accurate; that is the reason why a potentiostat is necessary to measure the current. However, it is immediately visible that for the couples of interested, aluminum 5083 + magnesium AZ91 and aluminum 6082 + magnesium AM50, the galvanic current will result lower, in the absolute value, for the second couples even if, from the electrochemical techniques and the corrosion potential, it is known that the couple aluminum 6082 + magnesium AM50 will corrode more than the other one.

Consequently, for each couple, the galvanic current is measure with the potentiostat for 90 second and the results are the following:

EN AW 5083 + AZ91 D HP: I_e = 310 μA.

EN AW 6082 + AM50 HP: I_e = 150 μA.

EN AW 5083 + AM50 HP: I_e = 700 μA.

EN AW 6082 + AZ91 HP: I_e = 105 μA.

According to the prediction, the galvanic current for the couple aluminum 6082 + AM50 is lower than the one for aluminum 5083 + AZ91 but it is measure only for 90 seconds. Therefore to better understand what happens during the time, the galvanic current for the two couples of interest is measured for 8 hours with the potentiostat (to compare also with the hydrogen evolution).

Table 6.11 reports the trend of the galvanic current for the couple EN AW 6082 + AM50 HP during 8 hours. The galvanic current starts around 110 μA and increases rapidly in the absolute value for 2 hours, and then it reaches slowly asymptotically ca. 800 μA. The Table reports the current with the negative values so it decreases during the time. The surface of magnesium present parts with pitting corrosion and parts than do not seem visible corroded while the entire surface of aluminum is corroded but not deep. During the test, both metals present the formation of bubbles on the surface due to corrosion.

Table 6.12 reports the trend for the couple EN AW 5083 + AZ91 HP. The galvanic current starts around 150 μA and increase very rapidly in the absolute value for 600 minutes until 640 μA but then it decrease, returning at the end of the tests around the same value of beginning. During the test, both metals present again the formation of bubbles on the surface but on aluminum 5083 the production is higher. The surface of magnesium presents some pitting corrosion while the entire surface of aluminum is completely corroded but less than aluminum 6082.
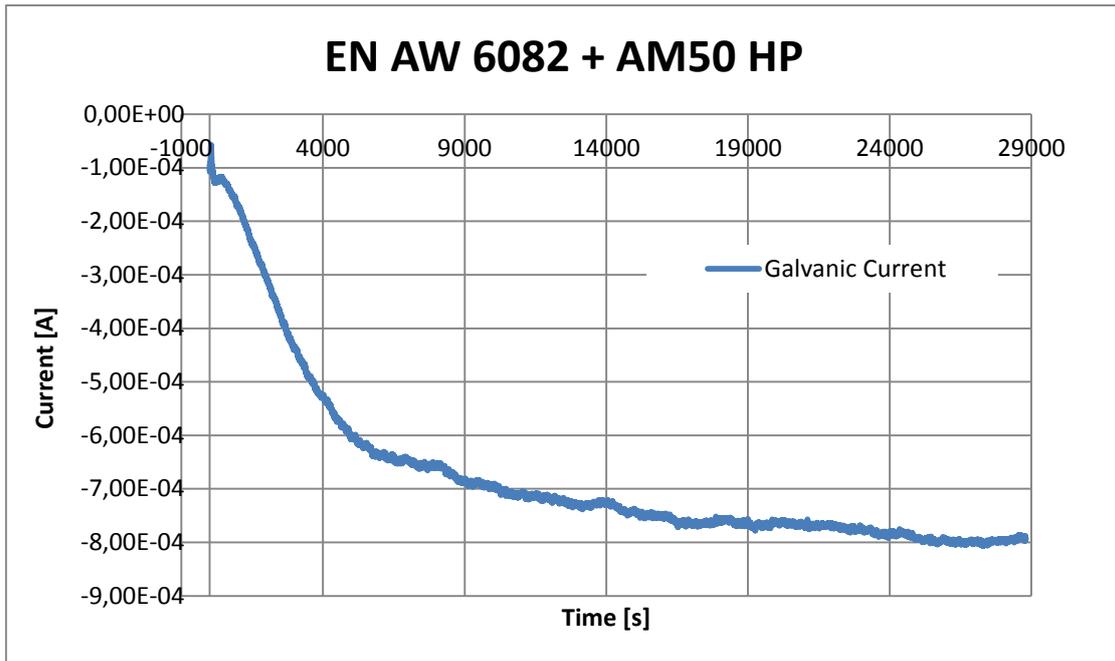
Table 6.11: Trend of galvanic current during 8 hours test for couple EN AW 6082 + AM50 HP.
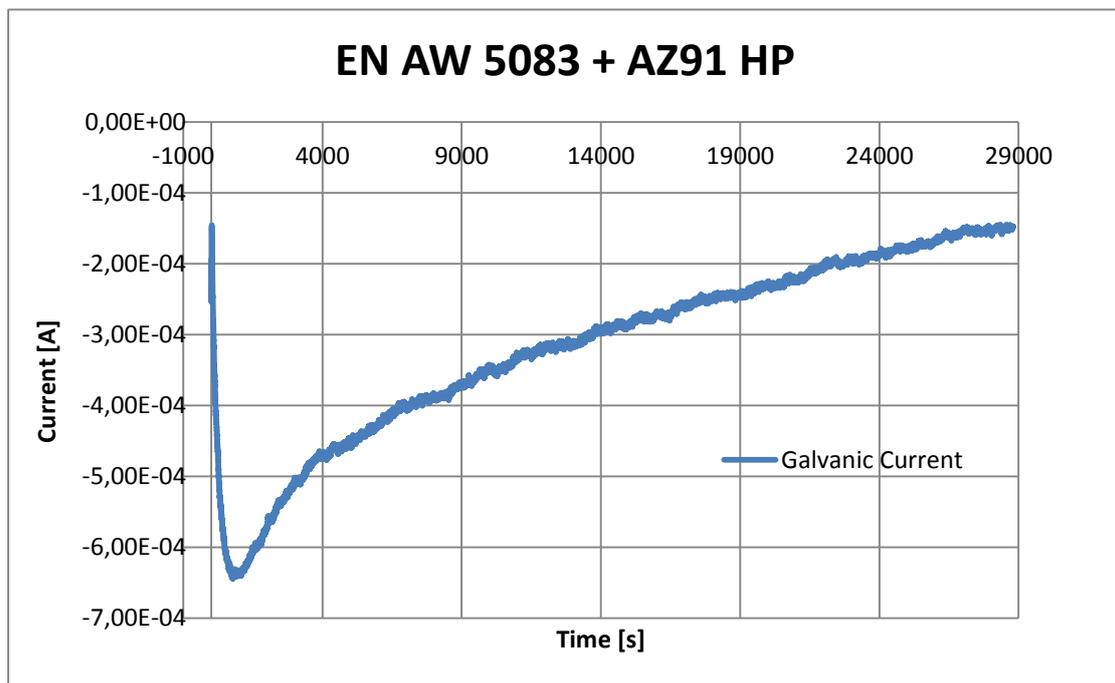
Table 6.12: Trend of galvanic current during 8 hours test for couple EN AW 5083 + AZ91 HP.

6.4. Immersion test: coupled aluminum and magnesium alloys in contact

The hydrogen evolution for both couples measuring during the immersion test is reported in the charts below in function of the time. In the Table 6.13, the result for the couple EN AW 5083 + AZ91 HP is reported: the hydrogen volume increases linearly for about 180 minutes until 2 ml and then it increase less fast reaching 3 ml at the end of the test. The result for the other couple, EN AW 6082 + AM50 HP is reported in Table 6.14: the hydrogen evolution rate is linear ad reach 7/8 ml of hydrogen at the end of the test.

For the couple EN AW 5083 + AZ91 HP the rate of hydrogen evolution decreases during the time until the end of the tests: it is high at the beginning, higher than the rate for the other couple, but very small after 200 minutes, as displayed in Table 6.15, taking the derivation of the hydrogen evolution reported in Table 6.13. For the couple EN AW 6082 + AM50 HP the rate for hydrogen evolution starts at a value smaller than the previous couple but increases from the beginning for 250 minutes and then decreases lightly until the end of the test (Table 6.16).
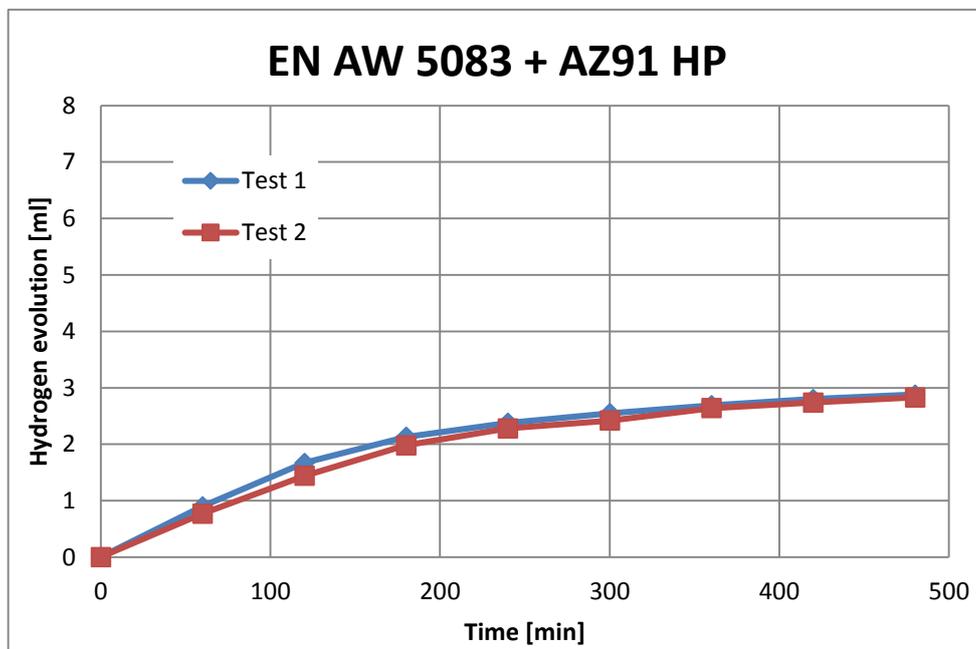
Table 6.13: Hydrogen evolution in the immersion tests of couple aluminum 5083 + magnesium AZ91.
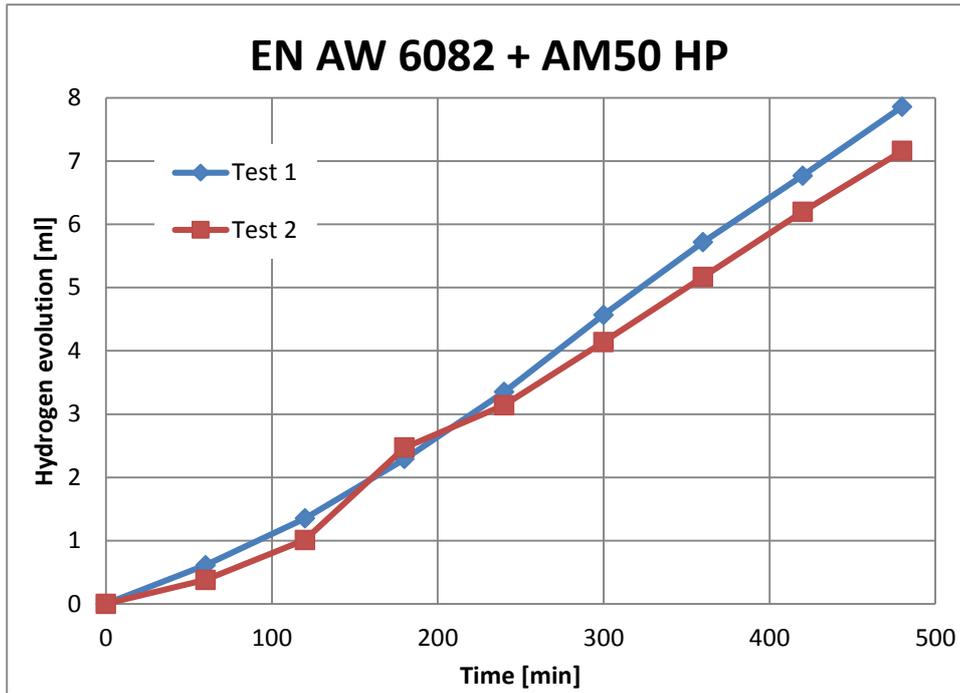
Table 6.14: Hydrogen evolution in the immersion tests of couple aluminum6082 + magnesium AM50 HP.
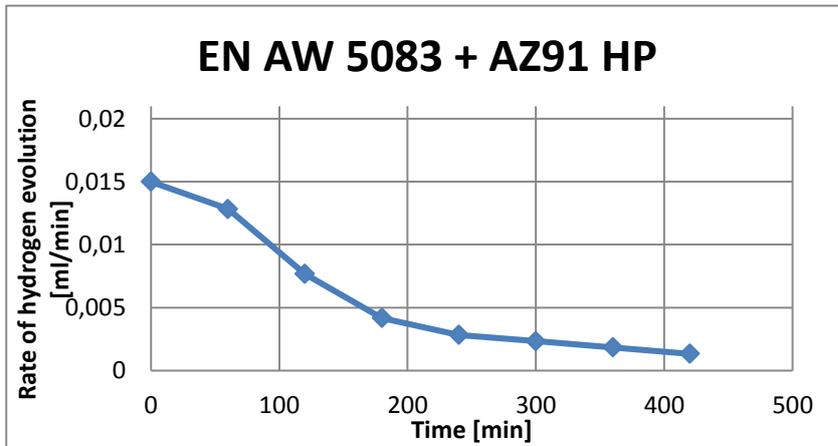
Table 6.15: Rate of hydrogen evolution in the immersion tests of couple aluminum 5083 + magnesium AZ91.
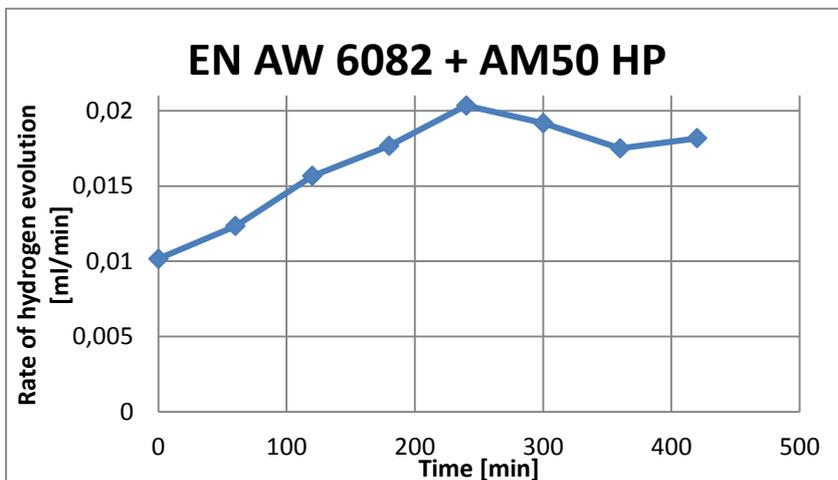
Table 6.16: Rate of hydrogen evolution in the immersion tests of couple aluminum 6082 + magnesium AM50.

The pH for the couple aluminum 5083 with magnesium AZ91 starts around neutral condition and increase until 9,75 / 10 after 300 minutes to decrease again until 9,60 / 9,65 at the end of the test, after 480 minutes. At the beginning of the experiment, the production of hydrogen, i.e. the corrosion rate, is high and visible, but then it decreases fast. The magnesium alloy shows signs of pitting corrosion at the beginning that increases until the end when the major part of the surface is corroded. The corrosion for aluminum is less relevant and starts after the initiation of corrosion for magnesium but it is uniform on the surface.

Figure 6.1 shows the corroded surfaces of aluminum and magnesium after the test: the magnesium alloy presents part of the surface not corroded and other with relevant pitting corrosion while the aluminum alloy is completely corroded. Figure 6.2 shows the border between the two materials: a lot of corrosion products are visible.

The pH for the couple aluminum 6082 with magnesium AM50 starts again around neutral condition but continues to increase until around 10,6 / 10,7 after 480 minutes. The production of hydrogen is continuous and linear, aluminum surface corrodes completely before 200 minutes and also pitting corrosion on aluminum surface starts early.

Figure 6.3 shows the corroded surfaces of aluminum and magnesium after the test: the magnesium alloy presents part of the surface not corroded but a higher percentage of the surface is corroded in comparison to the other couple, while the aluminum alloy is again completely corroded but not deep. Figure 6.4 shows the border between the two materials: a lot of corrosion products are visible also in this couple.
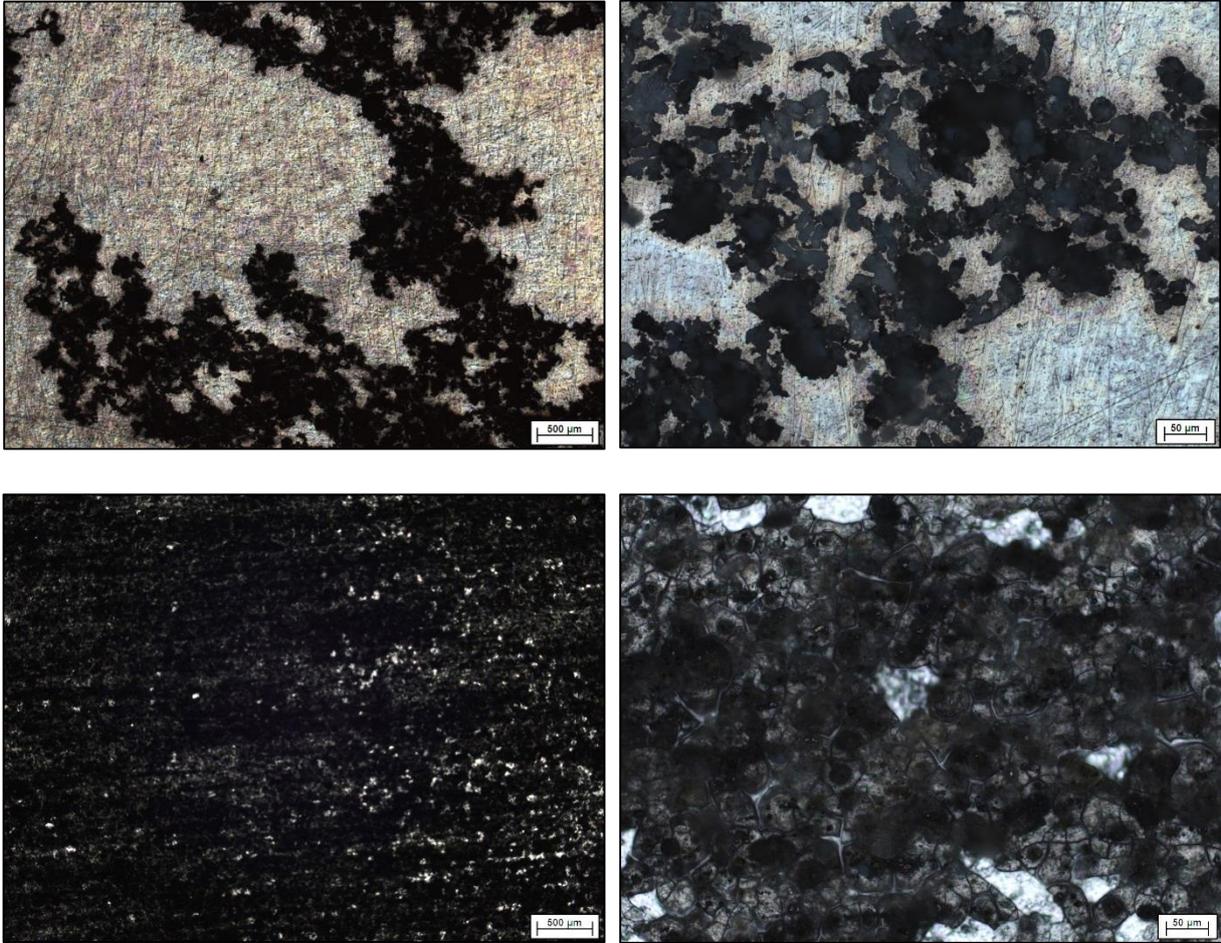
Fig. 6.1: Coupled EN AW 5083 + AZ91 HP after 480 minutes of immersion in 0.1 M NaCl – optical microscope: (up-left) magnesium 25x; (up-right) magnesium 200x; (below-left) aluminum 25x; (below-right) aluminum 200x.
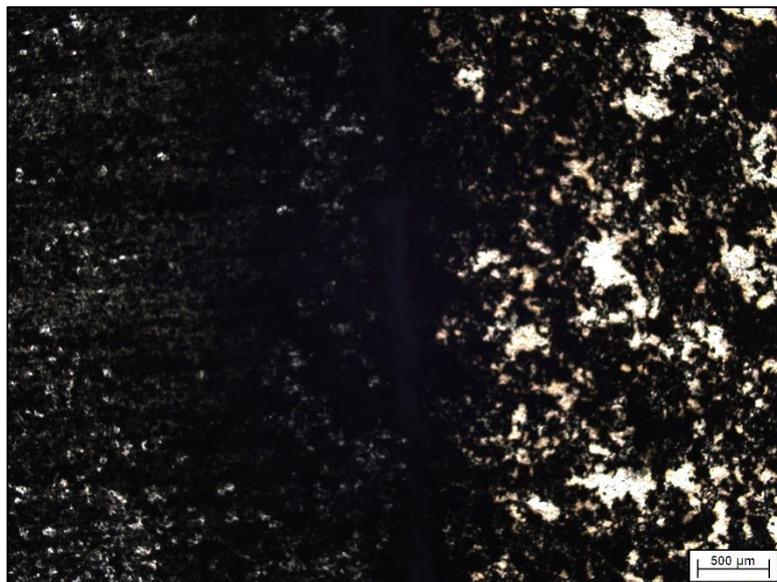
Fig. 6.2: Border between EN AW 5083 and AZ91 HP with a lot of corrosion products – optical microscope 25x.

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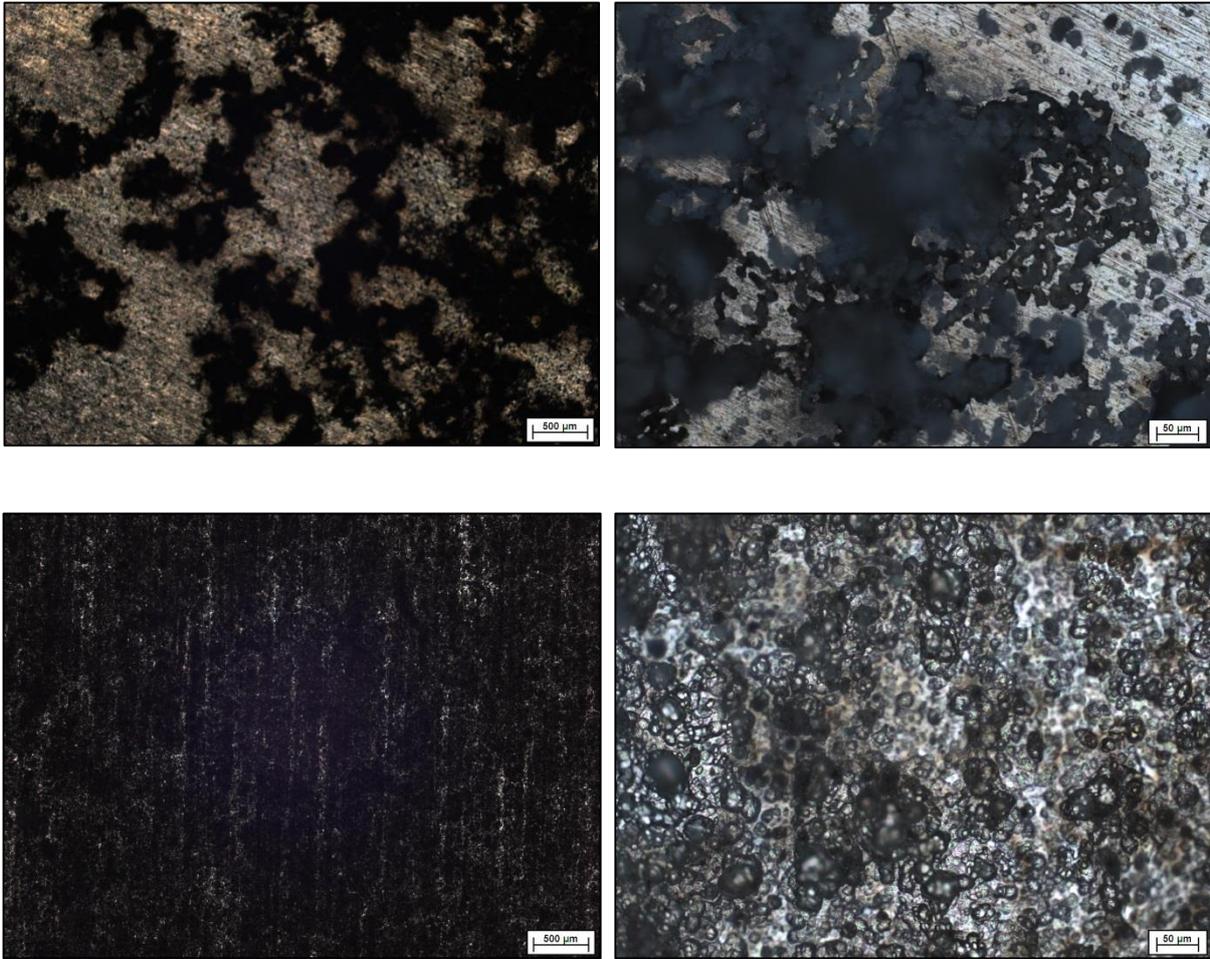
Fig. 6.3: Coupled EN AW 6082 + AM50 HP after 480 minutes of immersion in 0.1 M NaCl – optical microscope: (up-left) magnesium 25x; (up-right) magnesium 200x; (below-left) aluminum 25x; (below-right) aluminum 200x.

Fig. 6.4: Border between AM50 HP and EN AW 6082 with a lot of corrosion products – optical microscope 25x.

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Figure 6.5 shows the samples after the immersion test: the surface of aluminum is completely corroded in both couples but less in aluminum 5083; the surface of magnesium AZ91 is a little bit less corroded than the surface of AM50 but both presents pitting corrosion.
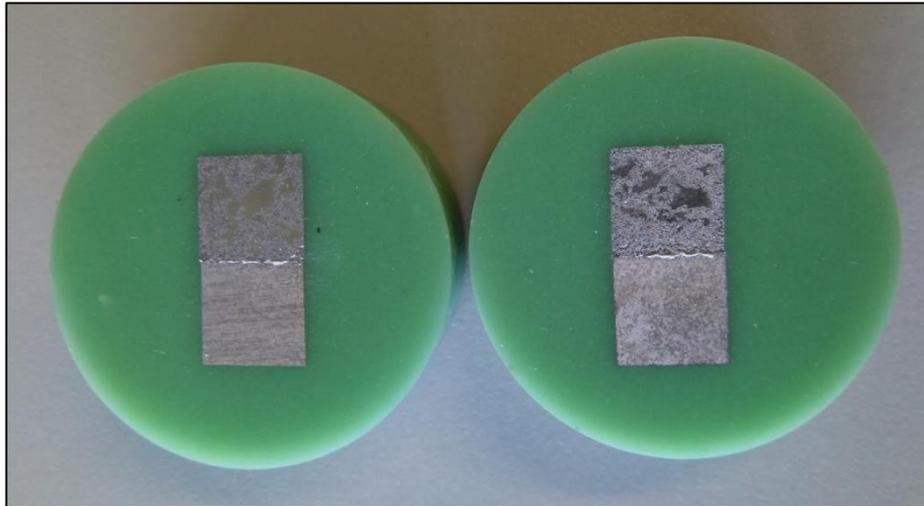
Fig. 6.5: Samples after immersion test: (left) EN AW 5083 + AZ91 and (right) EN AW 6082 + AM50 HP.

As last step, the samples are cut to analyze with the optical microscope the deepness and the appearance of the corrosion on the surface of the materials and on the border between the two. Figure 6.6 show the border after the test of the couple EN AW 5083 + AZ91 HP: magnesium presents a severe metal loss, more near the contact with aluminum, and the deepest of the corrosion on the surface is much higher than the one for aluminum. The figure shows also the aspect of the aluminum and magnesium surface far from the point of contact between the two. The situation visible is the same for the couple EN AW 6082 + AM50 HP: magnesium is severely corroded and aluminum visible less.
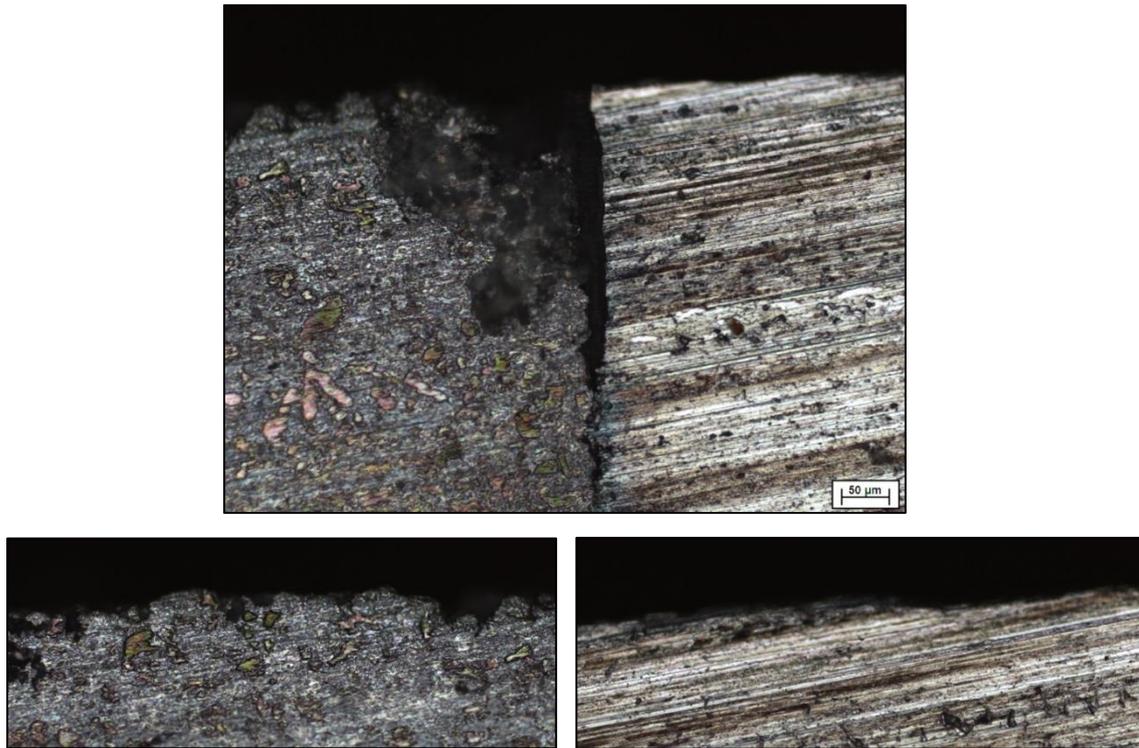
Fig. 6.6: Couple EN AW 5083 + AZ91 HP after 480 minutes of immersion in 0.1 M NaCl – optical microscope 200x: (up) border; (below-left) magnesium; (below-right) aluminum.

6.5. Immersion test: diffusion bounded pure aluminum and magnesium couples

After 10 minutes of immersion, the bounded couples show immediately signs of corrosion (Figure 6.17): in both couples, magnesium shows signs of pitting corrosion uniformly distributed while aluminum presents few signs of filiform corrosion. The intermetallic interface is not affected by visible corrosion. The sample with aluminum + magnesium 6 days presents more corrosion on both elements than the sample with aluminum + magnesium 7 days because the layer in the first one is thinner and the galvanic corrosion is accelerated, in comparison on a thicker intermetallic layer. During the test a high production of bubbles is visible on the surface of magnesium due to the hydrogen evolution on magnesium surface during corrosion.

In Figure 6.18 there are reported the images of aluminum, magnesium and the intermetallic interface for the aluminum + magnesium 6 days, taking with the optical microscope. Magnesium present products of corrosion on the surface, lighter than the

base metal, and also magnesium presents products of corrosion but darker than the base material.

After 20 minutes of immersion, the situation does not change a lot: the corrosion proceeds on both materials in both couples, with a higher rate in the couple with the diffusion process of 6 days, the same as during the first 10 minutes.

After 40 minutes, the magnesium shows important signs of corrosion in both couples and also aluminum presents more filiform corrosion on the surface.
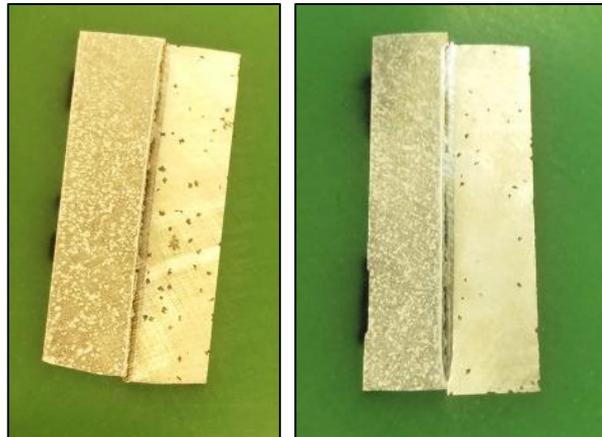
Fig. 6.17: Samples aluminum + magnesium after 10 the immersion tests: (right): 6 days of diffusion, more visible signs of corrosion on aluminum, (left) 7 days of diffusion; in both couples, magnesium is on the left and aluminum on the right.
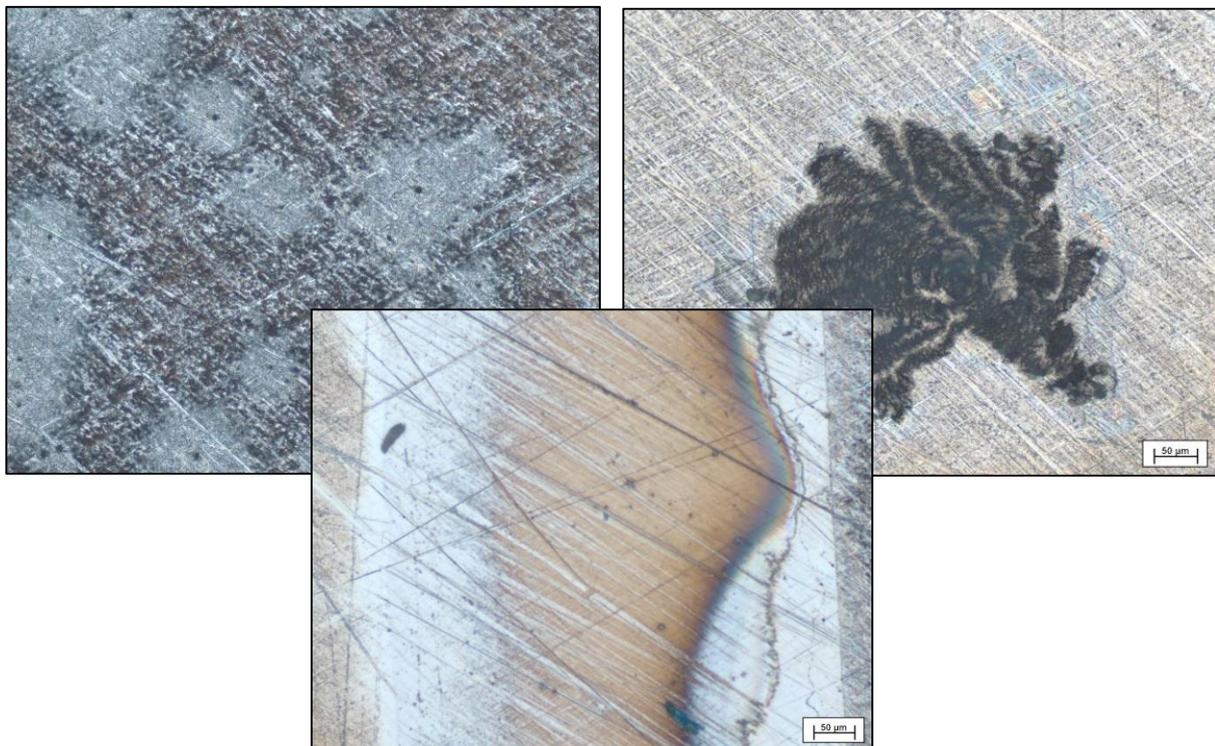
Fig. 6.18: Samples aluminum + magnesium 6 days after 10 minutes of immersion tests: (up, left) magnesium, (up, right) aluminum, (down) intermetallic layer – optical microscope, 200x.

Figure 6.19 reports the situation of the samples surface while in Figure 6.20 there are images taken with the optical microscope of aluminum + magnesium 6 days: magnesium surface is almost all corroded while aluminum presents the same shape of corrosion as before but more extended.
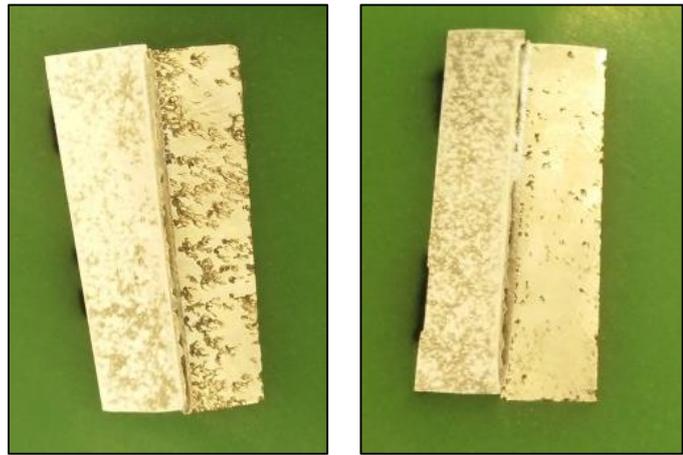
Fig. 6.19: Samples aluminum + magnesium after 40 the immersion tests: (right): 6 days of diffusion, more visible signs of corrosion on aluminum, (left) 7 days of diffusion; in both couples, magnesium is on the left.
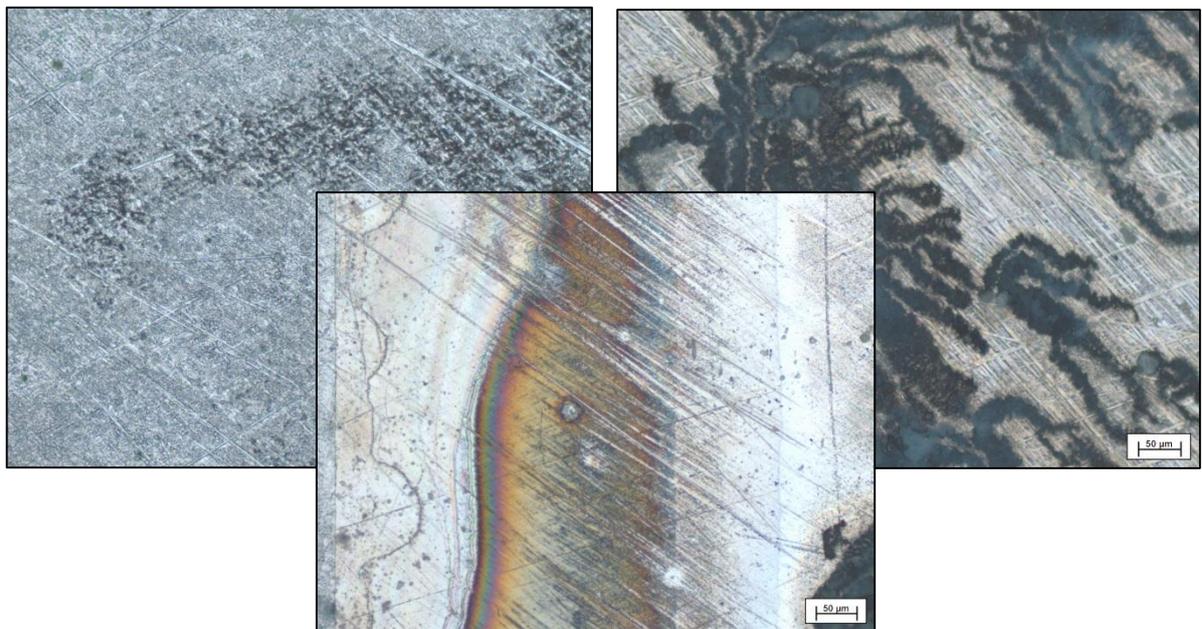
Fig. 6.20: Samples aluminum + magnesium 6 days after 40 minutes of immersion tests: (up, left) magnesium, (up, right) aluminum, (down) intermetallic layer – optical microscope, 200x.

After 100 minutes, as visible on Figure 6.21, in the couple aluminum + magnesium 6 days, aluminum presents great parts with corrosion, while in the other couple the surface is also corroded but visible less. For both couple the surface of magnesium is almost completely corroded and covered by the corrosion product as visible also in

Figure 6.22 taken by the optical microscope. The layer between the two elements is not corroded also after 100 minutes of immersion.

Fig. 6.21: Samples aluminum + magnesium after 100 the immersion tests: (right): 6 days of diffusion, more visible signs of corrosion on aluminum, (left) 7 days of diffusion; in both couples, magnesium is on the left.
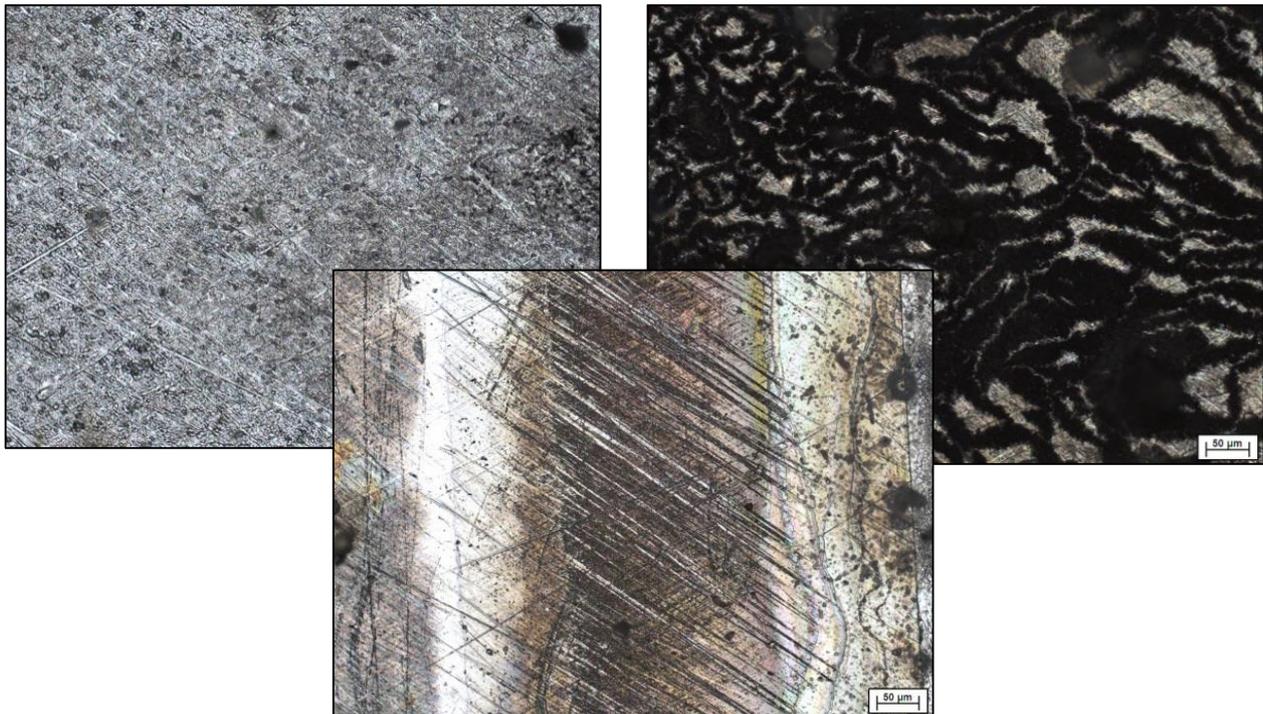
Fig. 6.22: Samples aluminum + magnesium 6 days after 100 min the immersion tests: (up, left) magnesium, (up, right) aluminum, (down) intermetallic layer – optical microscope, 200x.

CHAPTER 7

Discussion of results

7.1. Rotating disk electrode

The goal of the corrosion tests with the polarization scan is to obtain the polarization curves, which show the corrosion potentials, to compare different aluminum alloys and different magnesium alloys to choose the best combination of the two. The best combination of aluminum and magnesium is that one that presents the less galvanic corrosion and to decrease galvanic corrosion there should not be a big difference in the corrosion potential of the materials.

The RDE setup is useful for the magnesium alloys because the rotation of the electrode and the convention of the electrolyte contrast the high effect of alkalization of the solution near the surface of the samples. This effect of alkalinization is more accentuated in the standard three electrode setup because there is no movement in the solution, so the RDE is indicated to use in the polarization scan for magnesium; indeed the results for magnesium alloys are good with this setup.

For aluminum alloys the results are not very clear, both alloys show scattering in the curves and dispersion in the value of corrosion potential. This could depend on the start potential chosen for the aluminum, i.e. -1 V; probably it is too far from the corrosion potential and the long-time anodic measurement influences the scattering behavior when the corrosion potential is reached. It is better for aluminum to measure the anodic curve and the cathodic curve separately to contrast this situation.

Table 7.1 show the results for the RDE tests: for the magnesium alloys the difference in the corrosion potential is minimal, so it is possible to assert that the choice of the magnesium alloy to use in the galvanic couple is not very sensitive for the results, even if AZ91 presents a little less negative corrosion potential than AM50, due to the higher amount of aluminum that swifts the curve in the part closer to aluminum. Aluminum alloys show some dispersion in the results, but aluminum 6082 presents a more negative

corrosion potential, closer to the magnesium alloys potential curves, in comparison to aluminum 5083. In fact, the difference is not high (in the Table only one curve is reported for each alloy but the other presents some difference in the corrosion potential then, in conclusion, the difference in the corrosion potential of the two aluminum alloys is not very high) but these results for aluminum do not agree with the theoretical assumption that the curves for the potentiondynamic scan for aluminum 5083 should be closer to the ones for magnesium in comparison to aluminum 6082, due to the higher percentage of magnesium in the aluminum alloy 5083. That could be explain by the fact that, in these tests, aluminum presents scattering curves and not well defined corrosion potentials due to the choice of -1 V as start potential of measurement, and also the electrode rotation speed chosen changes the behavior of the alloys. It is necessary to investigate the influence of the rotation speed on the results for the aluminum alloys. Different rotation speeds could place the corrosion potentials in a more or less negative value and switch the position of the curves for aluminum 5083 and 6082 obtained.

For this reason the galvanic corrosion tests are referred as background to the results obtained from the polarization curves with the standard setup described in the next chapter because the RDE setup and the electrode rotation speed need to be more investigated.
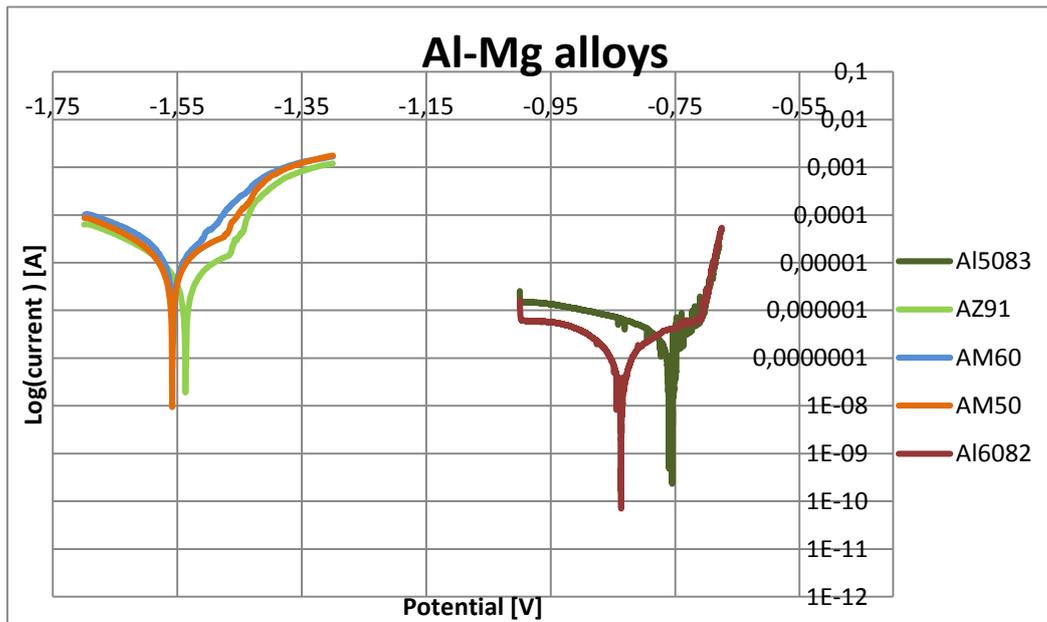
Table 7.1: Comparison between aluminum alloys (EN AW 5083 and EN AW 6082) and magnesium (AM50 HP, AM60 HP and AZ91 D HP).

7.2. Standard three electrode setup

Table 7.2 shows the results of the polarization scan for the standard three electrode setup. Between the two aluminum alloys tested, aluminum 5083 and aluminum 6082, there is a big different in the corrosion potential. Aluminum 6082 presents a corrosion potential of -0,69 V because it has a lower amount of magnesium than aluminum 5083, so its corrosion potential is less negative and further from the corrosion potential of magnesium alloys. Aluminum 5083 present a corrosion potential of -0,87 V and it is closer to the magnesium alloys because it has a higher amount of magnesium. The experimental results agree with the theoretical prediction based on the chemical composition of the alloys. For magnesium alloys, AZ91 presents a less negative corrosion potential (-1,43 V) that AM50 (-1,48 V), due to the higher amount of aluminum that shift the corrosion potential in the direction of the aluminum corrosion potential.

For each aluminum alloy, only one polarization curve is reported but the results of the tests show very good reproducibility; for magnesium alloys also one curve for each one is reported but it is necessary to remind that there are some differences in the results for each alloy.
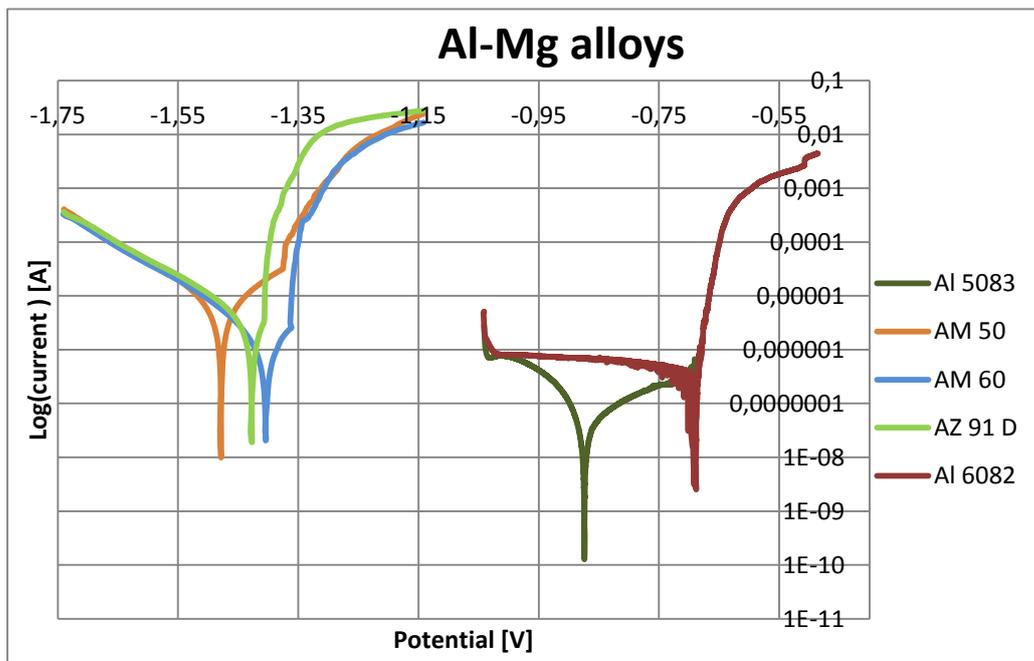
Table 7.2: Comparison between aluminum alloys (EN AW 5083 and EN AW 6082) and magnesium (AM50 HP, AM60 HP and AZ91 D HP).

7.2.1. Comparison of results between RDE and standard setup

It is not possible to real compare the results obtained from the two setups for different reasons. In the RDE, the rotation of the electrode create a convention in the solution, so the results are influenced by this phenomenon: magnesium alloys suffer less the effect of alkalization and aluminum alloys present not clearly defined results due to passivation and repassivation behavior and the choice of the rotation speed.

Moreover, the samples used in these test are different: the composition of the metals tested for each alloy of interest is the same investigated in the two setups but the microstructure is different. For the RDE test, the samples are smaller than the ones for the standard setup so they are taken from smaller parts of casting compounds. The different microstructures presented for the different thickness of the parts in the casting should also be investigated to better understand the difference in the results in the polarization curves.

7.3. Galvanic cell setup

With this setup where the two electrodes are coupled in a galvanic cell, potentials in different situation can be measured and investigated: the open circuit potential of anode and cathode, the potential of each electrode when it is coupled with the other one or also the corrosion potential between the two. As explained before, with the voltmeter it is impossible to measure the corrosion potential to calculate the galvanic current, so a potentiostat is necessary.

Analyzing the results obtained with the potentiostat, it is possible to assert that the galvanic current created between the two should be measured for a long time to understand the trend during corrosion; otherwise, measuring the current after some seconds after the beginning of the test or after minutes could change a lot the values due to the fact that the corrosion proceed at different rate for different couples, especially at the beginning, and then this could bring to wrong conclusion.

Indeed, at the beginning of the test, the couple aluminum 5083 + magnesium AZ91 seems to corrodes more in the 0.1M NaCl aqueous solution than the other one because the galvanic current is higher and increase faster but then the results agree with the results from the polarization scan and, after some hours of testing, this couple shows the best resistance behavior against corrosion. Therefore all the tests should set up considering a sufficient time of testing to get correct results.

7.4. Immersion test: coupled aluminum and magnesium alloys in contact

It is demonstrated again that the couple with aluminum 5083 and magnesium AZ91 presents better corrosion resistance in 0.1M NaCl aqueous solution in comparison with aluminum 6082 with AM50. The hydrogen evolution is higher at beginning in the couple EN AW 5083 + AZ91 HP but then it decreases as clearly visible analyzing the rate of hydrogen evolution. At the end of the test, the hydrogen measured is higher for EN AW 6082 + AM50 HP, it means that the corrosion rate for this couple is also higher than the one for the other couple. Also for this test, as for the previous one, the time of testing should be sufficient to show the behavior of the couples; short time of testing gives incorrect results.

The results of the hydrogen evolution are comparable with the research cited in chapter 2.8. The trends obtain for the two couples used in this set up and the trends obtained testing the Connection-Demonstrator I and II are the same [12]: for the couple EN AW 5083 + AZ91 HP, the hydrogen evolution is characterized by two regions, the first one, linear for the first 180/200 min, and the second one, linear again but with an hydrogen production less accentuated; while for the couple EN AW 6082 + AM50 HP, the hydrogen evolution is linear from the beginning until the end but sensitive higher.

The rate of corrosion is also visible with the optical microscope but even simply watching the surface of the metals in the samples. The aluminum alloys present the same time of corrosion but aluminum 5083 corrodes less than aluminum 6082, obviously because aluminum 5083 presents a higher percentage of magnesium, thus the gap in the potential between it and the corresponding magnesium alloy used in the couple is smaller. Both magnesium alloys present pitting corrosion and AZ91 results a little less corroded than AM50. At the interface between the two materials, the corrosion products are present in a high amount, while on the surface of the samples they are quite uniformly distributed.

7.5. Immersion test: diffusion bonded pure aluminum and magnesium couples

This test is useful to investigate how corrosion proceeds on the pure metals and if the intermetallic layer is useful to prevent galvanic corrosion. The intermetallic interface between pure aluminum and pure magnesium has been already studied to investigate the chemical composition [10] but understanding the corrosion behavior of it is also interesting. The diffusion bonding used in this test is a way to replicate the behavior of the two metals when they are connecting using a casting process because the formation of different layers with different composition during the casting implies that diffusion is the dominant mechanism in the compound casting. Indeed, in both cases, using the diffusion bonding or casting the metal, the intermetallic interface presents the tree layers reported in the literature.

The hydrogen production on the surface of the magnesium starts immediately after the contact with the solution and first signs of corrosion appear after few minutes on both material. Magnesium shows signs of pitting corrosion at the beginning and they increase until the end when almost the surface is corroded. Aluminum presents filiform corrosion, only some spot at the beginning and larger parts at the end of the test. Also in this case both metals corrode; there is no anodic protection of the anode for aluminum. It is important to underline that the way of corrosion of the pure metals is very different from the one for alloys because alloys presents not only different composition but also different microstructure depending on the alloying elements and on the solidification process. In particularly, aluminum never presents this filiform corrosion in the previous test but it usually corrodes uniformly and, in general, it presents filiform corrosion only under the coatings.

The intermetallic interface does not corrode so it could be used to decouple the two materials or to reduce the galvanic corrosion. The result of the corrosion process is the same in both couples but the couple with 6 days bounded process present evidently more corrosion because the intermetallic layer is thinner and the galvanic corrosion can act more. A longer time of diffusion bonding increase the thickness of the intermetallic layer and decrease the galvanic corrosion in the couple.

In all the three experiments with the galvanic couples, both aluminum and magnesium corrodes in the solution, so there is not anodic protection: magnesium does not act as sacrificial anode to protect aluminum; the corrosion is present on both metals but accelerated.

CHAPTER 8

Outlooks

The couples investigated present always a severe galvanic corrosion so it is necessary to find solutions to protect the hybrid structures made with aluminum and magnesium alloys. One of the most effective ways to prevent corrosion is to coat the base material. Coatings can protect a substrate providing a barrier between the metal and its environment and/or through the presence of corrosion inhibiting chemicals in them.

In order for a coating to provide adequate corrosion protection, the coating must be uniform, well adherent, pore free and self-healing for applications where physical damage to the coating may occur. From a corrosion point of view, a coating is rated in the resistance it provides against corrosion in a specific environment and because there are many variations in corrosively environment, there is also a great variety of corrosion protective coatings.

General coatings can be divided into three classes: conversion coatings, that are produced by chemical or electrochemical reactions between the substrate and the aqueous solutions to form an oxide layer, such coatings represent an effective way to increase corrosion resistance or as pre-treatment to enhance the adhesion of final deposited coating on magnesium and aluminum; organic coatings, including sol-gel, painting and powder coating, that are typically used after a primary surface treatment of the substrate; and inorganic coating, such as chemical vapor deposition, plasma spraying, laser and diamond like coatings. [31][32]

Some tests on the coatings are already been performed on the hybrid structure [12]. The standard profile was tested in according with the VDA 621-415 standard, during 6 cycles with each 1 x 24h salt spray testing (DIN EN ISO 9227), 4 x 24h humidity test with condensation-water atmosphere (DIN EN ISO 6270-2 CH) and 2 x 24 h drying in the temperature range from T = 18 °C to T = 28 °C (DIN 50014). Cathodic dip coatings (CDP) and wax sealing were applied and tested and, as result, both coatings indicated no visually perceptible corrosion damage.

Future activities will focus on a development of an inner protective layer to uncouple the aluminum and magnesium in the hybrid structure. This insert coating should be applied to the aluminum alloys sheets before being inserted in casting magnesium alloys. The main challenge is that the inner coating has to survive to the condition of high pressure die casting, the fastest, most economical and high productivity method to create the hybrid structures.

The resistance of the coatings at the method of casting should be tested following different step: first of all, sand casting should be used to cast magnesium around the coated aluminum insert; if the coating will survive at this conditions, it must be tested with die casting and at the end with high pressure die casting. An important element to take under consideration is the thickness of the walls in the magnesium casting because the coating could survive until a certain thickness but not more, due to the time necessary for the cooling.

When a coating is found to have a good behavior during high pressure die casting, the effectiveness against corrosion has to be investigated. Probably useful tests should investigate conditions near to real application of the structures, so the samples made with the coated aluminum sheet and the magnesium casting should be tested exposing the external surface at the corrosion environment of interest but the sample should not be cut destroying the role of the inner coating. Another useful test should consider how scratches on the coating act with the galvanic corrosion and how deep could be the damage of the surface to resist at the corrosion.

A good way to uncouple aluminum and magnesium could be the anodization of the aluminum. Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface; this increases the resistance to corrosion and provides also a better adhesion for paintings. Anodization of aluminum consists of converting aluminum to its oxide by applying an external current in the presence of an electrolyte. This type of coating for the aluminum sheet could be useful to protect the structures against galvanic corrosion.

All these topics could be done as next steps in the investigation of the best way to use the light metal hybrid structures.

Conclusions

The hybrid light metal structures have a growing role in the reduction of weight in the components for the automotive field. Aluminum and magnesium alloys in a hybrid structure represent the best solution for this proposal but they suffer from severe galvanic corrosion when coupled and in contact with an electrolyte.

Therefore, the reason for this work was to investigate the behavior of different aluminum and magnesium alloys to better understand how the galvanic corrosion acts. The alloys of interest were for aluminum, EN AW 5083 and EN AW 6082, and for magnesium, AZ91 HP, AM50 HP and AM60 HP.

First of all, electrochemical techniques were used to obtain the polarization curves and the corrosion potential of each alloy. The setups used were two: the rotating disk electrode and the standard three electrode setup, used as reference for the following galvanic corrosion tests. The polarization scan in the solution used, 0.1 M NaCl aqueous solution, shows that aluminum 5083 has a more negative corrosion potential than aluminum 6083, due to the higher amount of magnesium, and AZ91 has a less negative corrosion potential than AM50, due to a higher amount of aluminum.

The tests to investigate the galvanic corrosion take under consideration the couples EN AW 5083 + AZ91 HP and EN AW 6082 + AM50 HP. Two tests, one with the use of the galvanic cell setup to measure the galvanic current and the other one with the use of the immersion techniques to measure the hydrogen evolution, show that the corrosion proceeds faster at the beginning in the couple EN AW 5083 + AZ91 HP but after hours of testing, the other couple investigated corrodes more. It is possible to assert that EN AW 5083 + AZ91 HP have a better corrosion behavior than EN AW 6082 + AM50 HP in a 0.1 M NaCl aqueous solution. The last performed test investigates the behavior of pure aluminum and magnesium diffusion bounded sheets, in the same 0.1 M NaCl aqueous solution. Both materials corrode immediately but the intermetallic interface does not show corrosion signs, so it could be useful to decouple the two metals.

Even if a couple acts better than the other under galvanic corrosion, it is not possible to protect the metals from corrosion, so it is necessary to find a method to uncouple the two materials avoiding the contact between the two or with the electrolyte.

At the end of the research, this work could provide an improvement of the actual knowledge on the corrosion behavior of the most common aluminum and magnesium alloys used in the automotive field and also new notions about the galvanic corrosion when these alloys are coupled. As expected, the tests performed do not lead to positive results because there is no way to protect the materials without using coatings or other techniques but they show how much the corrosion is an important aspect to take under consideration. All the investigations made are useful to proceed in the study to find a way to protect the hybrid structures in the next challenges aimed to reduce the weight in the automotive field and save fuel.

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