Electrochemical consequences of inverse macro segregation in skin of high-pressure die cast (HPDC) AZ91 alloy

Emmanuel Rocca, Caroline Juers, Stéphane Mathieu
Institut Jean Lamour, UMR7198 CNRS – Université de Lorraine, BP 70239, 54506 Vandoeuvre-Les-Nancy, France - emmanuel.rocca@ijl.nancy-universite.fr

Abstract

In many cases, the corrosion behavior of different AZ91 alloys is difficult to compare and often seems to be opposite. So, the objective of this study is to bring to light the importance of the metallographic structure of surface named “skin”. Indeed, the change of concentration ratio between the α matrix and β ($Mg_{17}Al_{12}$) intermetallic phase can easily induce a drastic change of corrosion behavior of alloy, from passive to active state. In case of HPDC alloy, the phenomenon of inverse macro segregation is sufficient to greatly modify the electrochemical behavior of cast pieces.

Introduction

Nowadays, magnesium alloys are widely used in transport industries to lighten the structures of aircrafts or cars. The technique of high-pressure die casting is often implemented to manufacture medium or small pieces in great number. The main advantages of this casting process are to be rapid and to induce a very flat surface so that no further machining of cast pieces is required.

Many corrosion studies about magnesium alloys are reported in the literature, but the results are often not very consistent, and even contradictory in some cases. The good knowledge of the casting process and the surface preparation seem to be important parameters to compare the different studies.

The objective of this work is to emphasis the importance of the metallographic structure of the pieces skin for the corrosion resistance of HPDC AZ91 alloy. The skin thickness of cast pieces depends on velocity of liquid metal in mold and temperature of the casting process.

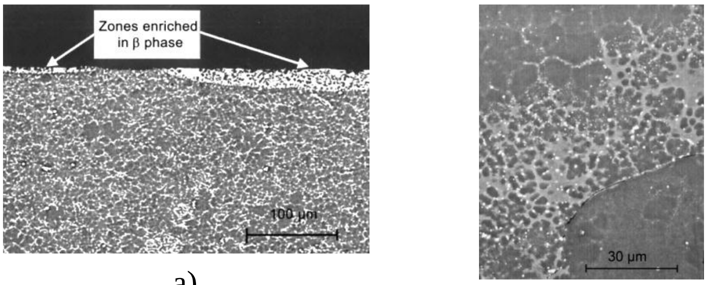
Experimental

AM50 alloy was cast by Technion (Haïfa, Israël) in plates with 3 mm thickness. The “skin” surfaces were prepared by soft polishing with alumina suspension (size: 0.5 µm) to suppress the thin layer of oxide on surface. The “bulk” surfaces were prepared by harder polishing with SiC paper (from 120 to 1200) followed by mirror polishing with alumina suspension.

The electrochemical measurements were performed in a three-electrodes cell in ASTM D1384 corrosive reference electrolyte (Na_2SO_4, NaCl, $NaHCO_3$) during 24 hours. The evolution of the electrochemical interface was characterized by electrochemical impedance spectroscopy (AC=20mV), followed by the recording of potentiodynamic curve. The anodic and cathodic parts of potentiodynamic curve were recorded separately.

Results and discussion

The metallographic analyses show significant and profuse inverse macro segregation at the surfaces of plates (Figure 1). In these inverse surface macro-segregation regions, the percentage of Al in the Mg matrix as well as the content of $Mg_{17}Al_{12}$ phase (β) grains are much higher than in regions without macro-segregation.

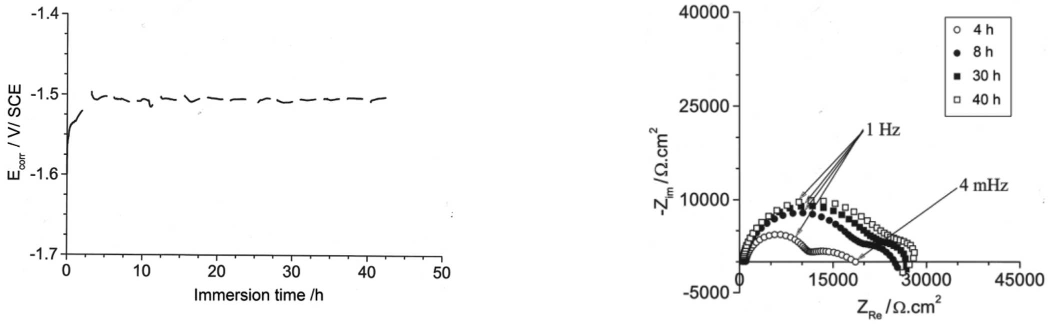


a)

b)

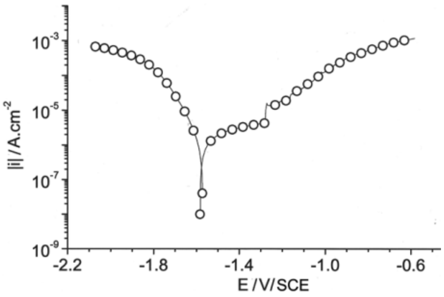
Figure 1: Example of SEM metallographic cross-section (a) and SEM surface observation (b) of inverse macro-segregation on HPDC AZ91 alloy

When the plate is sufficiently polished (“bulk” surface), the corrosion potential of samples is very stable around -1.5 V/SCE, and the global impedance of the surface is relatively high, above 24 hours of immersion. The potentiodynamic curve confirms that the “bulk” surface has a passive behavior in these medium.



a)

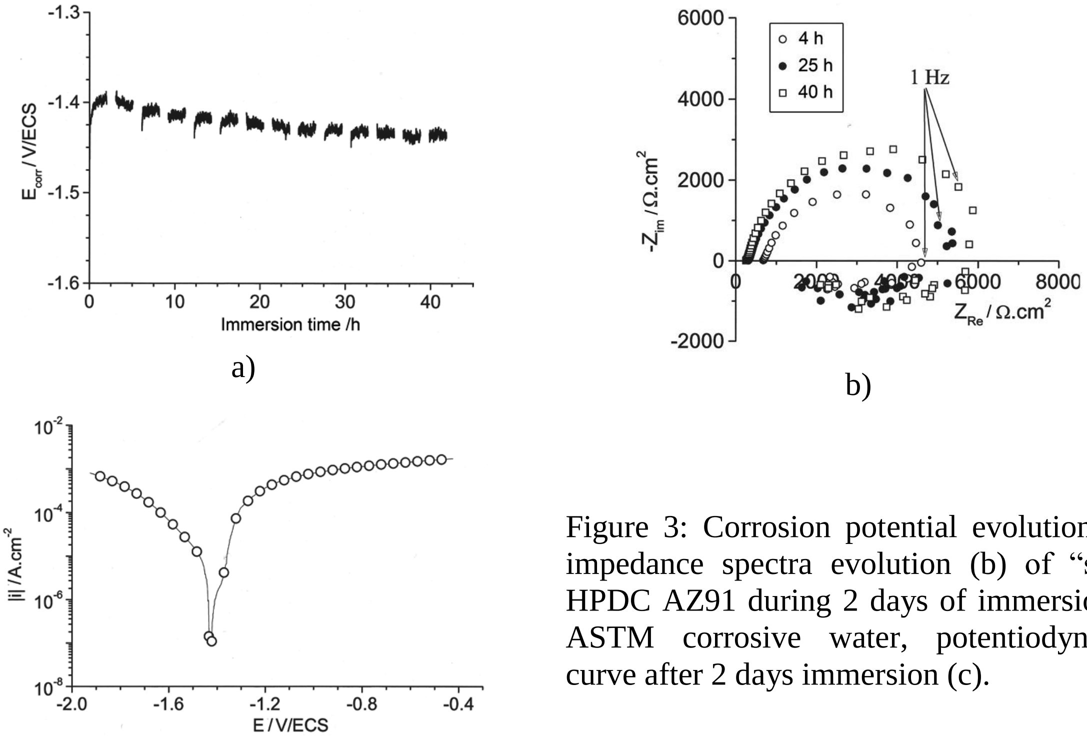
b)



c)

Figure 2: Corrosion potential evolution (a), impedance spectra evolution (b) of “bulk” HPDC AZ91 during 2 days of immersion in ASTM corrosive water, potentiodynamic curve after 2 days immersion (c).

This behavior is associated with the formation of stable passive layer containing aluminium.
In contrary, the corrosion potential of the skin of HPDC AZ91 is higher, around -1.4 V/SCE and unstable (Figure 3). The important surface concentration of β phase due to inverse macrosegragation increases the electrochemical potential of sample by galvanic coupling with α-Mg matrix. Along the immersion, the electrochemical impedance values of the surface are low and spectrum displays an inductive behavior at low frequency. In this case, the surface remains active without passivation plateau as shown by the potentiodynamic curve.
After immersion, metallographic analyses show the development of large pits in α-Mg matrix. Impedance spectra were interpreted with the model developed by G. Song et al. based on the hypothesis of adsorbed species [2]. This model is based on calculations of C. Cao [3]. This model can mathematically explain the occurrence of inductive loops in EIS spectrum, which is developed in this paper in the two cases. Nevertheless, the assumption of the existence of Mg^+ as adsorbed species to explain the NDE effect remains doubtful in the chemical point of view.



a)

b)

c)

Figure 3: Corrosion potential evolution (a), impedance spectra evolution (b) of “skin” HPDC AZ91 during 2 days of immersion in ASTM corrosive water, potentiodynamic curve after 2 days immersion (c).

Concluding remarks

The c ratio in surface of Al-Mg alloys determine the corrosion behavior of these alloys. Indeed, an important galvanic coupling between the two phases induce a depassivation of α-phase and the appearance of active-free surfaces (as shown by the inductive constant phase) which are a starting point of pitting phenomenon.

Acknowledgements

This study was performed in the framework of IDEA project funded by the FP6 of EC.

References

[1] G. Song, A. Atrens, D. St John, X. Wu and J. Nairn, Corrosion Science, 39, 1997, 1981-2004

[2] C. Cao, Electrochimica Acta, 35, 1990, 831-836