

# Influence of Casting Temperature on Electrochemical Behavior of Al-Zn-In Sacrificial Anodes

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**ABSTRACT:** Aluminum anodes have been widely used in the cathodic protection of marine structures. However there are conditions in which these anodes become passivated or face some localized or unwanted corrosion, which influences their efficiency. Addition of alloying elements such as Zn and In not only have improved the efficiency of the anodes but also the effect of casting parameters such as ultra melt temperature  $T_m$ , mold temperature and grain refiners can adversely influence the capacity of aluminum anodes. In this work the effects of ultra melt temperature and mold temperature have been studied on the potential and current capacity of Al-Zn-In anodes. Electrochemical polarization and NACE standard methods were used to evaluate the anodic behavior, potential and current capacity of the anodes. It is shown that metallic molds having higher temperatures could provide better condition for obtaining homogenous structures with minor inclusions. The optimum condition of anode operation may be provided where mold and pouring temperatures equal to 400 °C and 710 °C respectively, in which a fine structure, phase distribution and lack of casting faults are obtained. The microstructures that can provide a homogenous anodic dissolution bring by itself optimum efficiency of the anodes.

**KEY WORDS:** Al-Zn-In, Sacrificial anode, Casting parameters, Current capacity.

## INTRODUCTION

Application of commercial aluminum as sacrificial anode for cathodic protection systems is limited by the presence of an omnipresent oxide on the metal surface in aqueous environments, and its localized corrosion in halide containing environments [1- 4].

Although aluminum-based alloys have been developed as sacrificial anodes, understanding the role of alloying elements in promoting active dissolution of aluminum is

necessary for obtaining the high anode efficiency. Among these alloys, Al-Zn-In anodes are most common because of their low polluting effect on seawater environment compared with Hg-activated Al anodes, and because of their easy producing techniques compared with Sn-activated aluminum anodes which need to be heat treated after casting [5, 6].

Numerous theories have been proposed in order to

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explain the activating influence of In and Zn on aluminum in chloride aqueous media [7-10].

The attack initiation of Al-Zn-In alloy is related to In-Zn rich zones located at grain boundaries [9]. It has been previously shown that only the presence of In in true electric contact with Al is responsible for activating Al-In alloys [11]. It has been proved that there is a passivation-redeposition mechanism in activating of aluminum with indium [12,13].

A higher instability of the oxide layer due to the formation of  $ZnAl_2O_4$  spinel in Al-Zn-In alloys [14, 15], which facilitates the diffusion of  $In^{3+}$  ions in surface oxide layer, and preferential Zn dissolution and In accumulation, can explain the role of zinc on activation of process [16]. It has been also postulated that, as In to Zn concentration ratio increases the Al dissolution rate will decrease [17,18].

In addition to the amount of alloying elements presented in Al-Zn-In alloys, the distribution of these alloying elements and the grain size can affect the electrochemical behavior of the anode. It has been said that the current efficiency (i.e. attack morphology) depends on the solidification microstructure, which in turn depends on heat treatment and aging time [19]. The overall solidification rate can have a significant effect on both macro and microstructure features.

In general, faster solidification rates result in a thicker chill zone in relative to the thickness of both the columnar and equiaxial zones.

Therefore it's necessary to investigate the influence of casting parameters on electrochemical behavior of Al-Zn-In sacrificial anodes including current capacity and operating potential, in order to find the best anode having the highest efficiency. In this work the effects of casting temperature on the dissolution of Al-Zn-In alloy is studied.

## EXPERIMENTALS

The ternary alloy Al-5%Zn-0.02%In (composition according to Table 1) was prepared using pure Zn, In (99.99%) and commercial aluminum (99.8%) in a graphite crucible used for melting and graphite rods for stirring the melt. The pouring temperatures were 670 °C, 710 °C and 750 °C. Mold temperatures were 25 °C, 100 °C, 200 °C, 300 °C, and 400 °C. The alloys were casted in a cast iron mold (height = 60mm, cross section area = 25mm<sup>2</sup>).

**Table1: Composition analysis of Al-Zn-In.**

Elements	Al-Zn-In (wt.%)
Zn	5.097
In	0.021
Si	0.088
Fe	0.150
Cu	0.009
Cd	0.002
Pb	0.040
Al	Rem.

Samples were cut in a 2.5 Cm<sup>3</sup> cubes from each anode for the experiments and polished with 1200 emery papers, degreased in acetone rinsed thoroughly in double-distilled water and kept in a desiccators [20].

Accelerated dissolution tests at  $i = 4 \text{ mA.in}^{-2}$  in 0.5 M NaCl solution were performed over 14 days to determine the anode current capacity and potential vs. time curves according to NACE standard method TM0190-98 [20]. All potentials were measured relative to standard saturated calomel electrode (SCE). The potentiodynamic polarization were measured using by suspending the cubic samples in 0.5 M NaCl solutions at pH=5.

Two-liter electrochemical cells having steel cathodes were used for current efficiency tests. The used counter and reference electrode were platinum and calomel respectively. Potentials were applied at 2 mV.s<sup>-1</sup> scan rates using a potentiostat-galvanostat (EGG-M273A) after 15 minutes stabilization at rest potential.

## RESULTS AND DISCUSSION

Accelerated galvanostatic dissolution tests at 4 mA in<sup>-2</sup> in 0.5 M NaCl were performed on the anodes over 14 days and the effects of pouring and mold temperature on the electrochemical behaviors are shown in Table 2. It is shown that at higher pouring and mold temperature the current capacities improved.

The potential variations vs. time curves are shown in Fig.1, the Potential is shifted to more negative values by increasing the mold temperature.

The macrostructures of Al-Zn-In at pouring temperature of 710 °C and mold temperatures of 25 °C, 100 °C,

**Table 2: The effect of pouring and mold temperatures on performance of anodes.**

Anode No.	Casting Condition (°C)		Performance	
	Melt	Mold	Current Capacity (Ah Kg <sup>-1</sup> )	Potential (mV <sub>SCE</sub> )
1	750	25	2308	1000
2	710	25	2280	990
3	670	25	2264	985
4	750	100	2356	1010
5	710	100	2349	1005
6	670	100	2327	990
7	750	200	2469	1000
8	710	200	2461	1020
9	670	200	2452	1010
10	750	300	2562	1010
11	710	300	2568	1030
12	670	300	2561	1030
13	750	400	2578	1020
14	710	400	2595	1040
15	670	400	2530	1050

200 °C, 300 °C and 400 °C are shown in Fig. 2 in which a finer structure is obtained at higher mold temperature.

The effect of mold and pouring temperatures on polarization behavior of Al-5%Zn-0.02%In anode are shown in Fig.3 and Fig.4 respectively. The anodic parts are similar but lowering in oxygen reduction, limiting current at higher mold temperature is seen. Figs. 5 and 6 shows some corrosion pits formed at the surface of Al-5%Zn-0.02%In after polarization.

Fig. 7 shows optical images of corroded Al anodes

after 14 days of polarization test at pouring temperature 710 °C and mold temperature 400 °C. An Al anode performs a uniform corrosion and reveals a decrease in inherent corrosion.

Due to the fact that metallurgical history of cast specimens determines the solid solution and segregates distribution, both the solidification macrostructure (i. e. chill, columnar and equi-axial zones) and microstructure (i. e. dendrites arm spacing) strongly depend on the cooling rate during the casting process. Therefore, such casting

conditions and the zinc and indium solid solubility in aluminium define their final distribution in the alloy. In the case of Al-Zn-Sn anodes, it has been claimed that casting conditions define the Zn-Sn enriched zone distribution at interdendritics or grain boundary regions, which in turn define the anodes current efficiency.

In practice all Al sacrificial anodes are based on the binary Al-Zn system [23, 24, 21] and in such Al-Zn alloys, Zn tends to be pushed to interdendritic zones or grain boundaries [21]. This effect is favored by the cooling rate and the alloying element characteristics lower melting point than aluminum.

Under anodic polarisation this local composition variation will favor the initiation and propagation of macro- and micro-local phenomena (i.e. galvanic corrosion or pitting). These phenomena responsible for lowering the anode efficiency either by electrochemical or mechanical mass loss (grain or particles drop). In Al-Zn with chill structure, the alloying elements are concentrated at the grain boundaries due to the segregation process [21] promoting a more concentrated and reactive  $\alpha$ -Phase in these places than the equiaxial structure with the same Zn content.

The columnar structure was disregarded due to the band segregation effect, which produced a heavy mechanical loss, and a very poor anode efficiency [21].

During the addition of In into molten aluminum, indium may be oxidized because of its high melting point. So it's possible to avoid it from oxidation by increasing the cooling rate.

Solubility limit of indium in aluminum is about 0.017 wt.% and if alloyed indium is more than this value the rest appears as precipitation in aluminum matrix [21].

During the addition of In into molten aluminium, indium may be oxidized at higher casting temperature. If the casting temperature is kept at 710 °C and mold temperature at 400 °C, the potential will be negative enough for accessing maximum efficiency.

More increase in temperature of molten alloyed Al-Zn causes Zn vaporization and less precipitation of Zn in the aluminum matrix. On the other hand it can promote the oxidation of indium during alloying. For this reason anodes produced in high melting temperature have less current capacity comparing to ones produced in low temperatures. In the presence of oxide layers (In, Zn, Al), which are increased in high temperature, there will be

some un homogeneity in alloy causing a decrease in efficiency and current capacity (Figs. 2, 3, 4).

The uniform consumption of Al-Zn-In anode during its service time is crucial for cathodic protection aims. Hence, it is necessary to control major casting parameters for getting uniformity of the cast anodes.

Casting and solidification parameters play important roles not only on obtaining sand casting, but also on introducing castings with well distributed alloying elements, such as In and Zn in aluminum.

It is well established that any increase in cooling rate will contribute in reducing segregation of alloying elements and improving the homogeneity of microstructures.

Casting temperature is an important factor, if the casting temperature is not selected properly phase segregation and porosity in grain boundaries may lead to some variation in properties (potential, current capacity, rate of corrosion, efficiency) specially the electrochemical potential of the anode.

Selection of a high super heat during casting encourages the oxidation of alloying elements (Fig. 5).

Keeping the mold temperature at 400 °C and pouring temperature at 710 °C results in optimum electrochemical behavior at Al-5%Zn-0.02%In anode. From the appearance point of view, anodes perform a uniform corrosion (Figs. 6 and 7). In This condition, alloying elements are well distributed in the micro and macrostructures.

It should be noted that any changes in microstructure resulting from altering the casting parameters may seriously affect the electrochemical properties of the anodes.

## CONCLUSIONS

1 - The casting parameters such pouring and mold temperature has a significant effect on structural refinement and alloying element distribution necessary for uniform corrosion of Al-5%Zn-0.02%In anodes.

2 - A mold temperature at 400 °C and pouring temperature of 710 °C results optimum electrochemical behavior at Al-5%Zn-0.02%In anode.

3 - At optimum casting temperatures more stable potential and higher current efficiency are obtained. The optimum casting and mold temperatures, lead to equiaxial structure, which promotes general corrosion of the anode. Casting conditions that produces better distribution of alloying elements in enriched zones, will give higher anode efficiency too.

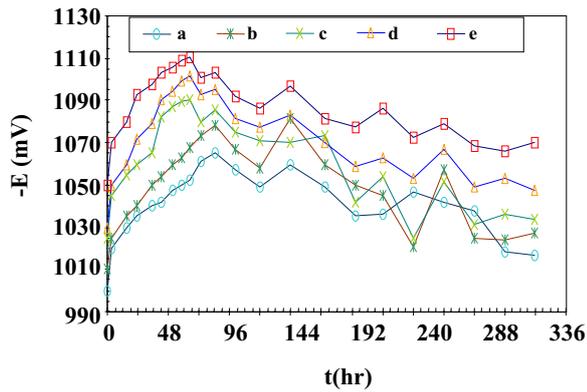


Fig.1: Potential variation vs. time plot at pouring temperature 710 °C and mold temperatures: (a) 25 °C; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C.

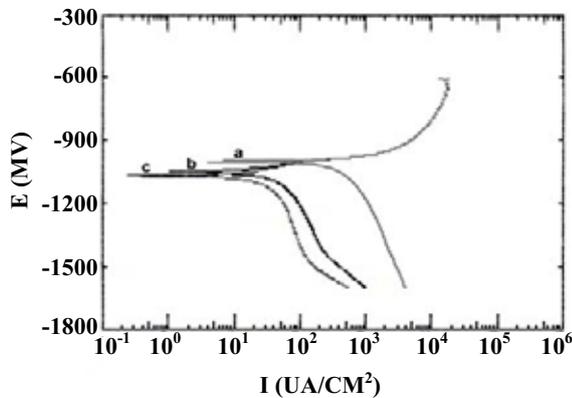


Fig. 3: Potentiodynamic polarization plots of Al-5Zn-0.02In alloy at pouring temperature 710 °C and affect mold temperatures: (a) 25 °C; (b) 200 °C; (c) 400 °C, Anode No. (Are shown in table 2).

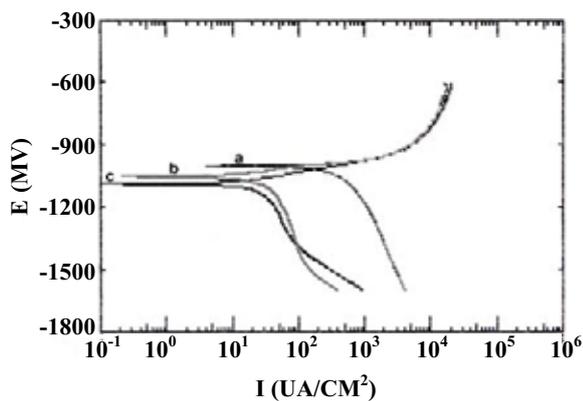
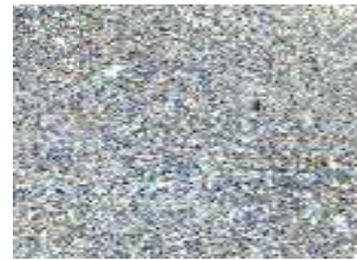


Fig. 4: Potentiodynamic polarization plots of Al-5Zn-0.02In alloys at mold temperature 400 °C and pouring temperatures: (a) 750 °C; (b) 710 °C; (c) 670 °C, Anode No. (Are shown in table 2).



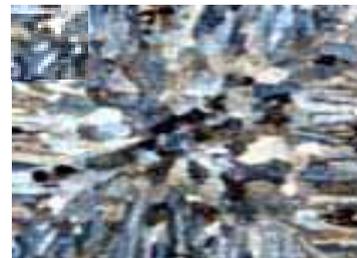
10 mm (a)



(b)



(c)



(d)



(e)

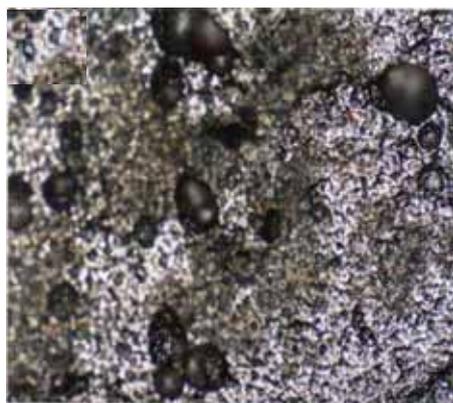
Fig.2: Macrostructures of Al-Zn-In at pouring temperature 710 °C and mold temperatures: (a) 400 °C; (b) 300 °C; (c) 200 °C; (d) 100 °C; (e) 25 °C, 1 X.



100  $\mu\text{m}$  (a)

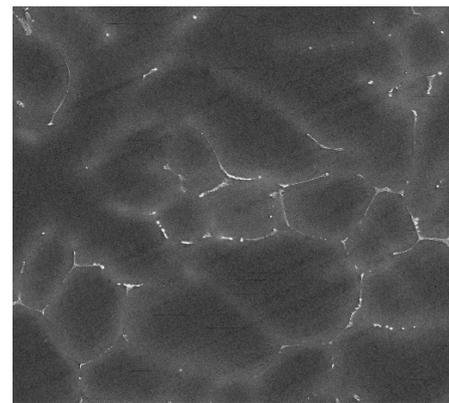


200  $\mu\text{m}$  (b)

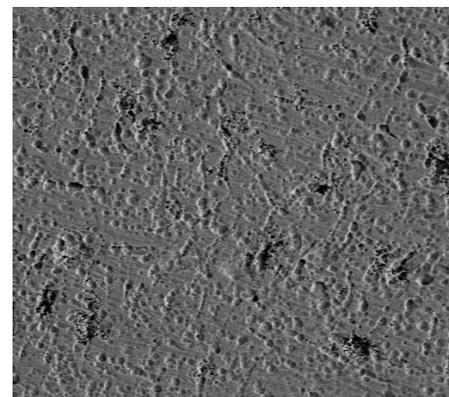


300  $\mu\text{m}$  (c)

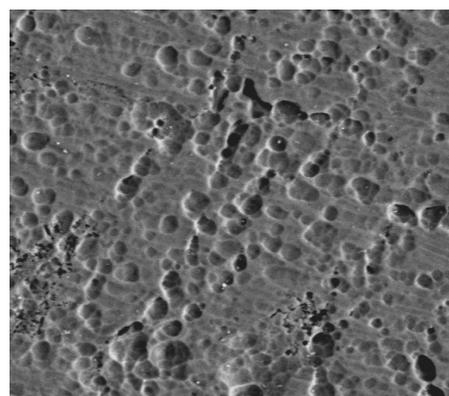
**Fig. 5:** Microstructure of sample Al-5%Zn-0.02%In at mold temperature 400 °C and high pouring temperature 750 °C: (a) Before polarization, 100 X; (b) Corrosion pits formed at the surface after polarization, 50 X; (c) after polarization, 500 X.



(a)



(b)



(c)

**Fig. 6:** Microstructures (SEM micrograph) of sample Al-5%Zn-0.02%In at mold temperature 400 °C and pouring temperature 710 °C: (a) Before polarization, 500 X; (b) After polarization, 200 X; (c) After polarization, 500 X.

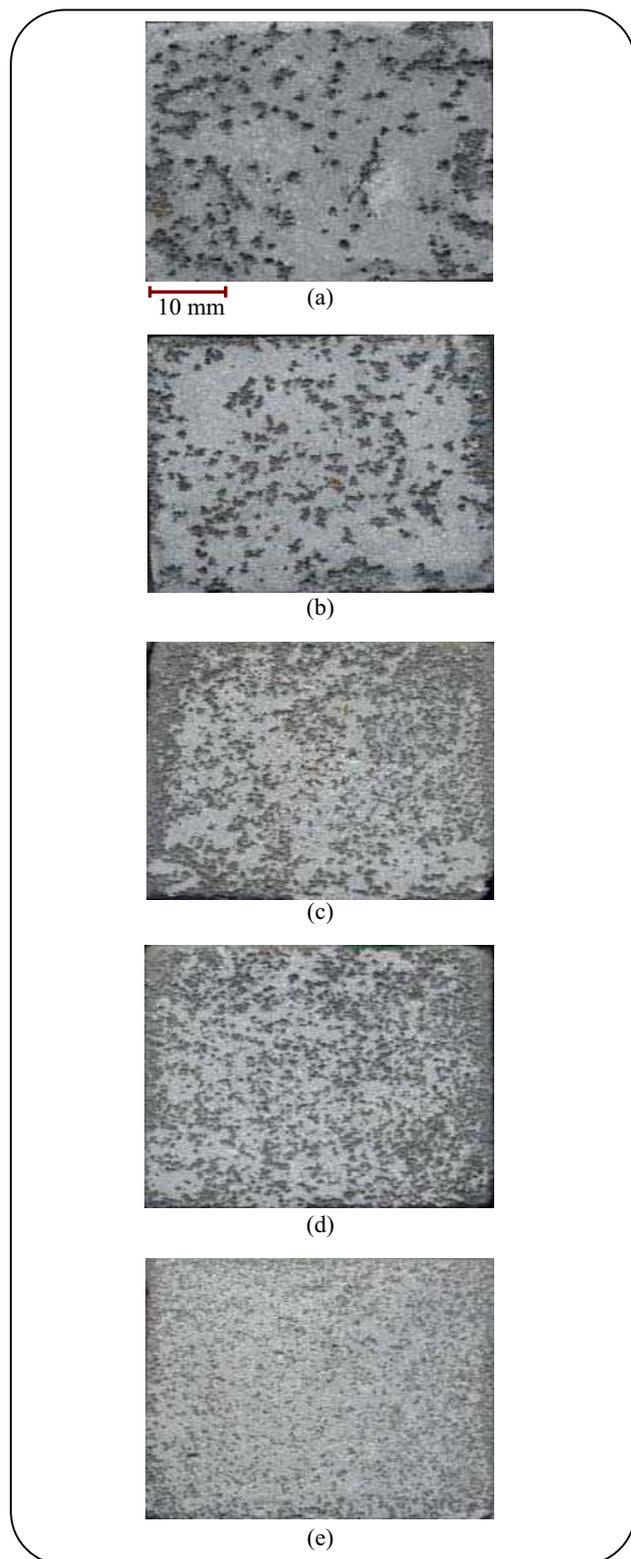


Fig. 7: The optical images of corroded Al anodes after 14 days of polarization test. Casting temperature 710 °C and mold temperatures: (a) 25 °C; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C, 1 X.

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