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Corrosion Resistance of Al-Cu Alloys in Function of the Microstructure

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Abstract. Aluminum and its alloys are characterized by low density, high electrical and thermal conductivity, and good resistance to corrosion in certain media such as air. The mechanical strength alloy is achieved. The objective of the present research consist on studying the type of structure (columnar, equiaxed or with columnar to equiaxed transition, CET) using parameters of the solidification process and electrochemical parameters in Al, Cu and Al-Cu alloys with different concentrations. In order to obtain columnar, equiaxed and CET structures, the alloys were directionally solidified upwards in an experimental set up with a set of thermocouples in the samples which permit to determine the time dependent profiles during the process. The electrochemical studies of the samples were realized by using an electrochemical impedance spectroscopy (EIS) technique and potentio-dynamic polarization curves immersed in 3% NaCl solution at room temperature. In general, we observed that the susceptibility to corrosion of the different structures depends on the size of the secondary dendritic spacing and the proportion of Al2Cu phase and Al-rich phase.

Introduction

Pure aluminum is characterized by good corrosion resistance because, when exposed to air or aqueous media, spontaneously form protective oxide films [1]. However, it is too soft to be used as a high strength material in large structures. For this reason, aluminum base alloys have been developed to improve specific properties. Copper is commonly used as an alloying element due to their presence in small amounts greatly increases the hardness of the resulting material. Currently, Al-Cu alloys are considered of great technological importance, finding numerous applications in industry due to their low density, their good both electrical and thermal conductivity, and its good corrosion resistance in certain environments [2, 3].

Galvele et al. [1] report that the presence of Al-Cu couple produces an adverse effect on the behavior of solutions containing aluminum chloride.

Some authors report that in addition to the solute redistribution pattern, the microstructural features play a fundamental role in the corrosion behavior of Al-Cu alloys [1, 3-6]. Osorio et al. [4] studied the effect of the presence of intermetallic materials in Al-4, 5% Cu alloys, and concluded that the Al-2wt.%Cu alloys are more susceptible to corrosion than pure aluminum. The same conclusions found Ares et al. [3] studying aluminum-based binary alloys.

The aim of this work is to study the corrosion behavior of diluted Al-Cu dendritic alloys with different weight percentages of copper in NaCl 3%, at room temperature, using electrochemical cyclic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) technique, complemented with the analysis of the resultant microstructures.

Materials and Method

The Al-Cu alloys analyzed in this work are: Al -1wt.%Cu, Al-4,5wt.%Cu and Al -15wt.%Cu . The alloys were obtained by directional solidification technique [3]. The development of the macrostructure was carried out with two different solutions: for the samples containing less than 10wt.%Cu was used a solution of 15 ml HF, 4.5 ml HNO_3, 9 ml HCl and 271.5 ml H_2O, and for Al -15wt% Cu alloy was used a solution containing 320 ml HCl, 160 ml HNO_3 and 20 ml HF. By visual observation was identified the presence of columnar and equiaxed grain zones; both separated by a columnar-to-equiaxed transition (CET) zone. Figure 1 provides a macrography of Al -4.5wt.% Cu, which indicates the different zones of grains.

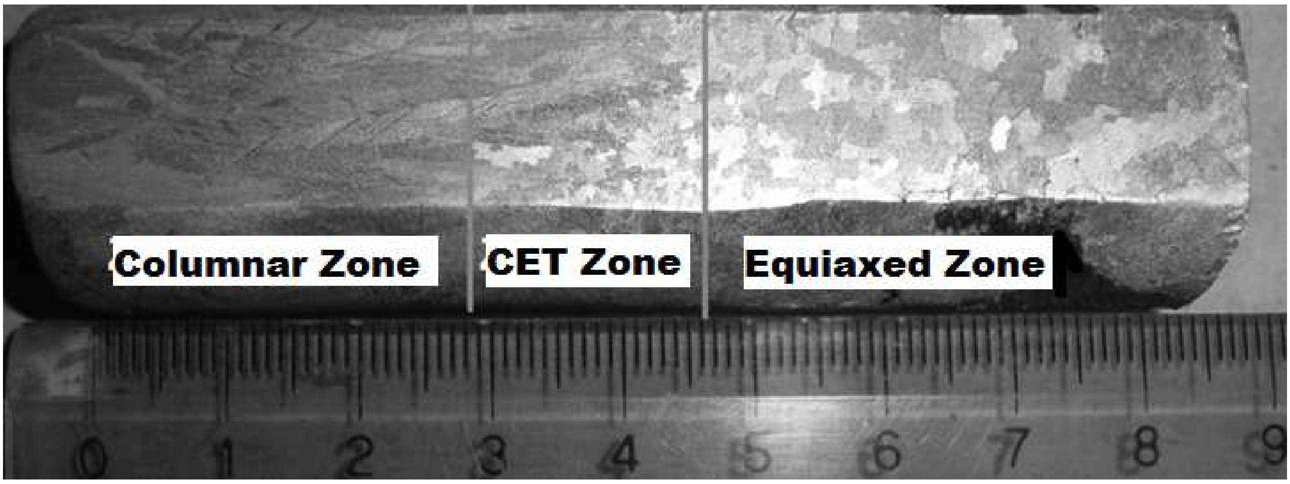


Fig. 1. Macrostructure of Al-4,5wt.% Cu sample [8].

These samples were cut longitudinally in order to obtain working electrodes of each of the zones for electrochemical measurements. Grinding was performed using different graded papers of CSi. Then, samples were washed with deionized water and dried with natural flow of air.

Were performed cyclic potentiodynamic polarization curves, following the Standard G61 -86, using a potentiostat model M7 LYP Electronics Argentina. An electrochemical Pyrex ® glass cell with conventional three electrodes (ASTM G-5), with a saturated calomel (SCE) as reference electrode and a platinum foil as counter electrode. The scanning of polarization curve was started from a lower potential of 300 mV at open circuit potential to more anodic potentials. Upon completion of these experiences, the working electrodes were examined using Nikon® metallographic microscope to visualize the effects of corrosion on the microstructure.

Measurements were also performed using Electrochemical Impedance Spectroscopy (EIS) technique, using a Gamry® Instruments, in combination with a potentiostat. EIS is a technique used in corrosion studies, based on the application of an AC signal on the electrode, obtaining in response an impedance spectrum, which is interpreted by equivalent circuit [6]. Potential amplitude of 10 mV/s was used at open circuit potential with an initial period of stabilization system of 600 seconds. For adjustment of the results the method of nonlinear least squares designed by Bouckamp [7] was used.

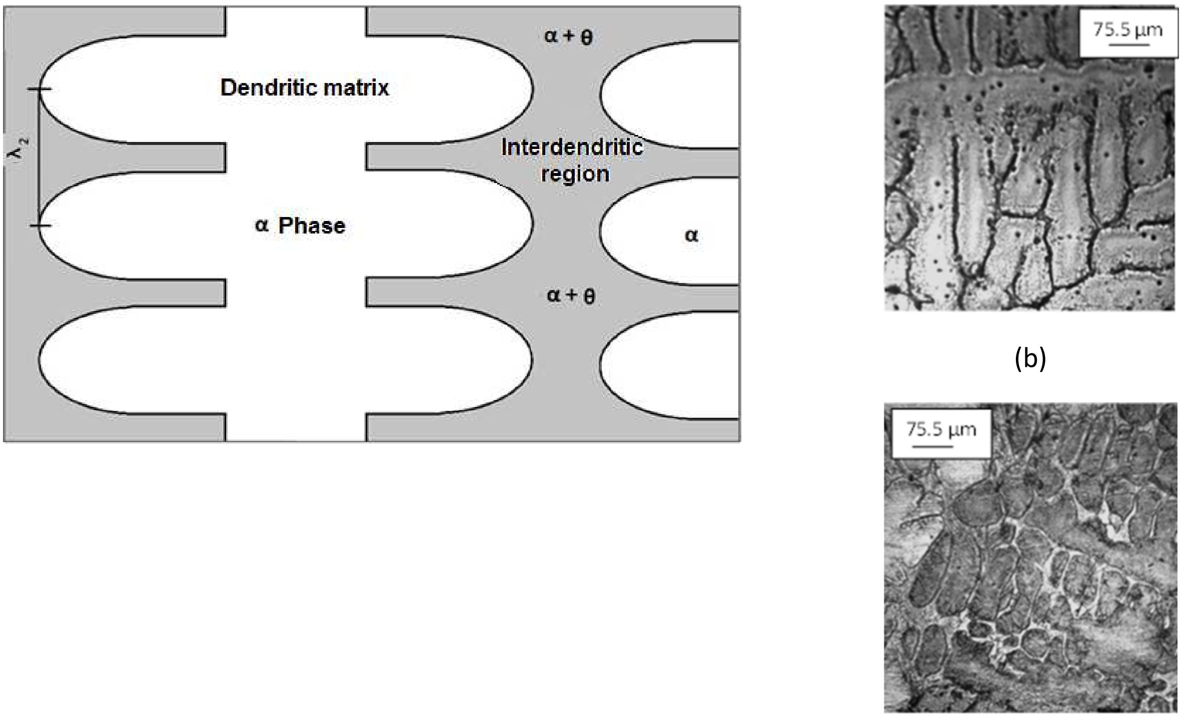
For all electrochemical tests was employed as electrolyte a solution of 3% NaCl, pH = 5 at room temperature, which previously removed oxygen by nitrogen bubbling during 20 minutes.

For analysis of the microstructures, the samples were grounded with CSi papers up # 1200 grain size and polished with 0.3 micron of alumina. Then, etching was performed at room temperature with a solution of 2.5 ml HNO_3, 1.5 ml HCl, 1 ml HF and 95 ml H_2O, during different periods of time, depending on the composition of the samples and to achieve the development of the microstructure (5 sec. for Al-1% Cu, 15 sec. for Al-4, 5% Cu and 35 sec. for Al-15% Cu). Using an Arcano® optical microscope (MO), and with the help of image processing program TSView were obtained the values of secondary dendritic spacing, λ_2 in each of the samples.

Results and Discussion

Microstructure Analysis

In general, Al-Cu alloys can develop different morphologies; they go from a solid solution phase to a polyphase structure. The appearance of these different morphologies will depend on the copper concentration, solubility of copper and how these phases are formed during the solidification process [8]. Figure 3 shows a diagram of the microstructure of a hypoeutectic Al-Cu alloy. Dendritic matrix is formed by a solid solution phase called α, which has a content of less than 0.1% of Cu. Interdendritic region is constituted by two phases which are in the form of alternating sheets: α phase, and the Al-rich phase called θ, corresponding to the intermetallic Al_2Cu, with content of Cu between 52.5% and 53.7%.



(b)

(c)

Fig.3. (a) Schematic of the microstructure of a hypoeutectic Al-Cu alloy. (b) and (c) Microstructures of: Al-4,5wt.%Cu and Al-15wt.%Cu [8].

From the study of micrographs (Figure 3 (b) and (c)) and following the phase diagram [9], was observed that increasing the Cu content in the samples, increases the interdendritic region. This brings a reduction of secondary dendritic spacing, λ_2. In the measurement of λ_2 was also found that this value increases with the distance from the base of the samples. Table 1 shows average values of λ_2 for each alloy at each of the zones. These results are consistent with those reported by Ares et al. previously [3].

Table 1. Averages values of λ_2, in each zones of the samples (μm).

Zone of the sample	Al-1wt.%Cu	Al-4,5wt.%Cu	Al-15wt.%Cu
Columnar	93,2	90,9	59,0
CET	102,4	85,3	61,2
Equiaxed	124,8	93,7	62,5

Potentiodynamic Measurements

For Al-1wt.%Cu alloy, in each of the areas analyzed showed a passivation zone, where lower currents remained virtually constant over a range of 100 mV (Figure 4). Then, there was a rapid increase in current and a rapid dissolution of the metal, with the highest pitting potential (E_P) in the columnar zone: -707 mV. Table 2 shows the measured potential for such pitting sample.

In the case of Al-4.5wt.%Cu alloy sample, passivation was only seen on the CET sample, commencing the increase in dissolution rate of the sample at E_P = -672.6 mV. For potentiodynamic curves of Al-15wt.%Cu alloy sample, the passivity was evidenced in Columnar (C) and Equiaxed (E) zones, being that intensity remains relatively constant at higher values in the columnar zone, which can be indicating the formation of a protective passive layer less than that corresponding to the equiaxed zone.

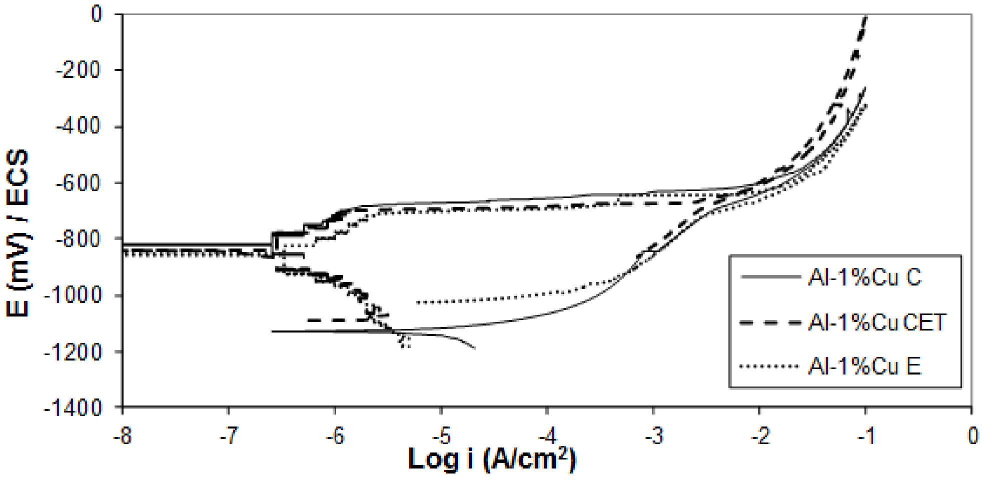


Fig. 4. Al-1%Cu potenciodynamic curve.

However, the E_P for the Equiaxed zone was equal to -703.6 mV, which is nobler than the E_P in the Columnar zone, equal to -643.5 mV. By evaluating the relationship between the copper content of alloys and potentials, it was found that in columnar and equiaxed zones, the corrosion potential (E_C) appears nobler to Al-4,5wt.% Cu Alloy. This composition is the nearest to commercial Al-Cu alloys. So too, the lowest E_C was evident for samples with lower copper content. In the case of the CET region was found that the corrosion potential increases with increasing solute content in the alloy. Table 3 presents the E_C measured for each ssmple worked.

Table 2. Pitting potentials in columnar, equiaxed and CET for Al-1wt.% Cu alloy.

Zone	E_P (mV)
Columnar	-707
CET	-731
Equiaxed	-733

Table 3. Corrosion potentials for the three alloys studied.

	E_C (mV)		
Alloy	Columnar	CET	Equiaxed
Al -1wt.% Cu	-820	-833	-854
Al -4.5wt.% Cu	-645	-744	-707
Al -15wt.% Cu	-755,7	-639	-793

Figure 5 presents photographs of the micrographs obtained in the columnar zone after the potentiodynamic test was realized. Examination of the micrographs shows that the region most affected by localized corrosion match with dendritic area (α phase). This indicates that the interdendritic region, corresponding to intermetallic Al_2Cu, acts as cathode, favoring the dissolution of the copper-depleted metal matrix. This was exposed by other authors [1, 5] and consistent with the results in the present research. It is also evident that the higher copper content of the sample area affected by the attack decreases. This is explained by the growth of the interdendritic space (cathode areas rich in copper) with increasing solute in alloys.

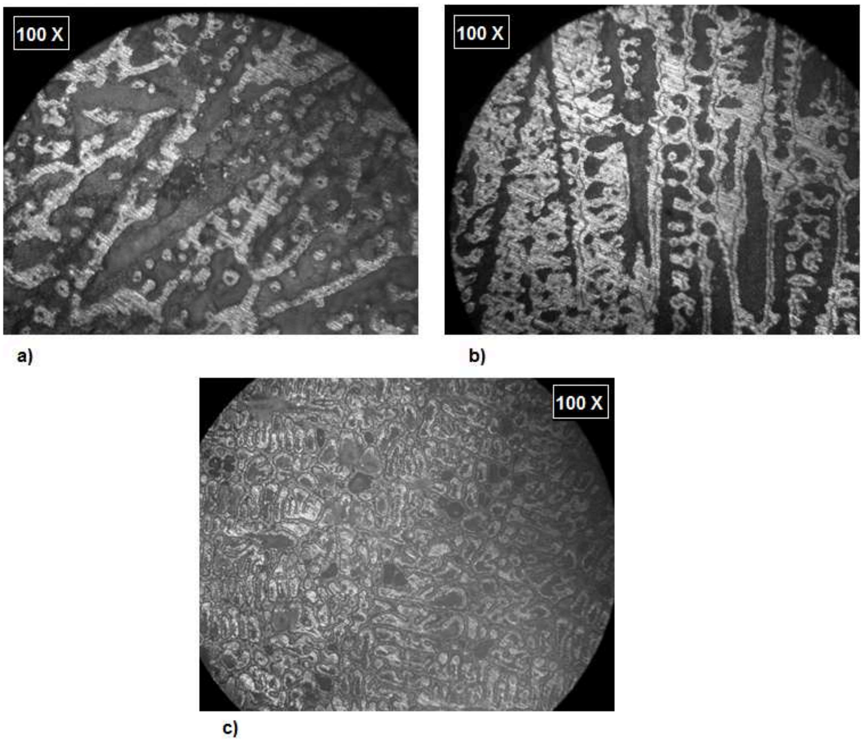


Fig. 5. Photograph obtained using optical microscope in columnar zones of the samples. a) Al –1%Cu; b) Al-4,5%Cu; c) Al-15%Cu

Electrochemical Impedance Spectroscopy (EIS)

The impedance response for three samples obtained for the various zones of the Al-1wt.%Cu, as well as corresponding to the CET zone of the alloy with a copper content of 15wt.% can be simulated by the circuit shown in Figure 6 (a). The parameters corresponding to EIS can be observed in Table 4. R_Ω corresponds to the resistance of the electrolyte and the R_1 resistance corresponds to the charge transfer that accompanies the double layer. Given that the values of n_1 are close to 0.8 which is can be attributed to this constant phase element, CPE_1 is the double layer capacity.

For the three regions of the Al-4,5wt.%Cu and columnar and equiaxed zones of the Al-15wt.%Cu, a proposed model was used to represent the impedance response of the electrodes having a coverage of porous surface film, where the reactions occur only in the exposed surface, i.e., the end of the pore. Within the pore, concentrations of different species differ from the concentration in the bulk solution [10] (Figure 6 (b)). Setting parameters are presented in Table 4. R_2 is considered the resistance associated with the porous oxides and constant phase element, CPE_2, correspond to porous oxides capabilities.

Observing the impedance setting parameters in the various zones for a given composition of the sample, shows that the Equiaxed zone has the lowest values of the charge transfer resistance,R_1, while the CET zone have the highest valued, assumed resistor values in the three alloys tested. Figure 7 shows the Nyquist plots for the three areas of the specimen of alloy Al-4, 5% Cu.

Fig. 6. Equivalent circuits obtained from adjustment of the experimental data. a) Al-1wt.%Cu. b) Al-4,5wt.% Cu and Al-15wt.%Cu.

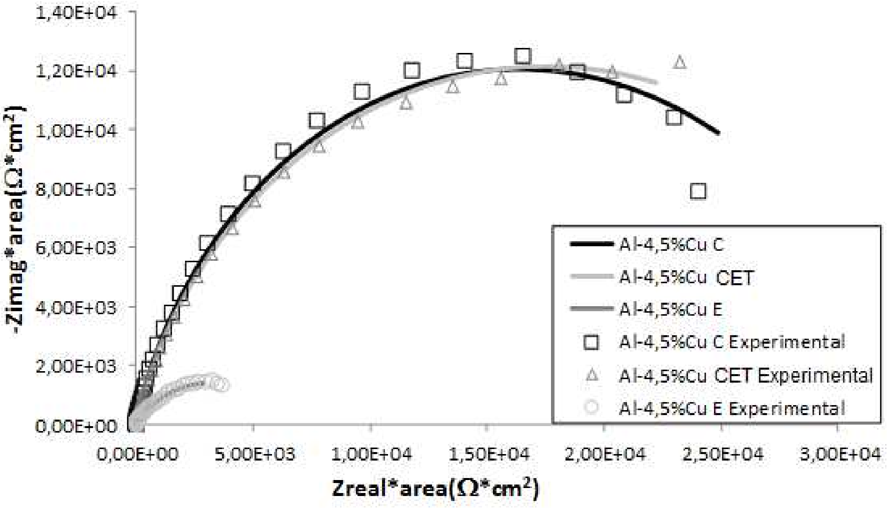


Fig. 7. Nyquist diagram for Al-4,5wt.%Cu.

Table 4.Parameters obtained from EIS adjustment.

Alloy	Zone	R_{omh} $(\Omega*cm^2)$	CPE $_1$ (Ω/cm^2)	n_1	R_1 $(\Omega*cm^2)$	R_2 $(\Omega*cm^2)$	CPE $_2$ (Ω/cm^2)	n_2	Circuit
Al-1wt.%Cu	Columnar	6.77	7.0E-05	0.82	25090	-	-	-	Fig.6. (a)
	CET	3.69	2.6E-05	0.82	113920	-	-	-	Fig.6. (a)
	Equiaxed	4.03	6.8E-05	0.80	13986	-	-	-	Fig.6. (a)
Al-4,5wt.%Cu	Columnar	4.93	5.8E-06	1.00	33420	47.3	2.4E^{-07}	1.00	Fig. 6. (b)
	CET	3.99	1.8E-05	0.53	33642	3826.2	2.2E^{-05}	0.88	Fig.6. (b)
	Equiaxed	1.89	1.8E-04	0.51	6400	12.4	6.6E^{-06}	0.99	Fig.6. (b)
Al-15wt.%Cu	Columnar	4.77	1.5E-05	0.75	30168	55.3	2.65E^{-06}	1	Fig.6. (b)
	CET	5.36	2.7E-05	0.84	43900	-	-	-	Fig.6. (a)
	Equiaxed	5.58	1.5E-05	0.69	17928	65.9	2.54E^{-06}	1	Fig.6. (b)

Conclusions

Electrochemical parameters do not indicate a relationship between the structure of the alloy and corrosion resistance. However, microscopic observations show that the interdendritic region, rich in copper, acting as a cathode favoring the dissolution of the metal matrix formed in a higher percentage of aluminum.

Given the presence of a passive region in the cyclic potentiodynamic polarization curves and high resistance values in the equivalent circuits of the electrochemical impedance spectra can be concluded that the alloy Al-1wt.% Cu exhibits good corrosion resistance.

Analysis of electrochemical impedance spectroscopy revealed that in general, for each of the alloy compositions, the equiaxed zone has the lowest values of resistance.

The impedance response for the three areas obtained alloy Al-4% Cu and columnar and equiaxed areas alloy Al-15% Cu has contributions from a porous oxide layer.

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