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Belkacem Korichi, Nacer Zazi, Stéphanie Delbrel, Kieu Ngo, Jean Paul Chopart. Microstructural, morphological characterization and corrosion behavior of sand cast AlSi10Cu(Fe) alloy in chloride solution. Chemical Papers, 2022, 76, pp.2947-2967. 10.1007/s11696-022-02064-9 . hal-03597124

HAL Id: hal-03597124

<https://hal.science/hal-03597124>

Submitted on 21 Nov 2022

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4

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Abstract

In order to examine the relationship between the microstructure and the corrosion behaviour in chloride solution, the microstructure of AlSi10Cu (Fe) sand cast aluminium alloy has been investigated by using different techniques including scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction analysis, and electrochemical measurements. The microscopic analysis and X-ray diffraction analysis show several phases in addition to matrix phase, including pores and phases at nano and micro scales. The average rate of micropores and nanopores is 4% and 5%, respectively. The nanoparticle size varies between 20 to 150 nm. Plates and corals-like silicon eutectic, rich-Cu phase and Chinese script phase ($\text{Al}_{15}(\text{Mn,Fe})_3\text{Si}_2$) have been observed. Energy dispersive spectroscopy analyses show the presence of a new phase ($\text{Cu}_{61.22}\text{Zn}_{25.39}\text{Ni}_{11.85}\text{Al}_{1.54}$) and the pitting corrosion has been demonstrated to be initiated at the nanopores. The electrochemical measurements exhibited the effect of several elements and porosities on the corrosion kinetics that is controlled by charge transfer and diffusion phenomenon. Wide passive windows, followed by the breakdown of passive film and excessive dissolution, have been observed in 0.3 and 3 wt. % NaCl solutions. The electrochemical measurements show a high corrosion rate which does not recommend the use of this alloy in seawater.

Keywords: AlSi10Cu(Fe) cast alloy, plates-like silicon eutectic, corals-like silicon eutectic, $\text{Cu}_{61.22}\text{Zn}_{25.39}\text{Ni}_{11.85}\text{Al}_{1.54}$ phases, aluminum corrosion, nanopores.

Introduction

Aluminum alloys are chosen as materials for construction in various fields due to their low density and their high corrosion resistance (Singh and Goel 1990). The aluminum-silicon alloys are economical and more lightweight due to the high quantity of silicon (Ahn et al. 2018). However, a high ratio of silicon in aluminum alloys can increase the cracking, the wear resistance and the fluidity of these alloys. Moreover, it can minimize the shrinkage porosity and reduce the melting temperature point (Ahn et al. 2018; Elzanaty 2015). Therefore, the use of these alloys is limited due to the variations of their properties and their limited performance, especially at high temperature (Stadler et al. 2011, 2012; Ceschini et al. 2015).

The mechanical properties of these alloys depend on their microstructure, their chemical composition and their defects (Zamani et al. 2015; Campbell 2003; Jiang et al. 2014). In order to enhance their properties, some metallic elements including Mg, Cu, Fe, Ni and Sr have been added in addition to the silicon. In fact, the alloys microstructure is characterized by various present parts such as α -aluminum phase, primary silicon particles, aluminum-silicon eutectic, intermetallics and precipitates (Tenekedjiev and Gruzleski 1990; Bogdanoff et al. 2016).

The coral-like eutectic structure can be obtained by heat treatment or by addition of low concentrations of elements such as Na, Sr, or Eu which change the silicone plate-like eutectic morphology to fine and round coral-like eutectic morphology (Barrirero et al. 2019).

The α -aluminum phase represents the matrix of cast aluminum-silicon alloys; it crystallizes in the appearance of non-faceted dendrites (Warmuzek 2004), and sometimes in appearance of non-dendritic forms (Zazi 2013). Moreover, the hard primary silicon particles distributed in the matrix are responsible for the good mechanical properties and the high wear resistance (Elzanaty 2015). (Oya et al. 2013) showed that the intergranular corrosion susceptibility increases as a function of the silicon content in the alloys.

Aluminum-Silicon-Magnesium alloys are polyphase materials and have good properties such as excellent castability, high ductility, high strength and low thermal expansion coefficient (Ahn et al. 2018; Cáceres et al. 2003). These properties explain why these alloys have occupied an important position in the field of automobile applications and are widely used in the production of engine components. The mechanical properties of these alloys depend on the size, the shape, the distribution, the degree of modification of eutectic phase, and the primary silicon particles (Ye 2003; Ma et al. 2017; Mohamed and Samuel 2012; Al-Hella and Kawther 2013). Moreover, the casting process plays a crucial role in the microstructure and mechanical properties of these alloys (Al-Hella and Kawther 2013).

In Aluminum-Silicon-Magnesium cast alloys, the Mg-containing phases formed during the solidification are Mg_2Si , Si eutectic crystals, and the π -Fe phase. The contents of Mg and Fe in these alloys and the solidification rate determine the fractions of the β -Fe and π -Fe phases and the concentration of Mg in solid solution. The π -Fe phase has a Chinese script or blocky morphology and it is often formed on the β -Fe plates. The Mg_2Si phase ratio increases with the Mg content in the alloys, *i.e.* from close to zero for 0.3 wt% Mg to 0.2 vol% for 0.7 wt% Mg (Sjölander and Seifeddine 2010). The secondary phases, including Mg_2Si , π -Fe, β -Fe and Si eutectic crystals can induce specific alloy properties, and therefore have an influence on the mechanical and corrosion behavior of these materials (Dobkowska et al. 2016; Cecchel et al.

2017). In aqueous media, the corrosion resistance of aluminum and its alloys is provided by the formation of an oxide film composed of Al_2O_3 , $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$ phases on the metallic surface (Barr 1977). However, for media containing chloride ions, an extensive localized attack or a uniform corrosion can be observed (Bessone et al. 1992; Munoz and Bessone 1999; Allachi et al. 2010; Zazi et al. 2010). The oxide film on aluminum surface is a poor electronic conductor and the cathodic reactions take place on the micron size intermetallic particles, or smaller precipitate particles (Zaid et al. 2008). The silicon rich phase can cause galvanic corrosion, and the porosities formed during the casting processes can generate crevice corrosion (Dobkowska et al. 2016)].

Several authors have showed the presence of Al_2Cu phase during the solidification of aluminum-silicon-copper alloys (Sjölander and Seifeddine 2010; Dobkowska et al. 2016; Cecchel et al. 2017; Barr 1977; Bessone et al. 1992; Munoz and Bessone 1999; Allachi et al. 2010; Zazi et al. 2010; Zaid et al. 2008; Djurdjevic et al 1999; Samuel et al. 1997; Li et al. 2003). This phase can be found in different shapes as compact block-like phase type, eutectic Al_2Cu phase type or mixture of both types. This Al_2Cu phase arises from β -Fe plate's phase or on coarse eutectic Si particles phase during the end of solidification process. Other phases including β - Mg_2Si , Θ - Al_2Cu , π - $\text{Al}_8\text{Mg}_3\text{FeSi}_6$, Q - $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$, α - $\text{Al}_{15}(\text{Fe},\text{Mn})_3\text{Si}_2$ and β - Al_5FeSi can also be present in the alloys (Zazi et al. 2010; Li et al. 2003; Dinnis et al. 2006).

Porosities are cavities which are formed during the metal solidification. They are regarded to be the first defect that occurs in aluminum–silicon casting alloys (Ammar et al. 2008). These porosities can cause various issues such as poor mechanical properties with limited strength and ductility, variable fracture toughness and crack initiation sites (Ammar et al. 2008). The porosity development in solidifying aluminum–silicon casting alloys is due to shrinkage resulting from volume contraction associated with the solidification, and the entrapment of gas (mostly hydrogen and air) resulting from a decrease in gas solubility in the solid alloy compared to the liquid (Ammar et al. 2008). The formation of microporosities during the solidification of aluminum alloys is responsible for problems in the production of good quality products. Moreover, the process parameters during the solidification have a significant effect on the microstructural development of the alloy and determine the final engineering performance of the casting. Other parameters such as dendrite segregation, nature, size, distribution and morphology of precipitates and porosities have also a significant influence on mechanical and chemical alloys properties (Ferreira et al. 2010; L. Kuchariková et al. 2021).

The present work is a part of a larger research project (corrosion of AlSi cast alloys), which was performed to examine and to offer a better understanding of the influence of porosities (nano and micro size) and intermetallics on the corrosion behaviour of AlSi10Cu(Fe) sand cast alloy containing zinc and to find the relationship between the microstructures and the corrosion behaviour. The study has been achieved by investigation of microstructure of AlSi10Cu(Fe) sand cast aluminum alloy before and after two weeks of immersion in chloride solution (0.3 and 3 wt. % NaCl) at room temperature and correlation with the observed corrosion phenomenon.

The microstructure was investigated by using optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and electrochemical measurements.

Experimental

Materials

The investigation materials was a hypoeutectic aluminum sand casting alloy AlSi10Cu(Fe) and the experimental samples were prepared from an industrial ingot from SNVI company (Aluminum Foundry Unit, Rouiba) Algeria.

The chemical composition of the alloy is shown in Table 1. The casting was carried out by gravitation in sand mold at temperatures between 700°C and 750 °C.

Table 1. Chemical composition of the elaborated AlSi10Cu (Fe) aluminum cast alloy.

<i>Element</i>	Al	Si	Fe	Cu	Mn	Mg	Zn	Ni	other
<i>wt. %</i>	85.40	9.53	1.21	1.25	0.91	0.51	0.65	0.29	0.25

The samples were cut into cubic form from the ingot by using a mechanical saw.

Alloy elaboration

152 The elaboration has been carried out by the use of melting and maintenance furnaces,
 153 and casting pockets with capacities of 350 kg, 150 kg and 50 kg respectively.

154 A mixture of 160 kg of AlSi10Mg ingots with dimension of (720x100x80) mm³
 155 delivered by PECHINEY added to 190 kilograms of returns (Runners, channels of casting,
 156 defective and rejected parts... etc.) was melted at a temperature between 700 to 750 °C, then
 157 cleaning and creaming were carried out, afterwards the liquid mass was subjected to a
 158 degassing treatment, and finally the liquid metal was cast in the maintenance furnace at
 159 750°C, where the refining operation and a second cleaning were performed. 15 kg of the
 160 liquid metal has been cast in a casting pocket and then in sand moulds. The obtained ingot
 161 was in dimension (300x100x60) mm³. No chemical composition correction, in the liquid
 162 mass, has been done during sand cast alloy elaboration.

163

164 ***Sample preparation and microstructure characterization***

165

166 Metallographic observations were performed using optical microscopy. The samples
 167 were prepared by means of the standard metallographic procedure as following: the samples
 168 were polished with emery paper from 600 to 4000 grit, then degreased with ethanol (from
 169 SIGMA ALDRICH Company, with purity $\geq 99.8\%$), cleaned with distilled water, and finally
 170 dried in air. The etching process was performed in the solution composed of 99.9 in wt. %
 171 H₂O (Monodistilled) and 0.1 in wt. % NaOH (from SIGMA ALDRICH company, and purity
 172 $\geq 98.8\%$).

173 The sample surfaces were observed by optical microscopy and scanning electron
 174 microscopy before and after immersion during two weeks in aerated chloride solution of 0.3
 175 wt. %. Microstructural analyses of the samples were carried out using a metallurgical
 176 microscopy (Carl Zeiss ICM405 microscopy) and a scanning electron microscopy (FEG Zeiss
 177 Ultra 55) equipped with an energy dispersive spectrometer EDS (Brüker EDS Quantax).

178 The X-ray diffractograms of the materials were determined by XPERT PRO X-ray
 179 diffractometer at ambient temperature. The analyses of diffractograms (identification of
 180 aluminum peaks and intermetallic phases) were made by means of High Score software.

181

182 ***Electrochemical measurements techniques***

183

184 The electrochemical measurements for 1.13-cm² samples immersed in sodium
 185 chloride solution 0.3 and 3 wt. % NaCl at room temperature have been carried out. Using a

186 potentiostat/galvanostat GAMRY Reference 600+ controlled by software GAMRY
187 Framework. Input current /voltage range are 60 pA to 600 pA, -24 V to +24 V respectively.

188

189 A classic three-electrode method has been used. The reference electrode was a
190 saturated calomel electrode (SCE); the auxiliary electrode was a platinum grid (3-cm²).

191 Potentiodynamic polarization tests have been undertaken with a scanning rate equal to
192 1 mV/s from -1.2 V to -0.2 V according to the reference electrode.

193 The electrochemical impedance spectroscopy measurements were carried out in a
194 frequency range from 100 kHz to 1 mHz and with a 10 mV potential modulation amplitude.
195 To obtain accurate electrochemical impedance values, integration has been performed for
196 seven cycles.

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198

199 **Results and discussion**

200

201 The characterization of polished cast AlSi10Cu(Fe) aluminum alloy, both etched and
202 non-etched samples, using optical microscopy is shown in Fig. 1. As it can be observed, the
203 cast AlSi10Cu(Fe) aluminum alloy is characterized by a dendritic structure of the α -aluminum
204 solid solution phase and two forms for the aluminum-silicon eutectic (silicon plate-like
205 eutectic and coral-like eutectic). Firstly, unmodified silicon eutectic (silicon plate-like
206 eutectic) is observed as it is for industrial solidifying conditions. Secondly, a modified coral-
207 like eutectic phase is distributed over the entire sample surface with a low density as it is
208 visible in Fig. 1e. Other secondary phases in the microstructure of the aluminum alloy such as
209 rich-Cu phase and Chinese script phase $\text{Al}_{15}(\text{Mn},\text{Fe})_3\text{Si}_2$ have been observed (Fig. 1). In order
210 to identify the types of phases, EDS analysis has been used.

211 Micrographs of sand casting aluminum alloy AlSi10Cu(Fe) are shown in Fig. 2. For
212 all figures, presence of pores and phases has been observed at micro and nano scales. The
213 identified phases are α -Al matrix, Al-Si eutectic which appeared in the interdendritic space
214 and intermetallic compounds.

215 The observed micro and nanopores are due to hydrogen gas arising during melt casting
216 because of a low speed cooling in sand casting: hydrogen gas remains in the solidified melt in
217 pores and micro shrinkages, as described by (Michna et al. 2007). On the other hand, some
218 pores are due to the effect of iron castability in AlSi10Cu(Fe) alloy, as reported by several
219 authors (Taylor et al. 1995; Mbuya et al. 2003; Roy et al. 1996), iron may degrade the

castability of the alloys and an increase of iron content in alloy generates an increase of porosities rate. Moreover, the formation of iron rich intermetallic phases can lead to the formation of shrinkage and porosity defects (Taylor 2004; Berlanga-Labari et al. 2020). An increase of iron content in alloys leads to an increase in hydrogen gas pressure in equilibrium, which is related to a given rate of dissolved gas. Moreover, the iron β -Al₅FeSi phase can provide pore nucleation sites (Mbuya et al. 2003; Roy et al. 1996). In our case, the mass percentage of iron in the alloy is equal to 1.21 wt. % and the solubility of iron in the aluminum matrix is very low, *i.e.* 0.04 wt. % at 655 °C, and less than 0.01 wt. % at room temperature. As a result, several iron-rich intermetallic particles can form during solidification, leading to the formation of porosities in the alloys. Other phases, Al₂Cu and sludge for example, restrict pore growth and expansion (Roy et al. 1996). It should be noted that the nanopores were only observed at the surface of the matrix.

As described in literature (Tilloy et al. 2012), the size of micro and nanoparticles and the morphology of intermetallic phases depend on various parameters such as chemical composition, solidification conditions and particularly heat treatment process. The used AlSi10Cu(Fe) cast aluminum alloy samples have not undergone heat treatments, leading to the presence of micro and nanoporosities with an average rate of 4 % and 5 %, respectively. The size of the observed nanoparticles varies between 20 to 150 nm.

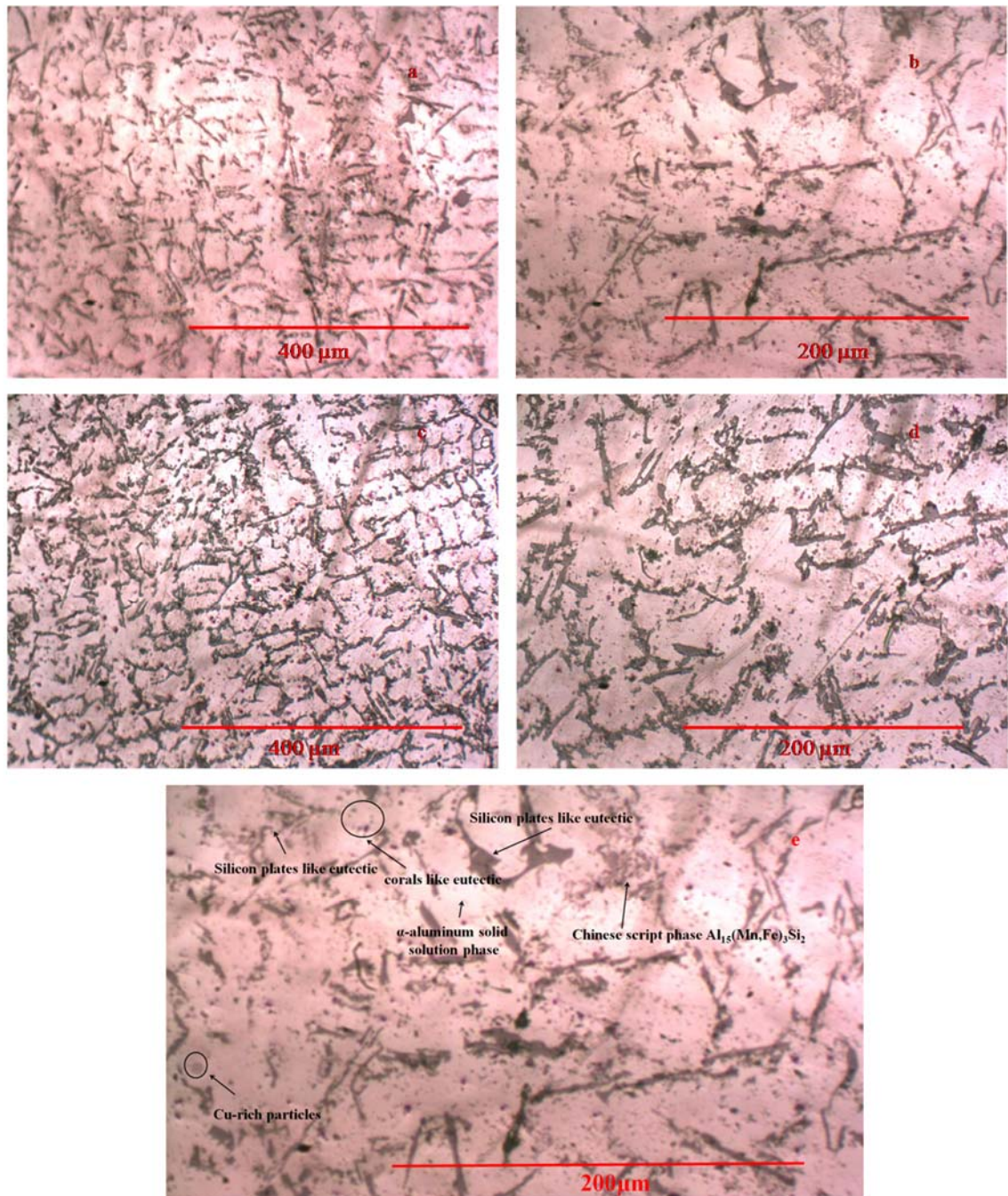
SEM images associated with EDS spectra and chemical composition of a polished AlSi10Cu(Fe) cast aluminum alloy sample before immersion in chloride solution, for three zones, are shown in Figs. 3, 4 and 5 - Tables 2, 3 and 4, respectively. These figures show the matrix phase, the eutectic phase and different other secondary phases and particularly numerous chemical compositions for each secondary phase. These figures and the EDS spectra highlight that the samples are multicomponent aluminum alloys with various elements (Al-Si-Cu-Fe-Mn-Mg-Zn-Ni). The details of chemical composition for each sample are shown in Tables 2, 3 and 4.

According to the literature, these elements have a low solubility at room temperature but in this case, their concentrations in the alloys are higher than their solubility in aluminum at ambient temperature (Mathers 2002; Reardon 2011; Ambat et al. 2006; McAlister and Murray 1987; Bannour et al. 2013; Skoko et al. 2009; Jia et al. 2018). It means that equilibrium is not reached; these elements may also exist in supersaturated solid solutions or in non-equilibrium intermetallic phases (Mathers 2002).

In Al-Si alloy, Al-Si multicomponent alloys or commercial and hypoeutectic alloys, several phases such as Al₂Cu, Mg₂Si, α -Al₁₂(Fe,Mn)₃Si₂, β -Al₅FeSi, etc. have been reported

254 by (Mbuya et al. 2003). In this work, a new phase $\text{Cu}_{61.22}\text{Zn}_{25.39}\text{Ni}_{11.85}\text{Al}_{1.54}$ has been
 255 evidenced, as it can be observed in Fig. 4 and Table 3.

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258 **Fig. 1.** Optical micrographs of AlSi10Cu(Fe) alloy: non etched sample(a-b), etched sample(c-
 259 d), zoom of fig. 1b (e).

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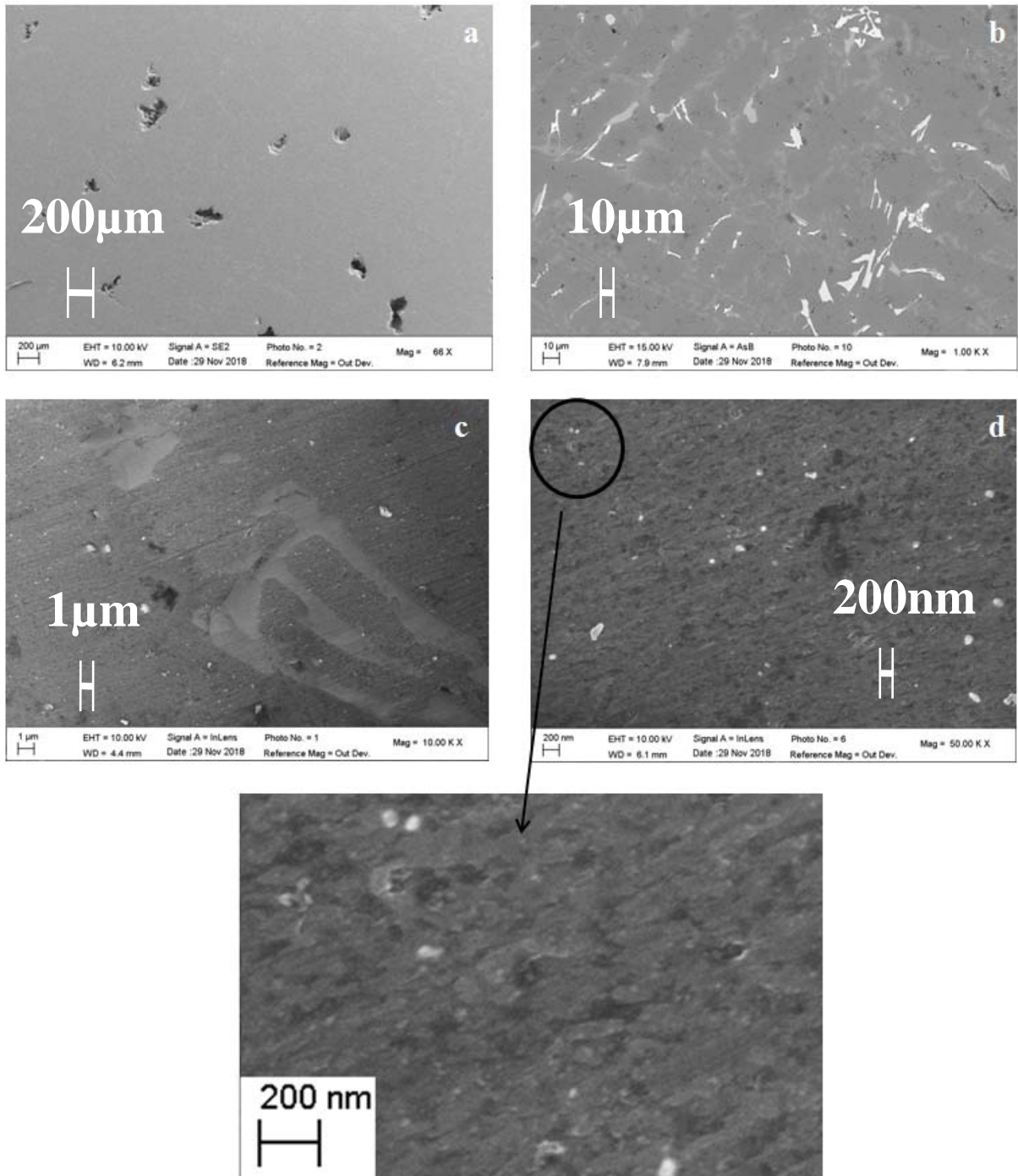


Fig. 2. SEM images of polished, non-etched samples of AlSi10Cu (Fe) cast aluminium alloy before immersion: (a-b) micropores, (c) microphases, and (d) nanophases and nanopores.

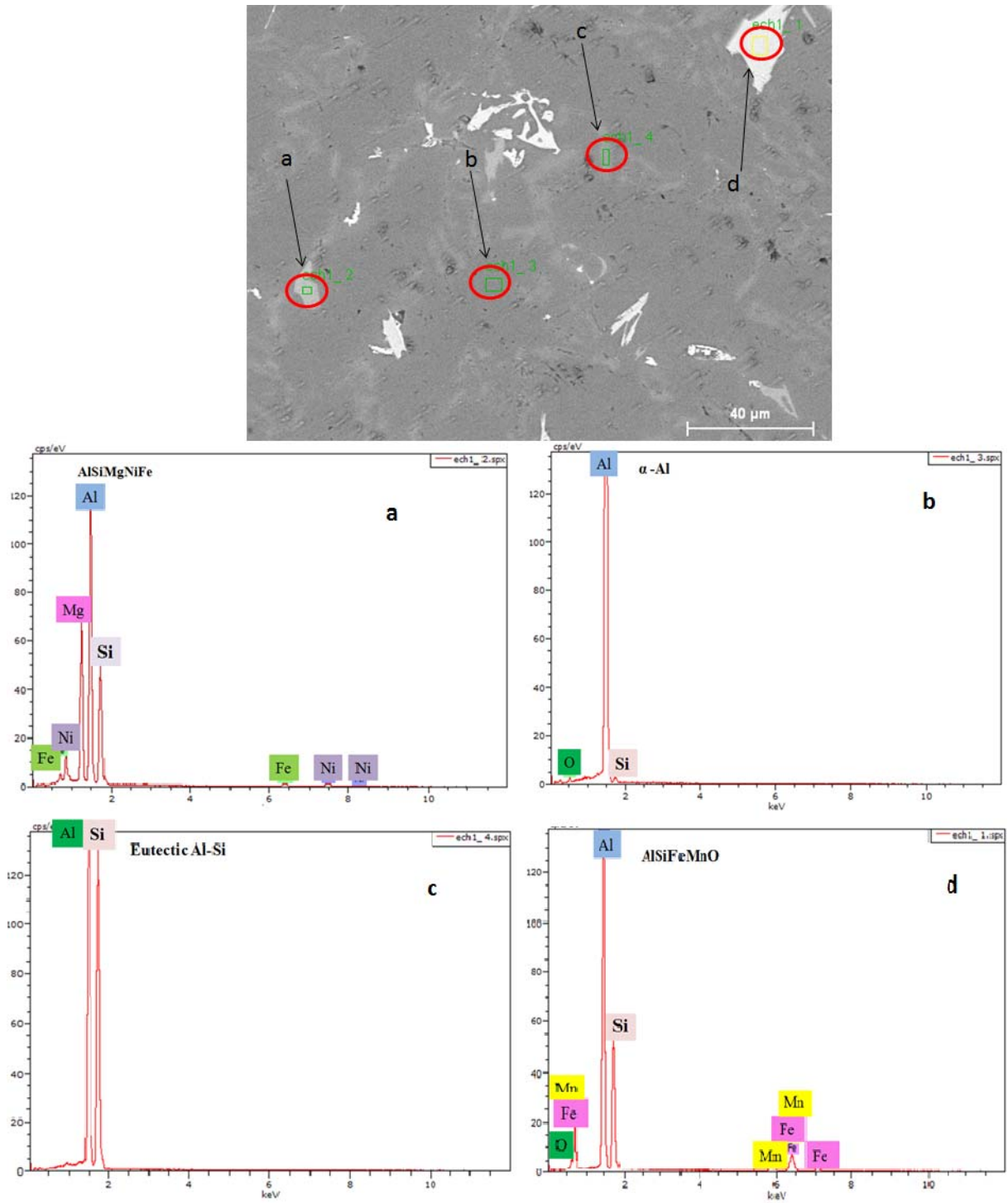


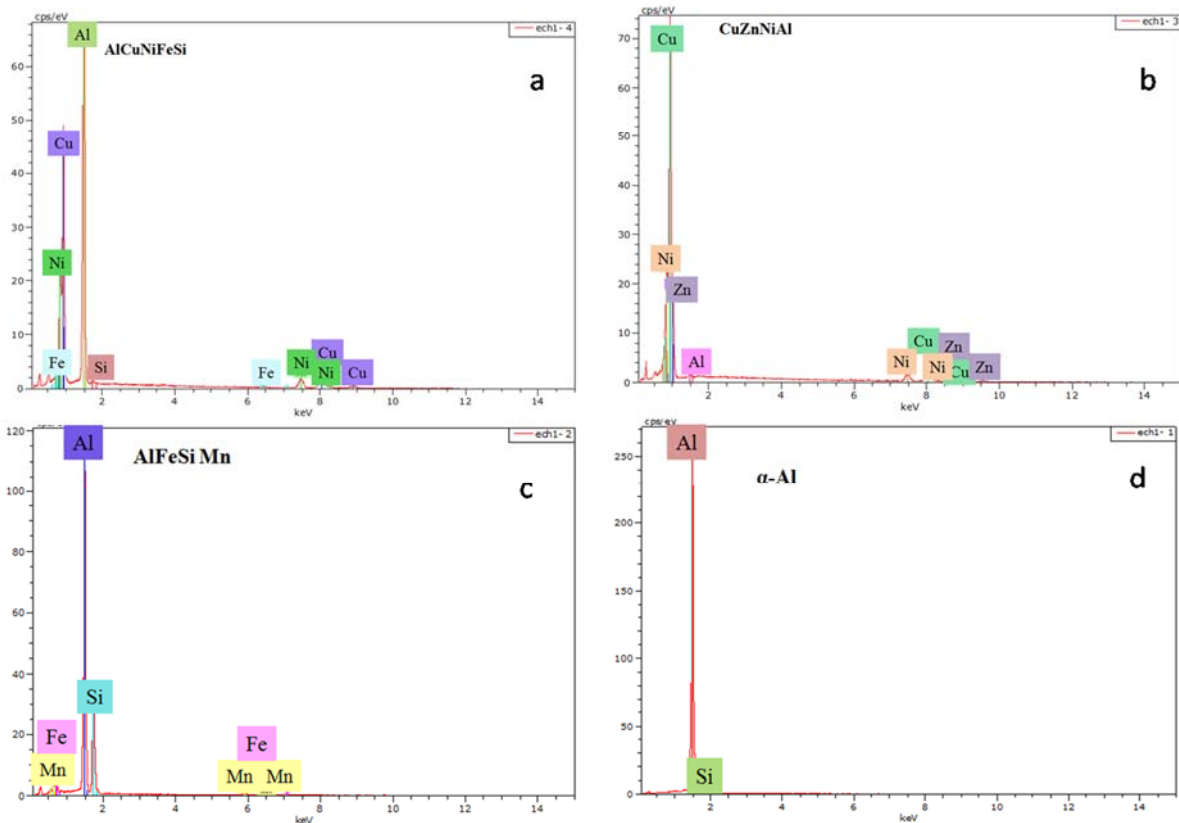
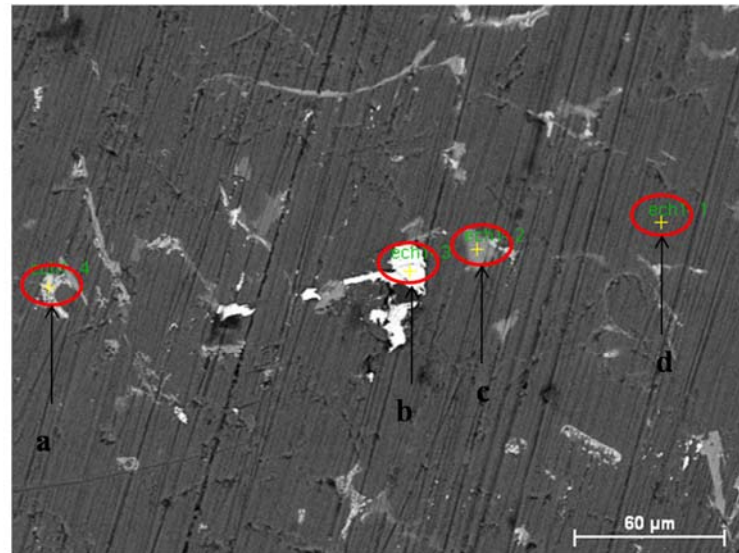
Fig. 3. SEM image and EDS spectra of points (a, b, c, and d) in zone 1 for non immersed sample.

278 **Table 2.** EDS results, chemical compositions, for some points of non-immersed sample in zone 1

279

<i>Point a, AlSiMgNiFe</i>			<i>Points b, α-Al</i>		
<i>Element</i>	<i>wt. %</i>	<i>at. %</i>	<i>Element</i>	<i>wt. %</i>	<i>at. %</i>
Mg _k	19.37	22.69	O _k	1.80	2.99
Al _k	42.05	42.05	Al _k	96.69	95.57
Si _k	26.77	26.77	Si _k	1.51	1.43
Fe _k	3.94	3.94			
Ni _k	7.87	7.87			
<i>Total</i>	100	100	<i>Total</i>	100	100
<i>Point c, Eutectic Al-Si</i>			<i>Point d, AlSiFeMnO</i>		
<i>Element</i>	<i>wt. %</i>	<i>at. %</i>	<i>Element</i>	<i>wt.%</i>	<i>at. %</i>
Al _k	46.47	47.47	Al _k	43.87	51.89
Si _k	53.53	52.53	Si _k	26.57	30.19
			Fe _k	25.84	14.77
			O _k	0.70	1.40
			Mn _k	3.02	1.76
			<i>Total</i>	100	100
<i>Total</i>	100	100	<i>Total</i>	100	100

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282 **Fig. 4.** SEM image and EDS spectra of points (a, b, c and d) in zone 2 for non immersed
 283 sample

284

285 **Table 3.** EDS results, chemical compositions, for some points of non-immersed sample in zone 2

<i>Point a, AlCuNiFeSi</i>			<i>Point b, CuZnNiAl</i>		
<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>	<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>
Al _k	35.40	55.73	Ni _k	11.06	11.85
Si _k	0.27	0.40	Cu _k	61.87	61.22

Ni _k	14.48	10.48	Zn _k	26.41	25.39
Cu _k	49.20	32.89	Al _k	0.66	1.54
Fe _k	0.65	0.49			
<i>Total</i>	<i>100</i>	<i>100</i>	<i>Total</i>	<i>100</i>	<i>100</i>
<i>Point c, AlSiFeMn</i>			<i>Point d, α-Al</i>		
<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>	<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>
Al _k	47.95	58.15	Al _k	98.09	98.16
Si _k	19.55	22.78	Si _k	01.91	01.84
Fe _k	29.28	17.16			
Mn _k	03.22	01.92			
<i>Total</i>	<i>100</i>	<i>100</i>	<i>Total</i>	<i>100</i>	<i>100</i>

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The Fe containing insoluble phases can take place in different forms including large or small needles or platelets, Chinese script, spheroidal or globular, rosette-like, polygonal, hexagonal, polyhedral, star-like, clusters. Other shapes can also be observed, for examples π -Al₈Mg₃FeSi₆ in a Chinese script morphology, Al₅FeSi as needles, β -Al₅FeSi in platelet form, Al₁₅(Fe,Mn)₃Si₂ in polyhedron forms, [Al₁₅(Fe,Mn,Cr)₃Si₂] in sludge form (Mbuya et al. 2003; Roy et al. 1996; Taylor 2004; Tillov et al. 2012). The large number of phases, the multicomponent aspect and the differences in the composition, form, and phase size, for the aluminum-silicon alloys, does not facilitate the study of the corrosion behavior of these alloys.

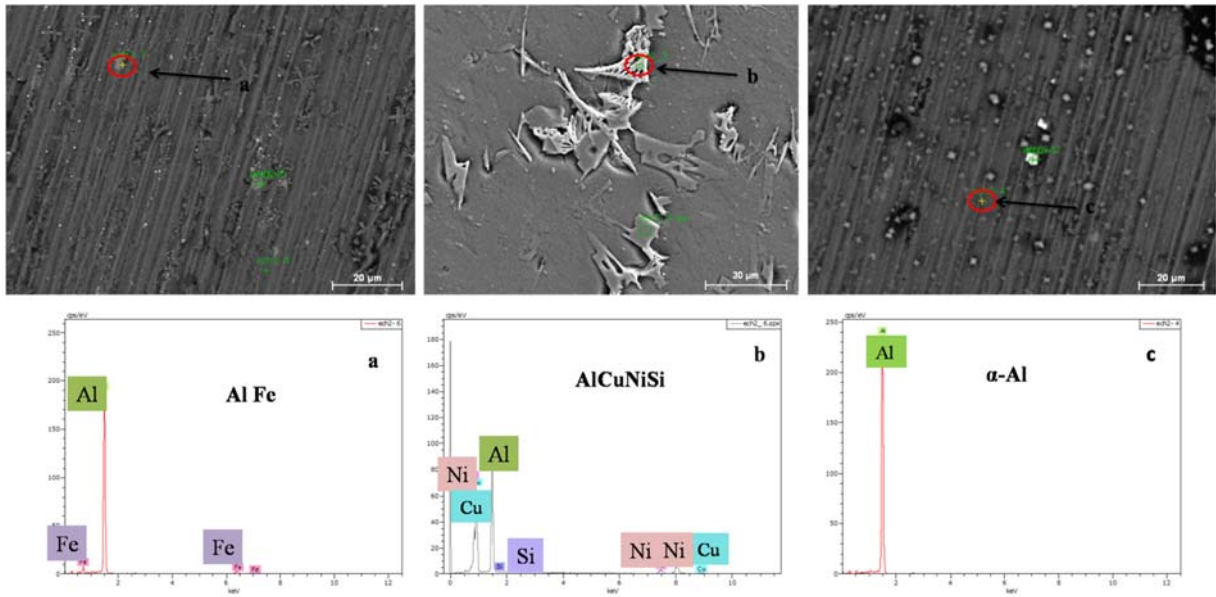


Fig. 5. SEM image and EDS spectra of non immersed sample: (a) zone 3, (b) zone 4, (c) zone 5

Table 4. EDS results, chemical compositions, for some points of non-immersed sample in zone 3

<i>Zone 3 (a) Al Fe</i>			<i>Zone 4(b) AlCuNiSi</i>		
<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>	<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>
Al _k	87.98	93.81	Al _k	38.38	58.73
Fe _k	12.02	0.49	Si _k	0.31	0.46
Total	100	100	Cu _k	44.12	28.68
			Ni	17.19	12.10
			Total	100	100
<i>Zone 5(c) α-Al</i>					
<i>Elements</i>	<i>wt. %</i>	<i>at. %</i>			
Al _k	100	100			
Total	100	100			

Fig. 6 shows the X-ray diffractogram of the aluminum AlSi10Cu(Fe) sand cast alloy. The aluminum peaks are observed in the diffractogram (Fig. 6a). All seventeen phases present in the alloy are shown in Fig. 6b and listed in Table 5. Three phases (7, 10 and 15) contain

zinc, the phase (7) is close to the phase observed by EDS as described in Table 3 and Fig. 4, which confirms the presence of the $\text{Cu}_{61.22}\text{Zn}_{25.39}\text{Ni}_{11.85}\text{Al}_{1.54}$ phase.

Figures 7-11 show the SEM images for several zones of AlSi10Cu(Fe) sand casting aluminum alloys, immersed in 0.3 wt. % NaCl solution during two weeks. The corrosion morphology of the material after immersion in chloride solution is very complex. Independently of the contact between the second phases and the matrix, it seems that the generalized corrosion is extended over the matrix phase, as shown in Fig. 7 (d, e), Fig. 9 (a, b), Fig. 10(c, d) and Fig. 11(a-c). The presence of second phases on the surface of the alloy promotes the formation of microgalvanic cells between the matrix and the second phases resulting in the corrosion of the matrix surrounding the second phases (Fig. 7(d, e), Fig. 9(a, b), Fig. 10(a- b) and Fig. 11(b, c, e)) or in the dissolution of second phases (Fig. 7(a-c), Fig. 10(c-d) and Fig. 11(b-c)). The corrosion occurring on the matrix surrounding the second phases is due to the higher corrosion potential of the existing phases, as $\text{Al}_2\text{Cu}(\theta)$, AlFeMnSi , AlCuFeMn , AlCuFeSi , and $(\text{Al,Cu})_x(\text{Fe,Mn})_y\text{Si}$, and the more active aluminum matrix. According to the work of (Birbilis and Buchheit 2005), the cathodic nature of these intermetallic phases compared to the matrix, causes the reaction of oxygen reduction on the intermetallic particles surface, leading to the formation of hydroxide ions. At the same time, a local increase in pH takes place, which provides a breakdown of the flimsy oxide film and the dissolution of the area surrounding the intermetallic particles phases. The presence of iron, copper and nickel in intermetallic phases has a determinant effect on the alloy resistance in chloride solution (Ambat et al. 2006; Seri et al. 1989; Hossain et al. 2015). The dissolution of intermetallic particle phases, and/or less noble segregated elements, is characterized by a perforation encircled by white circles, surrounding the β -Fe plate phases, as observed in Fig. 11f. In this case, the dissolved intermetallic particles are less noble than the surrounded phases and the matrix phases, the same phenomenon occurs between the nobler phases (matrix and surrounded phases) and the dissolved phase. According to (Birbilis and Buchheit 2005), this can be due to the fact that the dissolved phases contain one, two or all elements which are contained in the alloy, including zinc, magnesium and manganese.

The dissolution of the α -aluminum phase in silicon eutectic is showed in Fig. 7 (a-c), Fig. 10 (b-d) and Fig. 11 (a-c). This dissolution can be explained by the potential difference between α -aluminum phase and silicon phase since the silicon phase potential is always higher than the α -aluminum phase potential in chloride solution (Birbilis and Buchheit 2005).

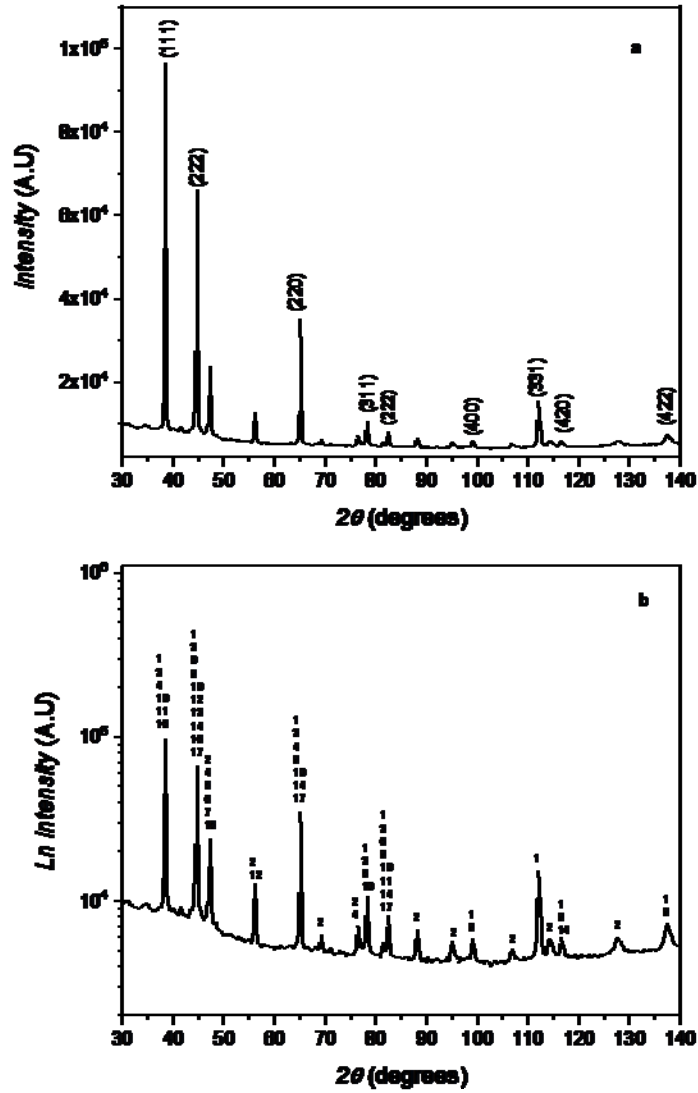


Fig. 6. X-ray spectrum of the aluminium AlSi10Cu(Fe) sand cast alloy: (a) aluminum diffraction plans and (b) all seventeen phases in the alloy.

Fig. 9 shows the formation of several hemispherical pits in certain zones or only one pit in other zones. The authors observed also a localized corrosion with crater shape in the nanopores of the matrix phases (Fig. 8). We assume that the pit beginning occurs at nanopore level.

358

359 **Table 5.** Seventeen phases present in AlSi10Cu(Fe) sand cast alloy

360

<i>Phase Number</i>	<i>Chemical Formula</i>	<i>Diffraction angle 2 θ (degrees)</i>	<i>Diffraction plans (hkl)</i>
1	Al	38.47, 44.718, 65.094, 78.226, 82.431, 99.081, 112.046, 116.574, 137.463	(1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 0 0), (4 0 2)
2	Si	47.313, 56.135, 69.144, 76.395, 88.054, 94.976, 106.937, 114.124, 127.587, 136.946	(2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1), (4 4 0), (5 3 1), (6 2 0), (5 3 3)
3	Al ₉ Si	38.498, 44.751, 78.289, 82.701	65.144, (1 1 1), (0 0 2), (0 2 2), (1 1 3), (2 2 2)
4	Al ₈ FeMg ₃ Si ₃	38.695, 65.003, 76.322	(2 0 2), (4 0 0), (3 2 2)
5	Al ₉ Fe ₂ Si ₃	45.603, 78.780	(8 2 0), (3 5 0)
6	Al ₂ Cu	47.569, 82.352	(3 1 0), (3 2 3)
7	Ni ₇ Cu ₃ Zn ₁₀	47.359	(2 0 0)
8	Al ₉ Fe _{0.84} Mn _{2.16} Si	44,682	(2 0 3)
9	Fe ₇ Ni ₃	44.762, 65.161, 82.524, 99.198, 116.732, 137.713	(1 1 0), (2 0 0), (2 1 1), (2 2 0), (3 1 0), (2 2 2)
10	Al _{3.8} Zn _{0.2}	38.568, 44.833, 78.451, 82.675	65.271, (1 1 1), (0 0 2), (0 2 2), (1 1 3), (2 2 2)
11	Al ₆ CuMg ₄	38.269, 82.352	(1 1 0), (0 2 2)
12	Cu _{3.17} Si	44.600	(1 0 0)
13	Al ₉ Mn ₃ Si	44.780	(0 2 3)
14	Mn ₃ Si	44.762, 65.161, 116.732	82.524, (2 2 0), (4 0 0), (4 2 2), (6 2 0)
15	ZnNi	47.488	(0 2 2)
16	AlCu	38.853, 44.763	(3 0 0), (3 1 0)
17	Cu ₃ Si	44.537, 65.238, 82.267	(0 1 2), (0 0 3), (2 5 0)

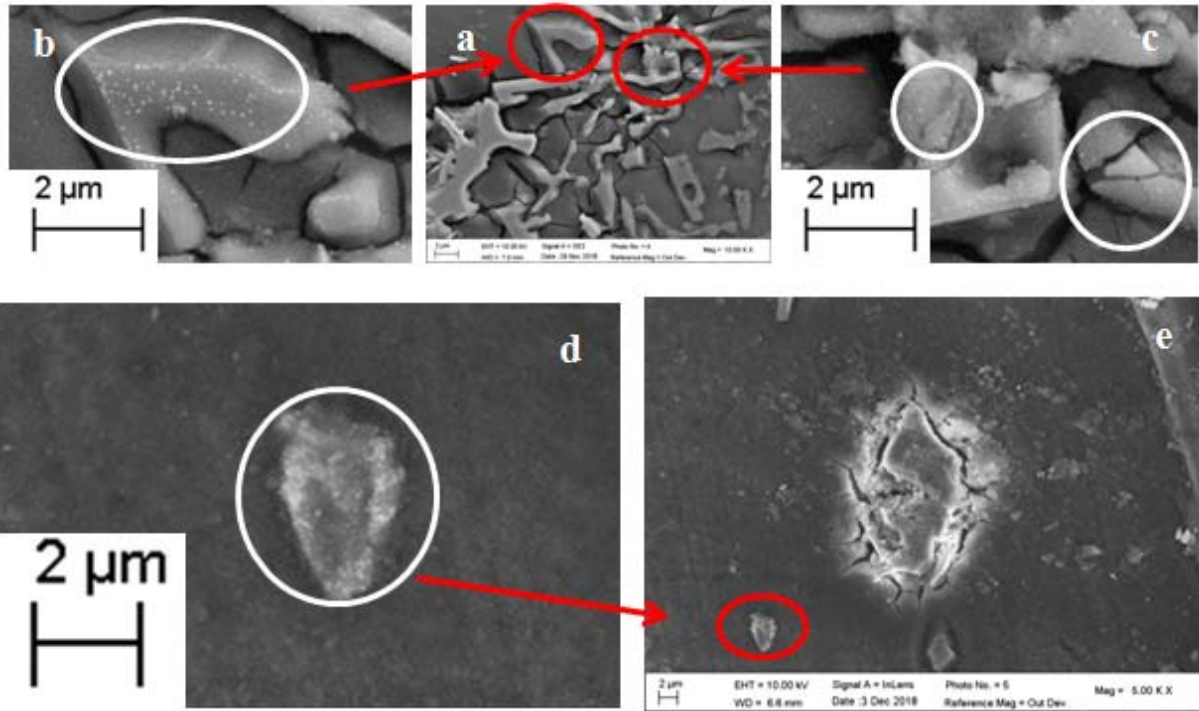
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362

363 Small white 50-200 nm size intermetallic particles can be observed in Fig. 7 (b, c, d), Fig.
 364 10 (c-d) and Fig. 11 (e-f). Particles of approximately 50 nm size were observed on the silicon
 365 plates-like eutectic (Figs. 7b and 7c) and coral-like eutectic phases (Fig. 7d). These particles
 366 were not dissolved after two weeks of immersion in chloride solution, meaning that their
 367 corrosion potential is higher than those of all other present phases.

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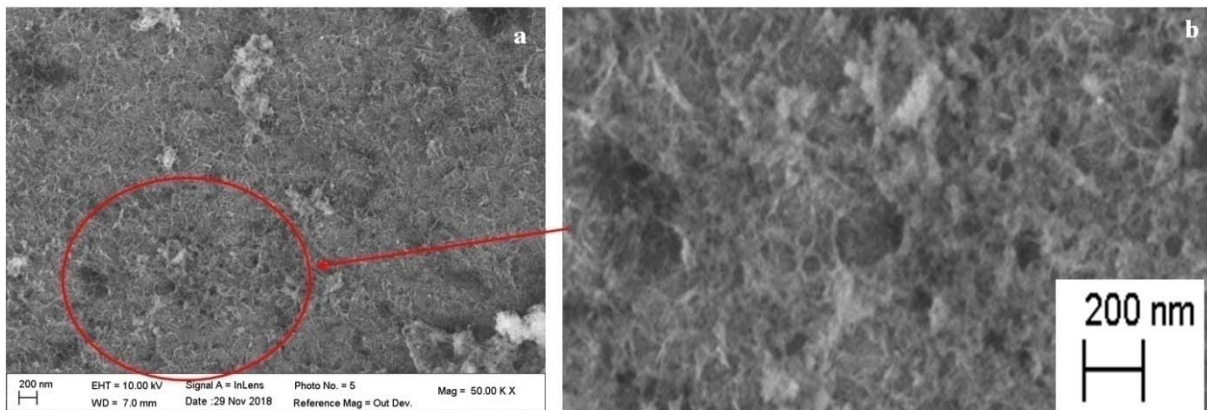


370

371 **Fig. 7.** SEM images of non-polished AlSi10Cu(Fe) sand cast aluminum alloy after two weeks
 372 of immersion in 0.3 wt. % NaCl solution (a, e). Dissolution of α -aluminum phase surrounding
 373 second phases, (b, c) magnification of SEM image presented in (a), (d) magnification of SEM
 374 image presented in (e), (b, c, d) small white intermetallic particles.

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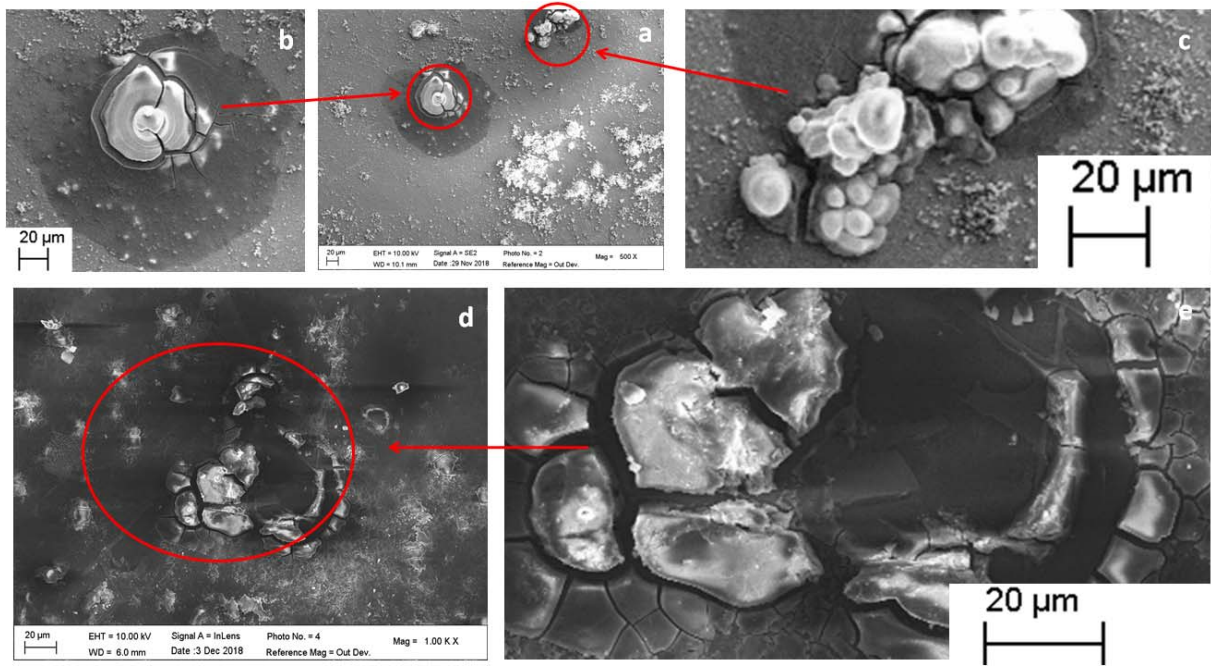
377

378 **Fig. 8.** SEM images of non-polished AlSi10Cu (Fe) sand cast aluminum alloy after 15 days of
 379 immersion in 0.3 wt. % NaCl solution: (a) corrosion presence at the nanopores, (b)
 380 magnification of SEM image presented in (a).

381

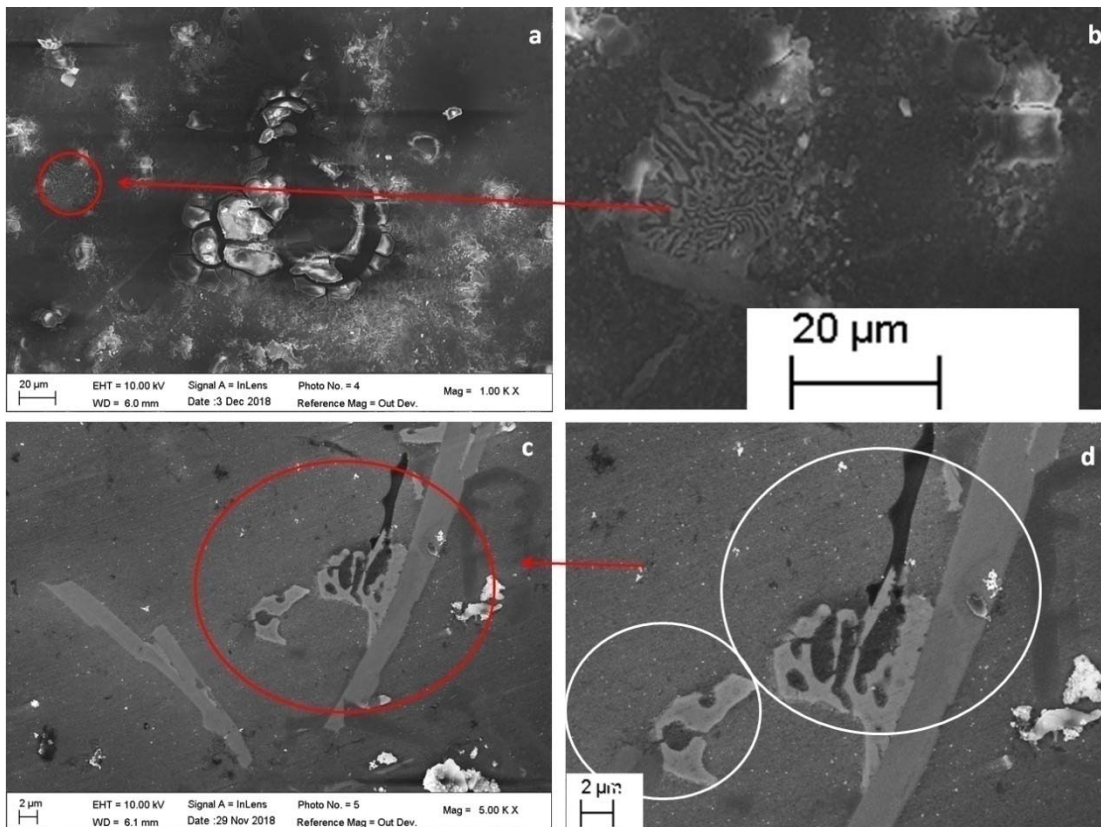
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384

385 **Fig. 9.** SEM images of non-polished AlSi10Cu(Fe) sand cast aluminum alloy after two weeks
 386 of immersion in 0.3 wt. % NaCl solution: (a, d) hemispherical pits, (b, c) magnification of
 387 SEM image presented in (a), (e) magnification of SEM image presented in (d)



388

389 **Fig. 10.** SEM images of non-polished AlSi10Cu(Fe) sand cast aluminum alloy after two
 390 weeks of immersion in 0.3 wt. % NaCl solution: (a, c) dissolution of α -aluminum phase
 391 surrounding eutectic phase, (b, d) magnification of SEM image presented in (a, c).

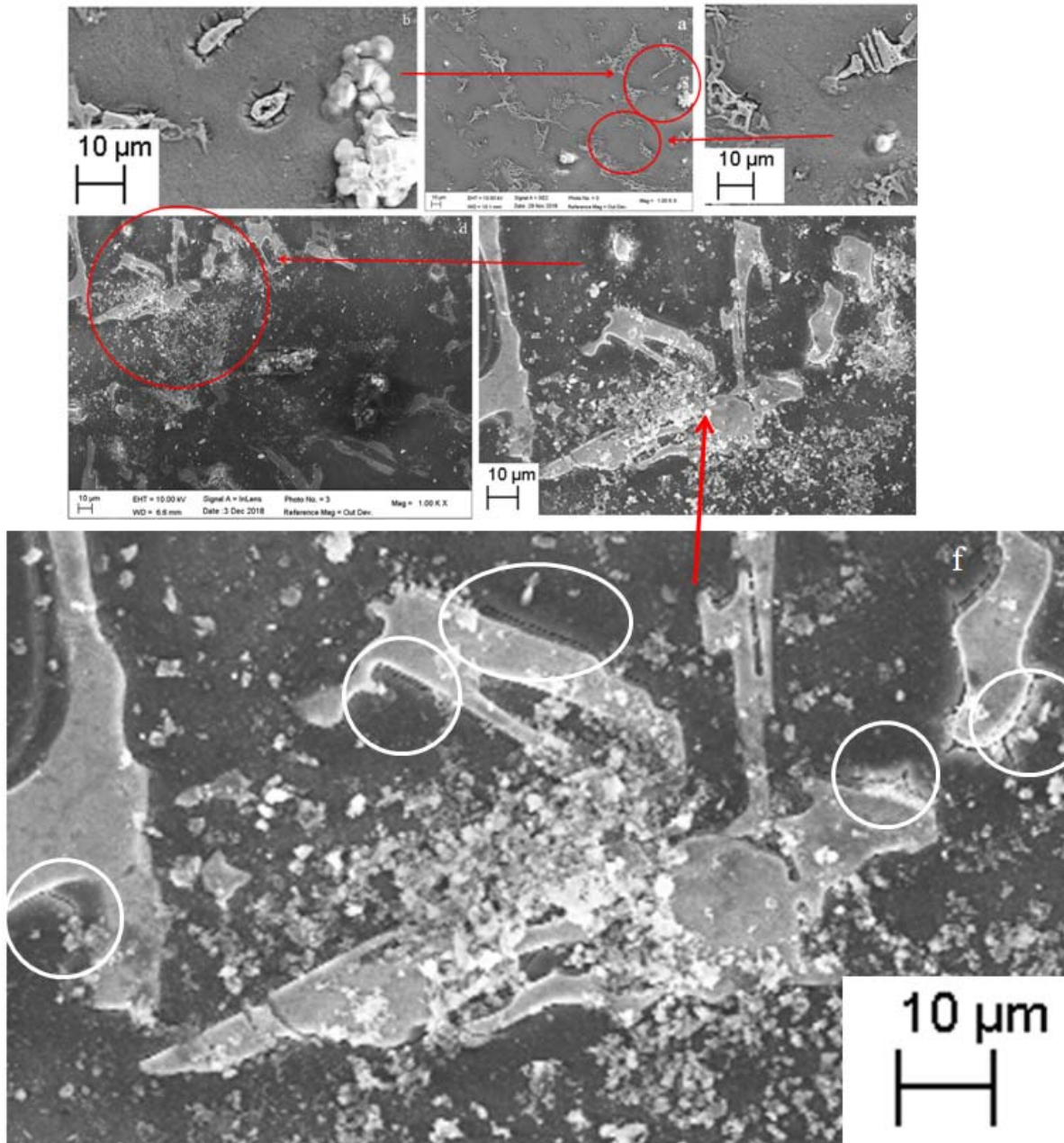


Fig. 11. SEM images of non-polished AlSi10Cu(Fe) sand cast aluminum alloy after two weeks of immersion in 0.3 wt. % NaCl solution: (a, c, d) extended generalized corrosion, (b, c, e) corrosion on the matrix surrounding the second phases, (b, c, f) dissolution of second phases.

SEM images associated with EDS spectrum and chemical composition of AlSi10Cu(Fe) cast aluminum alloy after two weeks of immersion in chloride solution are shown in Fig. 12 and Table 6, respectively. Two points (a and b) in zone 6 have been chosen in the areas adjacent to the pits.

We observe the presence of oxygen, magnesium, aluminum, chlorine, carbon and oxygen in point a, and aluminum, silicon, magnesium and chlorine in point b. This result is in accordance with (Yoo et al. 2011). Moreover, the formation of a homogeneous layer of hydrated aluminum oxide surrounding the pit has been identified, confirming a pitting corrosion mechanism. In fact, hydrated and dehydrated aluminum oxides can be formed when aluminum is exposed to a solution containing aggressive ions, as in our case (Pourbaix 1974). The EDS analyses showed also the presence of carbon traces.

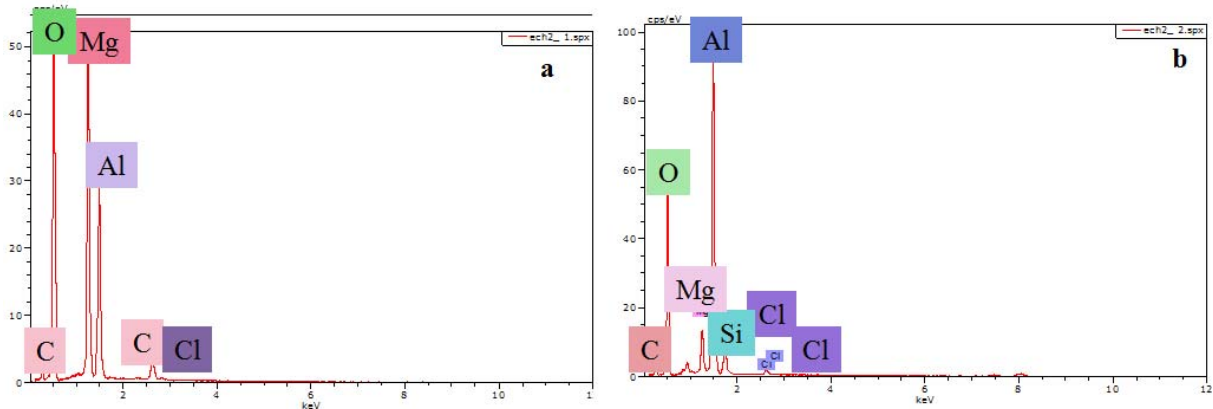
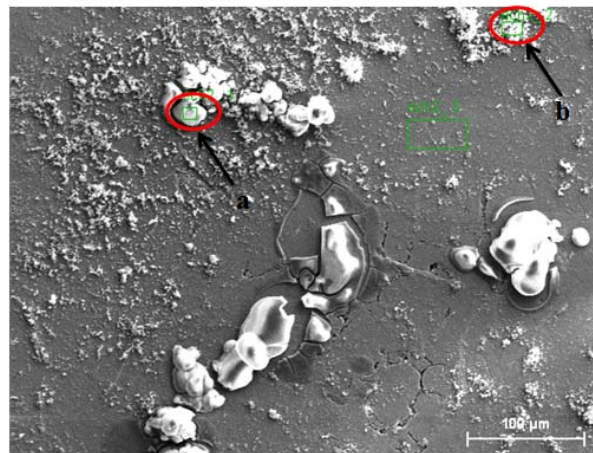


Fig. 12. SEM image and EDS spectra of points (a and b) in zone 6 of AlSi10Cu(Fe) sand cast aluminum alloy after two weeks of immersion in 0.3 wt. % NaCl

Electrochemical analyses including current-potential curves and electrochemical impedance spectroscopy of AlSi10Cu(Fe) sand cast alloy immersed in 0.3 and 3 wt. % NaCl solutions for different times are shown in Figs. 13, 14, 15, 16, 17, 18, 19 and 20 - Tables 7, 8, 9 and 10.

Table 6. EDS results, chemical composition, in some region of two weeks of corroded sample in 0.3 wt. % NaCl

<i>Point a</i>			<i>Point b</i>		
<i>Element</i>	<i>wt. %</i>	<i>at. %</i>	<i>Element</i>	<i>wt. %</i>	<i>at. %</i>
O _k	60.71	71.39	O _k	47,00	59,88
Mg _k	21.31	16.49	Mg _k	5.04	4,23
Al _k	15.46	10.78	Al _k	40.61	30.68
Cl _k	2.52	1.34	Cl _k	0.85	0.49
			Si _k	6.50	4.72
<i>Total</i>			<i>Total</i>	100	100

Fig. 13 shows difference in corrosion kinetics between the first hour immersion and after two weeks immersion in a 0.3 wt. % NaCl solution. A large decreasing of corrosion potential was observed, from -0.583 V after one hour- immersion to about -1.09 V after two weeks. Moreover, a weak increase of polarization resistance is observed after two weeks, i.e. from 2.5 kΩ to 2.8 kΩ (Table 7). In Figs.14 and 15, we observe a huge corrosion potential decrease from -0.583 V to -1.140 V, between 1h and 7 days immersion, followed by a corrosion potential increase up to -1.097 V after two weeks of immersion. A large increase of polarization resistance was observed between 1h and 24 h immersion, from 2.5 kΩ to 16.5 kΩ, thereafter a decrease until 7 days, from 16.5 kΩ to 2.1 kΩ, and finally an increase to 2.8 kΩ after 14 days (Table 7). The variations in corrosion potential and polarization resistance are due to an oxide layer formation and the dissolution of noble metals on the alloy surface.

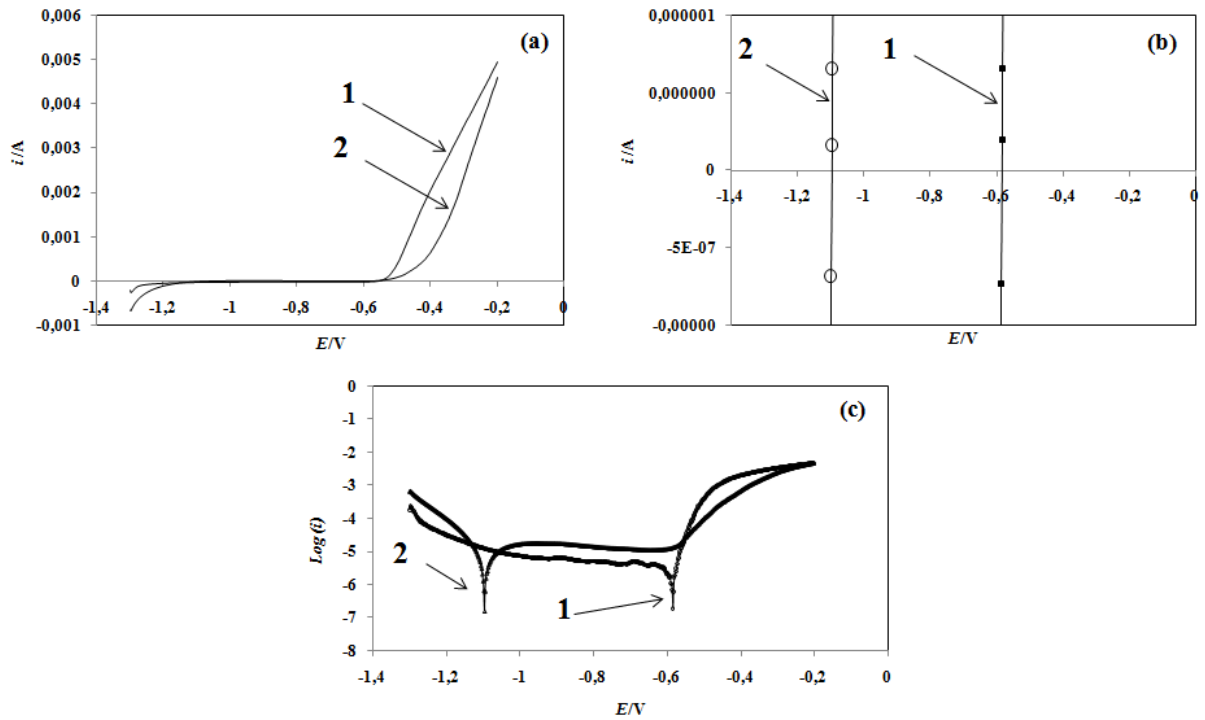
The corrosion rate is determined using the following relation (Rossi et al. 2007):

$$v = \frac{Ai_{corr}}{n.F.\rho} \quad (1)$$

Where A is Material molar mass (g/mol.), i_{corr} Current corrosion density ($\mu\text{A}/\text{cm}^2$), n Exchanged electrons number, F Faraday constant = 96500C, ρ Density of metal (g/cm^3).

The corrosion rate increases from 0.043 mm/year after 1 h of corrosion to 0.274 mm/year after 7 days immersion, and decreases to 0.172 mm/year after 2 two weeks.

Wide passive zones, followed by the breakdown of passive film and excessive dissolution, were observed after corrosion during three, seven days and two weeks, their values are ~570 mV, ~544 mV, ~500 mV respectively (Fig. 14).



449

450 **Fig. 13.** Polarization curves of AlSi10Cu(Fe) sand cast aluminum alloy after 1h immersion in
 451 0.3 wt. % NaCl solution (curve 1), and after 14 days of corrosion (curve 2) in 0.3 wt. % NaCl
 452 solution: (a) $i(E)$ curves, (b) magnifying effect of $i(E)$ polarization curves, and (c) $\log i(E)$
 453 curves.

454

455

456 The corrosion behavior of the alloy is similar in 3 wt. % NaCl solution. Figs. 16, 17
 457 and 18 show a difference in corrosion kinetics between the first hours until two weeks of
 458 immersion. A large corrosion potential decrease is observed, from -0.935V after one hour and
 459 -1.105 V after one week, then an increase to -1.092 V after two weeks . The polarization
 460 resistance decreases from 21 k Ω after one hour of immersion to 0.5 k Ω after 3 days of
 461 corrosion, and then increases up to 1.4 k Ω after two weeks (Table 8). The corrosion rate
 462 increases from 0.017 mm/year after 1 h of immersion to 0.466 mm/year after one week. Due
 463 to this high value, the use of this alloy is not recommended for seawater.

464 The increase of NaCl concentration in the solution greatly modifies corrosion potential values
 465 and polarization resistances during the first hour of immersion. In both cases the polarization
 466 resistance is the highest at the first hour and the corrosion potential converges to the same
 467 value after two weeks of immersion. The modification of the corrosion kinetics is probably
 468 due to pitting corrosion phenomenon (Figs. 9 and 10), appearance and disappearance of

microporosities and nanoporosities on the surface, presence of less noble elements segregated or not and particles dissolution as function of the immersion duration.

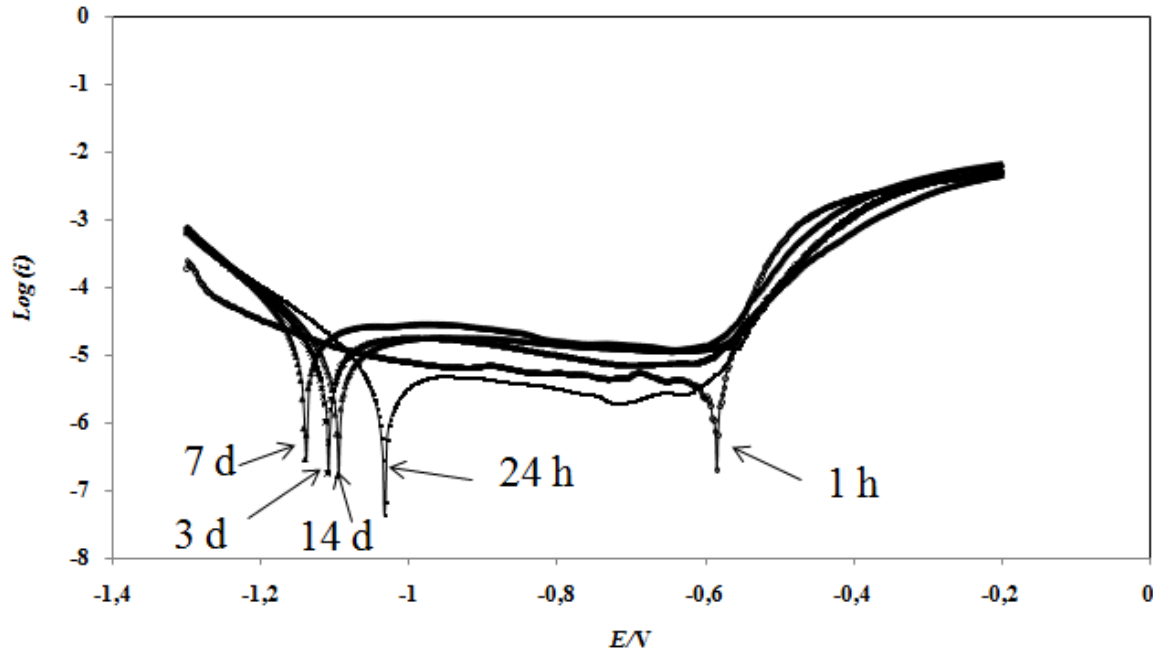


Fig. 14. Logi(E) curves of AlSi10Cu(Fe) sand cast aluminum alloy after immersion in 0.3 wt. % NaCl solution for duration of: 1h, 24h, 3days, 7 days, and 14 days.

Table 7. Corrosion potential, polarization resistance and corrosion current of the AlSi10Cu(Fe) sand cast aluminum alloy immersed in 0.3 wt. % NaCl solution

Immersion time	E_{corr} (V/SCE)	R_p (k Ω)	i_{corr} (μ A/cm ²)	V_{corr} (mm/year)
1h	-0.583	2.5	3.8	0.044
24h	-1.033	16.5	4.0	0.046
3days	-1.11	2.7	14.1	0.162
7days	-1.14	2.1	23.9	0.274
14days	-1.10	2.8	15.0	0.172

Wide passive windows, followed by the breakdown of passive film and excessive dissolution, were observed after twenty four hours, three days, seven days and two weeks of corrosion with values equal to ~429 mV, ~465 mV, ~493 mV, ~470 mV respectively (Fig. 18).

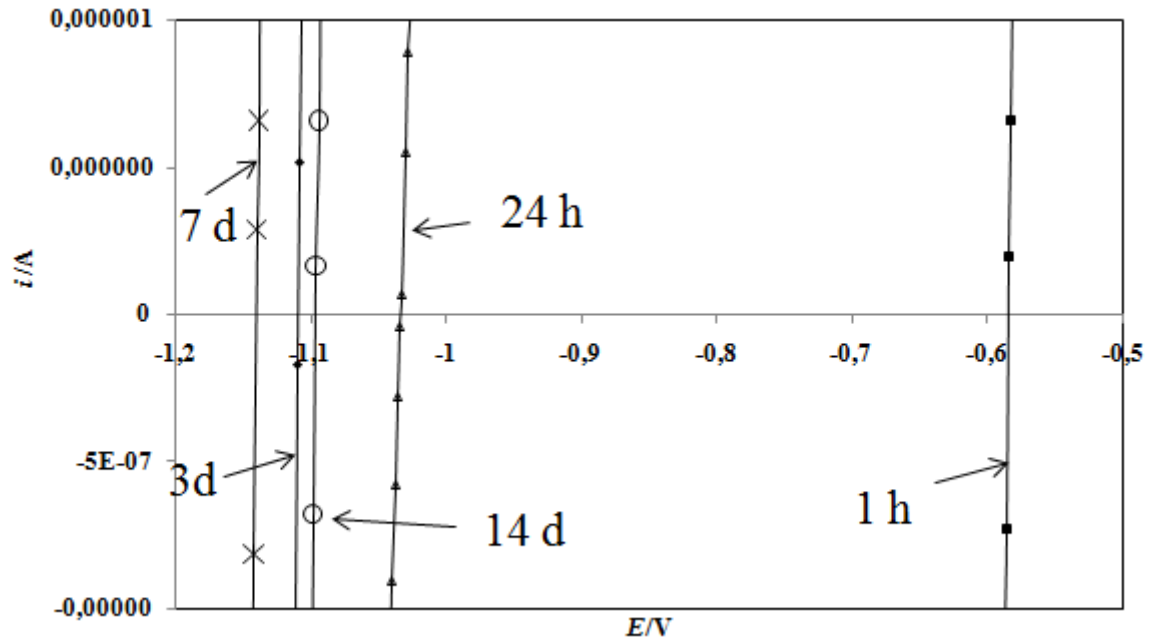


Fig. 15. Magnification of $i(E)$ curves AlSi10Cu(Fe) sand cast aluminum alloy after immersion in 0.3 wt. % NaCl solution for duration of: 1h, 24h, 3 days, 7 days, and 14 days.

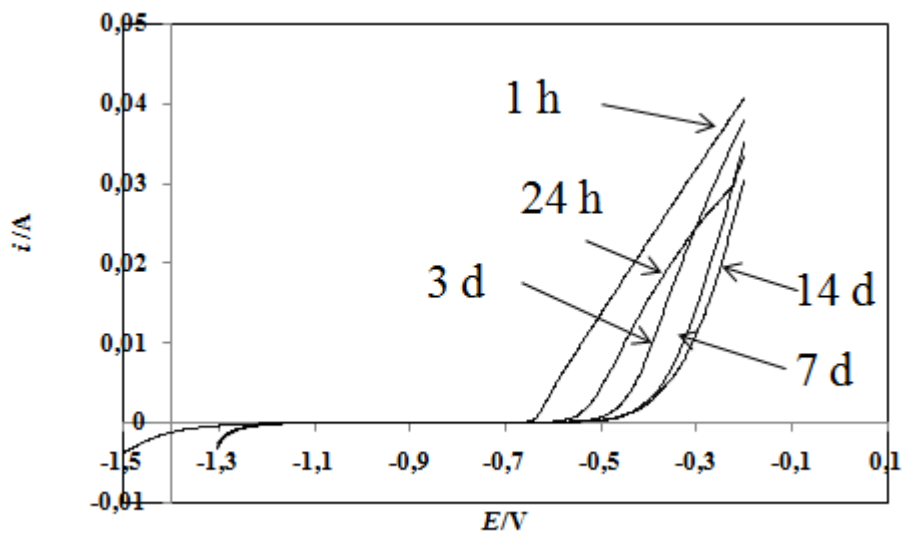


Fig. 16. $i(E)$ curves of AlSi10Cu(Fe) sand cast aluminum alloy in 3 wt. % NaCl solution after different immersion times.

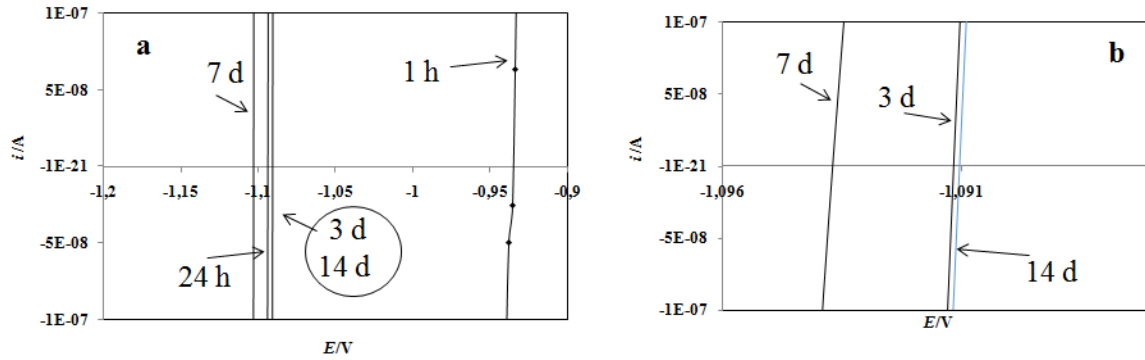


Fig. 17. Magnification of $i(E)$ curves of AlSi10Cu(Fe) sand cast aluminum alloy in 3 wt. % NaCl solution after different immersion times.

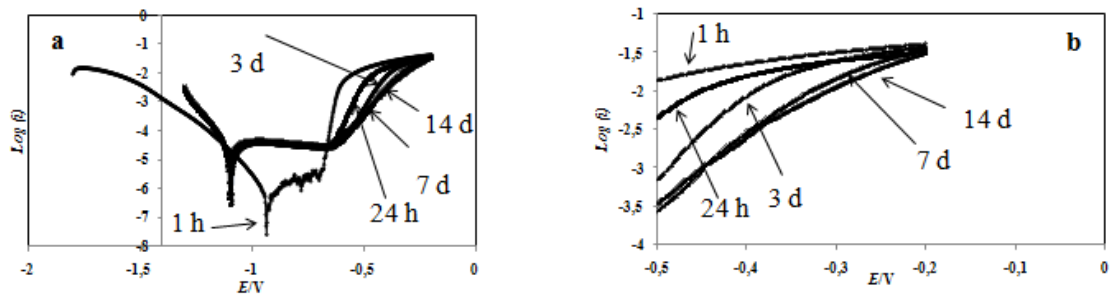


Fig. 18. Log $i(E)$ curves of AlSi10Cu(Fe) sand cast aluminum alloy in 3 wt. % NaCl solution after different immersion times.

Table 8. Corrosion potential, polarization resistance, and corrosion rate of the AlSi10Cu(Fe) sand cast aluminum alloy immersed in 3 wt. % NaCl solution

Immersion time	E_{corr} (V/SCE)	R_p (k Ω)	i_{corr} (μ A/cm ²)	V_{corr} (mm/year)
1h	-0.9350	21	1.5	0.017
24h	-1.0933	2.1	33	0.375
3days	-1.0917	0.5	34	0.385
7days	-1.1046	1.1	41	0.466
14days	-1.0921	1.4	34	0.385

516

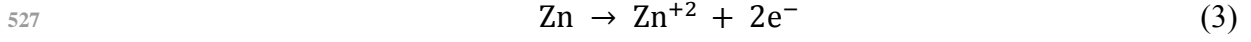
517 Fig. 19 shows the Nyquist plots of impedance of the alloy immersed in 0.3 wt. % NaCl
 518 solution. In all diagrams, a charge transfer loop at high frequency followed by a diffusion
 519 phenomenon at low frequency is observed; the result is in good agreement with (Frers et
 520 al.1990, Jafarzadeh et al. 2009 and Fernandes et al. 1989). The charge transfer loop is directly
 521 related to electrochemical transfer reactions, typically due to the metallic dissolution
 522 occurring on the alloy surface, for example:

523

524



526 And,



528

529

530 The transfer resistance value increases with immersion time, from 554 Ω after one
 531 hour to 2768 Ω after two weeks of immersion (Table 9).

532 The diffusion (Warburg) line is representative of the transport phenomenon, towards
 533 the porous surface layer of the alloy.

534 An analysis of the high-frequency loop allows determining the double-layer
 535 capacitance and transfer resistance values. The double-layer capacitance C_d values are not
 536 constant according to the immersion times (Table 9); this is probably due to an evolution of
 537 the passive layer thickness on the alloy surface, the localized corrosion process, and the
 538 presence of porosities. The increase of the transfer resistance value can be explained by the
 539 increase of the oxide layer thickness (Zazi et al. 2010).

540

541 The impedance spectra of AlSi10Cu(Fe) sand cast aluminum alloy immersed in 3 wt.
 542 % NaCl solution are presented in Fig. 20 and the characteristics of the impedances curves are
 543 given in Table 10. As for the previous case, the diagrams show a charge transfer loop,
 544 followed by a diffusion phenomenon. The charge transfert resistance (R_t) increases with
 545 immersion time, from 271 Ω after one hour up to 2536 Ω after two weeks of immersion.
 546 However, the double layer capacitance (C_d) values decrease from 587 μF after one hour up to
 547 323 μF after two weeks of immersion.

548

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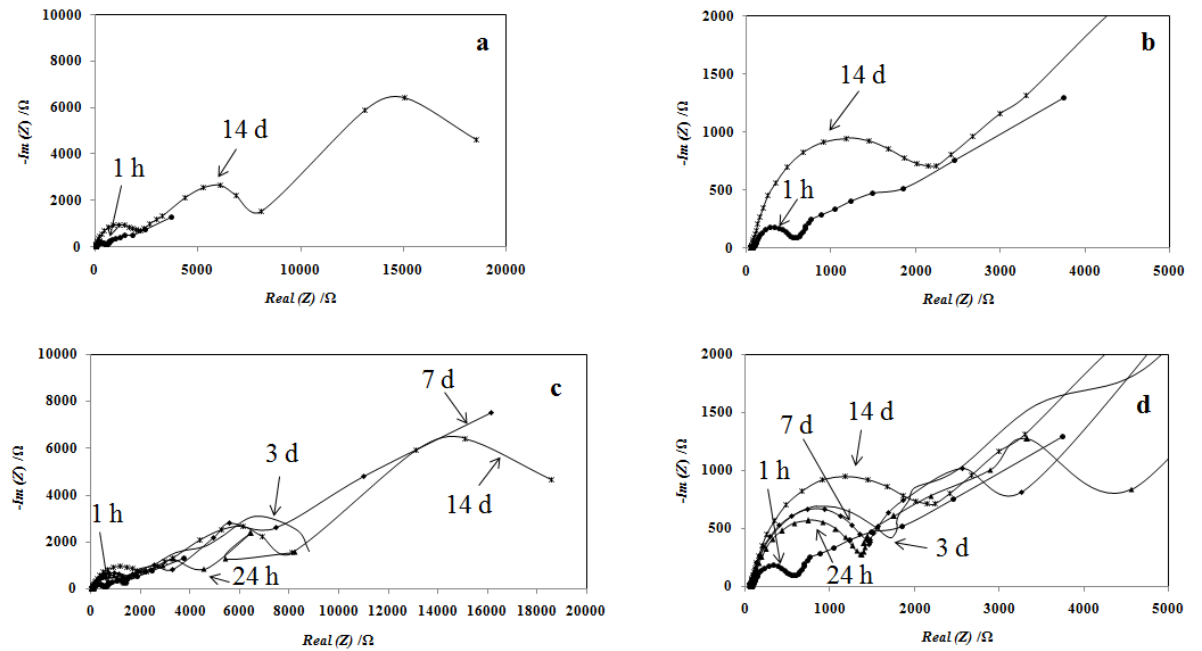


Fig. 19. (a) Nyquist plots of AlSi10Cu(Fe) sand cast aluminum alloy immersed in 0.3 wt. % NaCl solution after 1h of immersion and after 14 days of corrosion, (b) magnification of Nyquist plot of (a), (c) after different immersion times, (d) magnification of Nyquist plot of (c).

Table 9. Solution resistance (R_s), transfer resistance (R_t) and double-layer capacitance (C_d) AlSi10Cu(Fe) sand cast aluminum alloy of immersion in 0.3 wt. % NaCl versus time of immersion for sample area equal to 1 cm²

Immersion time	$R_s(\Omega)$	$R_t(\Omega/\text{cm}^2)$	$C_d(\mu\text{F}/\text{cm}^2)$
1h	70	154	201
24h	67	1616	136
3 days	59	2192	139
7 days	53	1898	230
14 days	53	2768	153

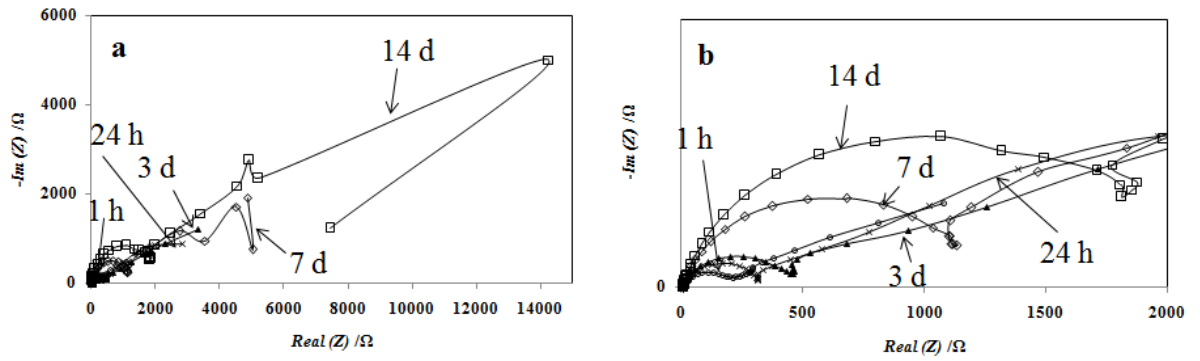


Fig. 20. (a) Nyquist plots of AlSi10Cu(Fe) sand cast aluminum alloy immersed in 3 wt. % NaCl solution after different immersion times

Table 10. Solution resistance (R_s), transfer resistance (R_t) and double layer capacitance (C_d) AlSi10Cu(Fe) sand cast aluminum alloy immersed in 3 wt. % NaCl solution after different immersion times.

Immersion time	$R_s(\Omega)$	$R_t (\Omega/\text{cm}^2)$	$C_d (\mu\text{F}/\text{cm}^2)$
1h	11	271	587
24h	12	260	613
3 days	9	542	407
7 days	7	1406	420
14 days	7	2536	323

Conclusions

The present work was performed to examine and to offer a better understanding of the influence of several intermetallics and porosities (nano and microporosities) on the corrosion behavior of AlSi10Cu(Fe) sand cast alloy containing zinc and to find the relationship between the microstructure and the corrosion behavior. Microstructure characterization and corrosion behavior of aluminum AlSi10Cu(Fe) sand cast alloy in chloride solution were investigated. The main results can be summarized as:

584 The chemical composition of the different second phases present in the alloy is variable,
 585 several phases and a new phase $\text{Cu}_{61.22} \text{Zn}_{25.39} \text{Ni}_{11.85} \text{Al}_{1.54}$, white nanoparticles on a silicon
 586 plate-like eutectic and coral-like eutectic have been observed.

587 Dissolution of aluminum phase surrounding the eutectic phases, and dissolution of fine
 588 particles and/or segregation surrounding the β -Fe plates phases occur. Nanopores on the
 589 surface of the samples have been characterized and can be responsible for the pitting
 590 corrosion, and the analysis of pitting zones shows that the zones contain oxygen, aluminum,
 591 silicon, magnesium, and chlorine.

592 The Nyquist plot evidences a charge resistance transfer at high frequency followed by a
 593 diffusion phenomenon (Warburg line) at low frequency. Impedance measurements show
 594 dissolution of metals on the alloy and electrolyte diffusion towards the porous surface layer of
 595 alloy, without adsorption phenomenon. It can be assumed that the corrosion phenomena are
 596 due to the appearance and the disappearance of porosities and the dissolution of less noble
 597 elements.

598 The transfer resistance is about 2.7 k Ω in 0.3 wt. % NaCl and 2.5 k Ω in 3 wt. % NaCl
 599 after two weeks of immersion, the double-layer capacitance is about 200 μF in the 0.3 wt. %
 600 NaCl solution and 300 μF in 3 wt. % NaCl solution after 14 days of corrosion. An increase of
 601 the transfer resistance and a change of the double layer capacitance with increasing immersion
 602 duration were observed. The change of double layer capacitance can be due to the presence of
 603 porosities on surface. The corrosion potential tends to -1.10 V after 14 days of corrosion in
 604 0.3 and 3 wt. % NaCl solutions. The polarization resistance is about 2.8 k Ω in the 0.3 wt. %
 605 NaCl solution, and 1.4 k Ω in the 3 wt. % NaCl solution. Due to its high corrosion rate value,
 606 in the 3 wt. % NaCl solution, the use of the alloy in sea water is not recommended. Wide
 607 passive windows, followed by the breakdown of passive film and excessive dissolution, were
 608 observed in 0.3% and 3 wt. % NaCl solution.

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