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ABSTRACT: The corrosion control of ductile cast irons becomes a technological challenge when supplying castings to customers due to the high reactivity of this alloy in contact with air. An interesting alternative to the protective systems such as coatings or corrosion inhibitors included in packaging processes is the chemical modification of the cast alloys by means of alloying elements addition which are able to improve the corrosion resistance of ductile cast irons. Ni, Cr and Al added to the cast alloys significantly affect their structure and properties, among them their corrosion response, when exposed to air. It has been observed that Ni and Al improve the corrosion behaviour while Cr additionally promoted pearlite and carbides formation. The results from the corrosion tests performed on ductile cast iron alloys which contain these three elements are discussed in the present work.

KEYWORDS: Alloying elements; Atmospheric corrosion; Electrochemical corrosion; Ductile iron

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RESUMEN: Efecto del Ni, Cr y Al sobre la resistencia a la corrosión atmosférica y electroquímica de la fundición de hierro con grafito esferoidal y matriz ferrítica. El control de la corrosión de las fundiciones esferoidales supone un reto tecnológico a la hora de suministrar piezas a la industria por su alta reactividad en contacto con la atmósfera. Una alternativa interesante a los sistemas de protección que emplean inhibidores de corrosión vía aplicación directa o en embalaje es la modificación de las fundiciones esferoidales. Elementos de aleación que mejoren el comportamiento frente a la corrosión de las fundiciones esferoidales. Elementos como el Ni, Cr y Al en la composición de la fundición, aportan cambios significativos en la microestructura y en las propiedades de estos materiales, como su mejora en la resistencia a la corrosión atmosférica. Se ha observado que el Ni y el

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Al mejoran dicha respuesta a la corrosión, mientras que el efecto del Cr se manifiesta, además, en la estabilización de la perlita y la formación de carburos en la matriz, no observada en las aleaciones que contienen sólo los otros dos elementos. En el presente estudio se describen y discuten los resultados encontrados con fundiciones esferoidales modificadas con estos elementos.

PALABRAS CLAVE: Corrosión atmosférica; Corrosión electroquímica; Elementos de aleación; Fundición esferoidal

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1. INTRODUCTION

Low-alloved steels and cast irons are used to manufacture castings which are part of components used in different aggressive conditions (Pourbaix M. and Pourbaix A., 1989; Rajani and Kleiner, 2003; Tiedje, 2010; Morcillo et al., 2011). Exposure to environment condition provokes atmospheric corrosion on castings which negatively affect the properties of these metallic alloys, reduces the life span of the components and increases the costs due to additional cleaning, reparation and/or replacement (Melchers, 2013; ASM Handbook, 2017). There are different protective strategies that minimise the corrosion attack of these iron-based alloys. The main techniques used to increase the corrosion resistance of cast alloys are based on the use of protective coatings and the optimization of its chemical compositions (Lou et al., 2006; Kim et al., 2007; Gulzar et al., 2009; Arenas et al., 2014; ASM Handbook, 2017).

When iron-based alloys are exposed to the atmosphere, the environmental parameters such as level of pollutants, mainly chlorides and SO_2 , temperature and relative humidity will play a crucial role on its corrosion behaviour. Because of its exposition, oxides, hydrated oxides, hydroxides together with other compounds that can be formed depending on the ionic pollutants present in the environment, are formed on the surface (Morcillo *et al.*, 2011). The composition of the corrosion products will also depend on the alloy composition, the exposure time and the changes of the climatological conditions.

Metallic matrix in cast iron alloys are similar to steel alloy though graphite particles are also present in the former case. The shape, size and distribution of these particles are mainly affected by the composition of the alloy, the solidification path (stable versus metastable) and the cooling rates (Larrañaga *et al.*, 2006; Larrañaga and Sertucha, 2010; Sertucha *et al.*, 2010). When compared to the low-alloyed steels, cast irons become competitive due to low production costs (low pouring temperatures, low shrinkage tendency and heat treatments are not usually required) and their mechanical properties good enough for important applications, especially in case of ductile cast irons (Gulzar *et al.*, 2009; Tiedje, 2010; Sertucha *et al.*, 2012). However, the presence of graphite particles promotes heterogeneous boundaries with the matrix, which originate galvanic effects and favours the onset of corrosion attack (Ebel et al., 2018; Méndez et al., 2019). In general, both shape of graphite particles and the presence of carbides in the matrix also affect to corrosion resistance of cast iron alloys. Additionally, the different constituents of the matrix are also important in this corrosion resistance, being austenite the most resistant phase against corrosion followed by pearlite and ferrite (ASM Handbook, 2017). On the other hand, gas and/or shrinkage porosities also increase corrosion as they are defects which favour the attack of the material. If the application of a protective coating is not an option, an effective way to increase corrosion resistance of cast irons is to add limited contents of some alloying elements (Si, Ni, Cr, Cu, Mo, V, Ti, etc.) so as to avoid high manufacture costs (Zhou et al., 2007; Méndez et al., 2019).

The present work deals with the evaluation against atmospheric and electrochemical corrosion of different ductile iron alloys with and without Ni, Cr and Al additions. Although it has long been known that high Cr concentrations increases drastically the corrosion resistance of cast irons (Medynski *et al.*, 2019; Ali *et al.*, 2020; Stawarz and Dojka, 2022), little data and few analyses are available for low Cr concentrations. For this reason, the present paper firstly focuses on the manufacturing of cast irons with low content of Cr, Ni and Al. Secondly, the manufactured alloys were studied both at atmospheric corrosion exposure and in an aqueous solution in a high chlorides concentration electrolyte.

2. EXPERIMENTAL WORK

The atmospheric corrosion test was carried out using plate castings which were manufactured with the 9 compositions included in Table 1. The increase of the Si content due to the inoculation process is not considered in the data shown in Table 1 though such a contribution has been estimated as 0.2-0.3 wt.%. As it was mentioned before, the alloying elements selected in the present study are Ni, Cr and Al which different contents have been highlighted in Table 1. According to a primary aim for evaluating the effect of the cooling rate on microstructures of the alloys, the lay-out of the mould included two

| Alloy | С | Si | Mn | Р | S | Cr | Ni | Mg | Al | Ti | Cu |
|-------|------|------|------|-------|-------|------|------|-------|---------|-------|------|
| C1 | 3.80 | 1.97 | 0.09 | 0.053 | 0.010 | 0.03 | 0.04 | 0.050 | < 0.010 | 0.022 | 0.02 |
| C2 | 3.73 | 1.94 | 0.12 | 0.045 | 0.009 | 0.04 | 0.50 | 0.050 | < 0.010 | 0.025 | 0.02 |
| C3 | 3.85 | 2.07 | 0.12 | 0.038 | 0.009 | 0.04 | 0.99 | 0.065 | < 0.010 | 0.026 | 0.03 |
| C4 | 3.75 | 1.99 | 0.13 | 0.040 | 0.013 | 0.50 | 1.02 | 0.058 | < 0.010 | 0.026 | 0.02 |
| C5 | 3.74 | 1.97 | 0.14 | 0.035 | 0.012 | 0.92 | 0.99 | 0.051 | < 0.010 | 0.026 | 0.02 |
| C6 | 3.79 | 1.94 | 0.07 | 0.063 | 0.012 | 0.03 | 0.03 | 0.050 | 0.015 | 0.017 | 0.03 |
| C7 | 3.78 | 1.89 | 0.10 | 0.058 | 0.012 | 0.04 | 0.04 | 0.049 | 0.049 | 0.022 | 0.03 |
| C8 | 3.65 | 1.92 | 0.11 | 0.050 | 0.011 | 0.05 | 0.04 | 0.049 | 0.057 | 0.024 | 0.04 |
| C9 | 3.80 | 1.94 | 0.13 | 0.050 | 0.010 | 0.05 | 0.04 | 0.046 | 0.150 | 0.027 | 0.03 |

 TABLE 1. Chemical compositions of the 9 ductile iron alloys (wt.%). The content of the selected alloying elements have been highlighted in bold numbers.



FIGURE 1. Mould used to produce the casting plates: (a) drag and cope of the moulds and (b) bunch containing the two plates.

different plate castings called "A" and "B". The dimensions of these two plates were $190 \times 90 \times X$ mm, where X = 12 and 25 mm for the plates "A" and "B", respectively. The plates "B" were designed for other purposes, so only the plates "A" were used in the present study.

For each casting alloy, the batch melt was prepared in a 250 Hz medium frequency induction furnace (100 kW) with 120 kg as maximum capacity. In all cases, the metallic charges were prepared with 55% pig iron and 45% ferritic returns (these last coming from heavy-section castings produced for the eolic industry). Once accomplished the melting processes, the carbon and silicon contents of the obtained base alloys were adjusted adding high purity graphite from electrodes (wt.%, C = 98.8) and a FeSi alloy (wt.%, Si = 74.6; Ca = 0.3; Al = 0.7 and Fe = 24.4) respectively.

The different additions of Ni, Cr and Al into the base melts were performed by using high purity nickel briquettes (wt.%, Ni >99.9), a FeCr alloy (wt.%, Cr = 62.7; C = 7.5 and Fe = 29.8) and small aluminium ingots (wt.%, A1 = 98.3). After completing the required additions in each case, the temperature of the base melts was increased to 1490-1500 °C and about 50 kg were transferred to a 70 kg maximum capacity ladle to carry out the Mg-treatments according to the "sandwich" method. For this purpose, 0.6 kg of a FeSiMg 511 ferroalloy (wt.%, Si = 44.7; Mg = 5.6; Ca = 1.2; Rare Earths = 0.7and Fe = 47.8) and then 0.3 kg of steel scrap pieces were introduced in a reaction chamber located in the bottom of the ladle before transferring the 50 kg of the base melt batches to it. Once finished the Mg-treatments, the resulting melt batches were skimmed while remaining into the ladle and one chemically bonded mould (see Fig. 1a) was finally poured per cast alloy. Figure 1b shows a bunch extracted from one of the poured moulds where the two plates are observed together with the filling system and the pouring cup.

The inoculation process was carried out setting a piece of an inoculant ingot (wt.%, Si = 70-76; Al = 3.1-4.3; Ca = 0.3-1.3 y Rare Earths = 0.4-0.5) in the pouring cup just before filling each mould. In all cases, the inoculant addition was the 0.20 wt.% of the total amount of melt poured into the mould.

After cooling the casting plates up to room temperature they were removed from the bunches and then shot-blasted. In a subsequent step, the 9 plates "A" underwent an annealing treatment (heating to 920 °C, isothermal period at 920 °C for 1 h, cooling up to 300 °C at 1°C/min and cooling up to room temperature in open air) so as to obtain fully ferritic microstructures. A piece was obtained from each cast bunch (in the gating runner of plates "A") to prepare a metallographic sample and to identify the constituents of the as-cast matrices. Once the plates were heat-treated and then cooled to room temperature, another metallographic sample was obtained from the gating areas of plates "A" to confirm that all microstructures were fully ferritic. These samples were also used to determine nodularity (Nod) and nodule count (N) values. Final data from these parameters were obtained from three different inspection fields at 100x per sample. In each image the total number and the area of each graphite particle were determined with the software ImageJ. In these analyses, all graphite particles with an area lower than $25 \,\mu\text{m}^2$ were not considered. Once these data were available, the graphite particles were assigned to classes III, V and VI according to ISO-945-1 and considering their circularity and Feret ratio (Feret, 1931). The criteria used in these classification work are shown in Table 2. Those particles which could not be included in the ranges of Table 2 were classified by optical observation (less than 0.5% of cases).

| TABLE 2. Criteria used fe | or classifying th | e graphite | particles. |
|---------------------------|-------------------|------------|------------|
|---------------------------|-------------------|------------|------------|

| Class | Circularity | Feret ratio |
|-------|-------------|-------------|
| III | 0.00-0.60 | 2.0-1000 |
| V | 0.50-0.77 | 1.0-1.5 |
| VI | 0.77-1.00 | 1.0-1.5 |

Nod and N values were determined with equations (1) and (2) where A_{III} , A_v and A_{vI} , and N_v and N_v are the total areas and the total particle counts, respectively, of the particles assigned to classes III, V and VI. On the other hand, A_{Field} corresponds to the area of each inspected field or image. In a subsequent step, all samples were etched with Nital 5% reactant for 10-15 s and the contents of ferrite, pearlite and carbides were determined by visual inspection according to the corresponding standard (AFS, 1984).

Nod (%) =
$$\frac{A_V + A_{VI}}{A_{III} + A_V + A_{VI}} \times 100$$
 (1)
N (mm⁻²) = $\frac{N_V + N_{VI}}{A_{III}}$ (2)

Carbon and sulphur contents were determined by a combustion technique (LECO CS 200) while silicon contents were obtained by gravimetric methods. For the rest of elements, contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES Perkin Elmer Optima 5300).

An atmospheric corrosion test rack (see Fig. 2) was built according to the standard ASTM G50 where all the plates "A" where separately set with an inclination angle of 45° and oriented to south. Just before starting the exposure period, all plates "A" were shot-blasted again during 20 min so as to remove any dirt/oxide rest from the surfaces.



FIGURE 2. Atmospheric corrosion test rack used to expose all the plates "A" to atmosphere.

The location selected to perform the exposure test had an atmospheric corrosivity category C3 according to the standard UNE-EN-ISO 12944-2:2018 (industrial and urban atmospheres) with frequent rainy days. The total exposure period elapsed between September and March with 186 days. Table 3 shows the atmospheric parameters registered during this period. Chloride contents were not measured as the exposure test was made in an area among mountains and 25 km far from the sea coast.

After the exposure period, the corrosion attack of the plates was characterised by metallographic analyses. For this purpose, all plates "A" were cut at 15 mm from the edge of the shortest side. Metallographic samples were obtained from these areas and the oxide layer thickness (C_E) was determined. Each of these values was calculated as the average

| Parameter | Average | Maximum value | Minimum value |
|------------------------------|---------|------------------|------------------|
| Temperature (°C) | 11.9 | 19.5 | 1.5 |
| Relative moisture (%) | 81.60 | 95.19 | 45.50 |
| Rainfall (1/m ²) | 6.7 | 62.1 | 0.0 |
| $NO_{2} (\mu g/m^{3})$ | 29.4 | 70.5 | 11.7 |
| NO (µg/m ³) | 23.3 | 74.8 | 3.5 |
| $SO_{2} (\mu g/m^{3})$ | 4.53 | 8.33 | 2.09 |

 TABLE 3. Atmospheric parameters registered during the exposure test of the plates "A".

value from ten different width measures along the total oxide layer present in each sample. The corrosion rate (V_c in g/cm²) values were then calculated assuming that all plates underwent uniform corrosion process, and no loss of the corrosion products layer did occur.

The composition of the oxides formed on the surfaces was analysed by Scanning Electron Microscopy, SEM (Zeiss Ultra Plus) with an EDS detector and by X-ray diffraction on polycrystalline samples (Bruker AXS D8 Advance). The X-ray diffraction patterns were registered under a CuK α radiation in the 20 range 10-70° at 40 kV, 30 mA with a scanning rate of 0.6 °/min.

Electrochemical measurements were performed by triplicate on a conventional three electrode cell. The working electrode was the studied alloy while the reference electrode is an Ag/AgCl electrode (3M KCl) and the counter electrode was a platinum wire. The area of the working electrode was 1.20 cm². The electrode was a 0.6 M NaCl solution. All the tests were carried out at 23 ± 2 °C. Before testing, the samples were polished down to 600 grit.

Corrosion behaviour has been evaluated by potentiodynamic polarisation using an Autolab PGSTAT 302N potentiostat. The evolution of the open circuit potential (OCP) was recorded for 1 hour. The potentiodynamic curves were conducted at a scan rate of 0.166 mV/s. Before starting the scan, the samples remained in the solution for 20 min to stabilize the OCP. After this period the potential scan was started in the anodic direction from a potential value of -0.25 V with respect to the OCP, up to 0.25 V. Each test was repeated three times for a given sample to ensure the repetitiveness of the results.

3. RESULTS AND DISCUSSION

3.1. Effect of Ni, Cr and Al on microstructures

The microstructural features observed in the 9 plates "A" before and after the heat-treatment are shown in Table 4. All the samples led to Nod values higher than 90% and N values in the range of 347-575 mm⁻². Mainly ferritic microstructures are observed in the gating areas of the plates before un-

| Alloy | Nod (%) | N (mm ⁻²) | Heat treatment | Ferrite (%) | Pearlite (%) | Carbides (%) |
|--|---------|-----------------------|----------------|-------------|--------------|--------------|
| C1 (hass allow) | 02.8 | 442.1 | No | 70-65 | 30-35 | 0 |
| CI (base alloy) | 93.8 | 442.1 | Yes | 100 | 0 | 0 |
| C2 (0.500(N)) | 02.2 | 545 1 | No | 50-60 | 50-40 | 0 |
| C2 (0.30% N1) | 93.2 | 545.1 | Yes | 100 | 0 | 0 |
| $C^{2}(0,000(\mathbf{N}))$ | 07.0 | 246.6 | No | 40-55 | 60-45 | 0 |
| C3 (0.99% N1) | 97.0 | 340.0 | Yes | 100 | 0 | 0 |
| $C_{4}(0.500/C_{max} + 0.00/N_{c})$ | 05.6 | 500.2 | No | 20-25 | 78-73 | 2 |
| C4 (0.30% Cr y 1.02% NI) | 95.6 | 500.2 | Yes | 30-35 | 68-63 | 1-2 |
| $C_{5} = (0.020) C_{max} = 0.000 (NE)$ | 05.6 | 260.0 | No | 0 | 93-90 | 7-10 |
| C3 (0.92% CF y 0.99% NI) | 93.0 | 369.0 | Yes | Traces | 95-90 | 5-10 |
| C(0,0150/1) | 02.4 | 260.4 | No | 70-65 | 30-35 | 0 |
| C6 (0.015% AI) | 93.4 | 309.4 | Yes | 100 | 0 | 0 |
| C7 (0.0400/.41) | 08.0 | 450.0 | No | 70-75 | 30-25 | 0 |
| C7 (0.049% AI) | 98.0 | 450.0 | Yes | 100 | 0 | 0 |
| $C_{2}^{0}(0,0570/11)$ | | | No | 80-85 | 20-25 | 0 |
| C8 (0.037% AI) | 94./ | 445.2 | Yes | 100 | 0 | 0 |
| C0 (0.1500/ 1) | 01.4 | 252 6 | No | 90 | 10 | 0 |
| C9 (0.130% AI) | 91.4 | 555.0 | Yes | 100 | 0 | 0 |

TABLE 4. Nod and N average values and microstructure characteristics of the plates before and after heat-treatment.



FIGURE 3. Microstructure found in the heat-treated plates produced with alloys (a) C1, (b) C7, (c) C4 and (d) C5. High magnification images (c) and (d) show the presence of pearlite and carbides.

dergoing the heat-treatments, except in those castings produced with the alloys C4 and C5. These last plates with relevant Cr and Ni contents show matrices in which pearlite becomes the main constituent. Additionally, these two compositions also contain carbides distributed by the matrix in contrast with the rest of plates where this phase is not detected.

The effects of alloying with Ni or Al have shown to be the opposite according to the ferrite and pearlite contents in the as-cast plates C2 and C3 versus C6 to C9 (see Table 4). Thus, Ni promoted the formation of pearlite while Al acted as a ferrite promoter element when the heat-treatments were not still made. These two behaviours were already described in the literature (Lacaze *et al.*, 2012; Takamori *et al.*, 2002).

As it was mentioned before, the heat-treated plates show matrices only composed by ferrite (Fig. 3a and 3b) though the microstructure of those ones produced with Ni and Cr (alloys C4 and C5) are mainly pearlitic and they contain carbides (Fig. 3c and 3d). Taking into account that the plates manufactured with the C3 contain a similar Ni content than the ones produced with alloys C4 and C5 and the former one show fully ferritic microstructures after undergoing the annealing treatment, it is considered that Cr is the cause of pearlite and carbides formation and of their stabilization during the applied heat-treatments.

3.2. Effect of Ni, Cr and Al on atmospheric corrosion response

After one week exposed to the atmosphere, the surfaces of all plates already showed clear evidence of corrosion. Thus, non-homogeneous, thin and brown-orange oxides appeared on the surface which suggested the formation of iron oxides (Fig. 4a and 4b). The corrosion products composed of these ox-



FIGURE 4. General and detailed view of the surfaces after (a) 4 days and (b) 46 days of exposure to atmospheric conditions.

| Alloy | C _E (m | m) | V _c (g/n | V _C (g/m ²) | | |
|----------------------------|-------------------|------|---------------------|------------------------------------|--|--|
| Апоу | Average value | σ | Average value | σ | | |
| C1 (reference composition) | 92 | 15.6 | 167.9 | 28.4 | | |
| C2 (0.50% Ni) | 78 | 7.1 | 142.4 | 12.9 | | |
| C3 (0.99% Ni) | 66 | 14.1 | 120.5 | 25.8 | | |
| C4 (0.50% Cr y 1.02% Ni) | 48 | 5.7 | 87.6 | 10.3 | | |
| C5 (0.92% Cr y 0.99% Ni) | 40 | 7.1 | 73.0 | 12.9 | | |
| C6 (0.015% Al) | 71 | 8.5 | 129.6 | 15.5 | | |
| C7 (0.049% Al) | 67 | 7.1 | 122.3 | 12.9 | | |
| C8 (0.057% Al) | 57 | 8.5 | 104.0 | 15.5 | | |
| C9 (0.150% Al) | 28 | 4.2 | 51.1 | 7.7 | | |

TABLE 5. Average layer thickness (C_E) and corrosion rate (V_C) values obtained on the metallographic samples.

ides became a continuous layer in all tested plates after 46 days (Fig. 4c and 4d) and remained without evident visual changes until the end of the experiment.

Table 5 shows the average values of the oxide layer thickness (C_E) and of the corrosion rate (V_C), determined from the metallographic examinations. These analyses have shown that all the exposed surfaces are totally covered by a corrosion products layer with different thickness according to the type of alloy used for manufacturing the plates. Taking as a reference the fully ferritic alloy C1, the increasing Ni contents in alloys C2 and C3 reduces the C_E and V_C values,

thus improving their atmospheric corrosion resistance. This effect of Ni has been already described by Sun *et al.* (2012) and Hsu and Chen (2010) in electrochemical studies. These authors related this improvement to the decrease of the potential difference between graphite and metallic matrix. These authors also reported that Ni decreased the graphite particles count and, therefore, the number of interfaces graphite-matrix was reduced though this last aspect has not been observed in the present work.

When comparing the results from samples C2 to C5, it is observed that the combined addition of Ni and Cr

in samples C4 and C5 also decreased their C_E and V_C values respect to C2 and C3 samples. However, these two samples contain pearlite and carbides apart from ferrite while samples C2 and C3 are fully ferritic alloys. Arenas *et al.* (2014) investigated the effect of the matrix type on the corrosion response of cast iron alloys with flake and spheroidal graphite particles in 0.03 M NaCl solutions. These authors found that graphite shape and the different constituents of the matrix do not significantly affect the response against corrosion of these cast iron alloys with Si contents of about 2 wt.%. This result suggests that the low corrosion rate found in alloys C4 and C5 is related to their high Cr and Ni contents (ASM Speciality Handbook,1996).

In case of alloys C6 to C9, the addition of Al and the increasing content of this alloying element also decrease their C_E and V_C values. However, it must be noticed here that the required Al content to obtain a similar effect on these two parameters to that exhibited by Ni is about 20 times lower than Ni content. On the other hand, Al is an alloying element cheaper than Ni and/or Cr though it increases the risk of gas porosity formation (pinholes) and of spheroidal graphite degeneration during solidification of cast irons (Sertucha and Suárez, 2005) and it decreases castability of melts. This last aspect was only observed in this work when pouring the mould with alloy C9.

The V_c range required in the standard ISO-12944 for low carbon steels exposed to a C3 corrosivity atmosphere for the first year is 200-400 g/cm²·year. Therefore, all alloys included in Table 5 would meet such a requirement. This target would be especially achieved for those alloys with the highest Ni, Cr or Al contents (alloys C4, C5, C8 and C9) which V_c values extrapolated to one year exposure would be even lower than the range included in the standard. This result is especially important when the replacement of some steel parts by cast iron ones is approached, considering that, meeting the required mechanical properties,



FIGURE 5. X-ray diffraction patterns obtained from the corroded surfaces of samples C1, C5 y C9.

the cast iron alloys comparatively exhibit a lower risk of shrinkage formation, tearing and of slag inclusions incidence than steels. Additionally, it must be considered that the lowest V_c values included in Table 5 occur for ductile iron alloys despite of graphite nodules promote the onset of corrosion processes. However, once the attack starts, the corrosion resistance of the metallic matrix delays its progression.

The visual examination of the exposed plates did not show any relevant difference among the alloys when corrosion started (Fig. 4). This result could indicate that the protective effect of Ni, Cr and Al mainly affected the corrosion rates and likely, the kind of compounds formed, though it did not change the corrosion onset.

3.3. Characterization of the corrosion products

The identification of those compounds present in the oxide layers formed on the exposed plates are



FIGURE 6. (a) SEM image of the corrosion products found in the exposed surface of a plate produced with alloy C5. (b) High magnification SEM image which shows a detail of the corrosion products.

carried out in this section. Samples with dimensions 10×20 mm were prepared from one plate manufactured with alloys C1, C5 and C9 and then analysed by X-ray diffraction. Similar diffraction patterns were recorded in the three samples which correspond to lepidocrocite [γ -Fe³⁺O(OH)] as the main phase present in the oxide layers (Fig. 5).

The exposed surfaces and the corresponding cross sections of alloys C1, C3, C5 and C9 have been analysed by EDS-SEM. In all cases, the exposed surfaces are covered with lamellar compounds (see Fig. 6a and 6b for alloy C5) which contain Fe and O (main peaks) and Si (minor peaks), which is typically found for lepidocrocite (Morcillo *et al.*, 2011).



FIGURE 7. Cross section of the plates manufactured with alloys (a) C1, (b) C3, (c) C5 y (d) C9. The spectrum (e) was recorded in the oxide layer formed on sample C1 while the spectrum (f) represents to those registered from samples C3, C5 y C9.

 TABLE 6. Semiquantitative EDS analyses (wt.%) of the corrosion products present in different areas of samples C1, C3, C5 and C9.

 All values correspond to the average ones obtained from three different individual measurements made in a given zone.

| Alloy | Scale zone | Fe | 0 | Si | Ni | Cr | Al |
|-------|----------------|-------|-------|------|------|------|------|
| | Surface | 55.86 | 43.01 | 1.14 | - | - | - |
| C1 | Inner part | 58.12 | 39.54 | 2.35 | - | - | - |
| | Around nodules | 59.96 | 41.67 | 2.37 | - | - | - |
| | Surface | 56.23 | 42.00 | 1.13 | 0.62 | - | - |
| C3 | Inner part | 54.55 | 42.56 | 2.36 | 0.53 | - | - |
| | Around nodules | 56.84 | 39.96 | 2.52 | 0.67 | - | - |
| | Surface | 54.12 | 44.71 | 0.69 | 0.53 | 0.11 | - |
| C5 | Inner part | 64.64 | 3.43 | 2.07 | 0.67 | 1.18 | - |
| | Around nodules | 60.86 | 35.79 | 1.87 | 0.71 | 1.25 | - |
| | Surface | 56.76 | 42.45 | 0.79 | - | - | - |
| C9 | Inner part | 61.90 | 34.83 | 2.83 | - | - | 0.44 |
| | Around nodules | 53.33 | 42.35 | 3.85 | - | - | 0.21 |



FIGURE 8. Mappings obtained by EDS microanalyses of Fe, O, Si, Ni and Cr, performed on the metallic matrix and on an oxide layer surrounding a graphite nodule in sample C5.

When analysing the corrosion products found in the inner part of the oxide layer (cross sections shown in Fig. 7) by EDS-SEM, similar spectra to those measured from the corrosion products present on the surfaces have been found (main peaks obtained for Fe and O and small ones for Si and S). Sulphur detection should be due to the presence of this pollutant in the industrial atmosphere in the location. It might also be assigned to the sulphur contents present in the alloys (Stawarz and Dojka, 2022). Similar spectra are also obtained in the most internal areas which correspond to corrosion products mainly located around the graphite nodules (see Fig. 7a and 7b). This shows that the contact areas between the spheroids and the matrix are prone to initiate corrosion, since graphite always acts as a cathode compared to iron which is the anode of the corrosion cell. This provokes an electrochemical corrosion process between both phases (Reynaud, 2008).

The semiquantitative results obtained from the EDS analyses carried out on the corrosion products present in different zones of the oxide layers and the surrounding areas to the graphite nodules are shown in Table 6. It is observed in sample C1 that Si contents are higher in the inner part of the oxide layer and in the compounds, which surround the nodules, than in the external zones. A similar trend of the Si contents can be seen in the other three samples C3, C5 and C9.

Additionally, the inner part of the oxide layers and the compounds surrounding the graphite nodules found in samples C5 and C9 show relevant Cr or Al contents, respectively, according to their chemical composition. However, these two elements have been hardly detected in the surface. For alloy C3, the Ni content of the corrosion products formed on the surface and inner areas of the oxide layer is similar.

Figure 8 shows the Fe, Si, O, Ni and Cr mappings obtained for the oxide layer surrounding one of the graphite nodules present in sample C5. It is observed that Ni is uniformly distributed in the metallic matrix and also in the oxide layer located around the nodule which is in agreement with the semiquantitative data included in Table 6 for this element and the results reported by Sun *et al.* (2012). On the contrary, Si and Cr appear mainly distributed in the oxide layer around the nodule. Cr also seems to be in a likely last solidification area where is common to find small inclusions which can contain this element. The presence of Cr in the inner part of the oxidation layer could explain that alloy C5 has shown one of the lowest corrosion rate values among all alloys studied in this work (see Table 5).

3.4. Electrochemical characterisation

As it has been mentioned in the experimental section, the electrochemical corrosion tests were performed by triplicate showing high reproducibility in all cases. The evolution of the OCP with time is shown in Fig. 9. As it can be seen, the OCP values



FIGURE 9. Evolution of the OCP with time for samples C1, C3, C5 y C9 immersed in a 0.6 M NaCl solution.



FIGURE 10. Polarization curves recorded from samples C1, C3, C5 y C9 immersed in a 0.6 M NaCl solution.

remain stable after 20 min for all alloys. One representative polarization curve recorded for alloys C1, C3, C5 and C9 is shown in Fig. 10.

All alloys show a similar behaviour with a cathodic branch which is characteristic of a diffusion control, and an anodic branch with a small slope which is related to the high activity of the tested materials. According to these results, the four alloys can be considered as active materials under cathodic control. In this case, the corrosion current density (i_{corr}) is defined by the oxygen diffusion-limited current density (i_L) which is estimated from the current density measured in the middle of the cathodic branch. Table 7 collects the average values of i_{corr} and corrosion potential (E_{corr}) obtained from the polarization curves for samples C1, C3 C5 and C9.

Although the four polarization curves plotted in Fig. 10 exhibit a similar behaviour, the ones recorded from samples C3, C5 and C9 show a slight shift

| Alloy | E _{corr} (mA vs Ref) | i _{corr} (μA/cm²) |
|-------|-------------------------------|----------------------------|
| C1 | -712 ± 6 | 28 ± 7 |
| C3 | -671 ± 16 | 21 ± 5 |
| C5 | -657 ± 29 | 29 ± 1 |
| С9 | -691 ± 25 | 29 ± 1 |

TABLE 7. Average values of E_{corr} and i_{corr} obtained from polarization curves of samples C1, C3, C5 and C9.

of the corrosion potential towards more positive values (about 35 mV with respect to the reference alloy C1). This difference in the corrosion potential could be related to the additions of Ni or Al carried out on the alloys which modify the chemical composition of the matrix and thus the potential difference between graphite nodules and the ferritic matrix. Nevertheless, it is necessary to bear in mind that differences found in the curves are not significant. From a kinetics point of view, the corrosion current density is similar in all these cases, that is, about $20 \,\mu\text{A/cm}^2$. In any case, it should be noted that the electrochemical measurements provide instantaneous corrosion rates, while the corrosion rate values obtained from measurements determined from the oxide layers thickness formed under atmospheric exposure lead to average values over the whole process. Because of that both results are indicative of the behaviour of the material, though they are not comparable, especially considering that the experimental environment and conditions used in the electrochemical tests are more aggressive than those present in the atmospheric exposure.

Hsu and Chen (2010) found similar corrosion current density values for an unalloyed and heat-treated ductile cast iron and smaller i_{corr} values for a cast iron alloy with a high Ni content (4 wt.%) after an austempering treatment.

SEM images of the corroded surfaces of samples C1 and C5 after the electrochemical tests are shown in Fig. 11. The surface appearance of samples C3 (with 0.99 wt.% Ni) and C9 (0.15 wt.% Al) is similar to that presented in Fig. 11a for alloy C1, all of them with fully ferritic matrices. EDS analyses have confirmed the formation of deposits consisting of an iron oxychloride distributed on the surface of the four samples. In Fig. 11a, attack zones are observed at the interface between the graphitic nodules and the metallic matrix (indicated in the image by a white arrow) due to the galvanic couple generated between these two constituents. In samples C3 and C9, these zones have also been found with morphologies similar to those found for sample C1.

In sample C5, the matrix composition markedly differs from those found in the other three samples because it contains pearlite and carbides (Fig. 11b). In this particular case, the size of the deposits formed on the surface is smaller and they are more homogeneously distributed on the pearlite sheets and carbides. These differences with respect to samples C1, C3 and C9 with fully ferritic matrices are probably due to the presence of the carbides which act as cathodes in addition to the graphite nodules. Moreover, in sample C5 less attack is observed at the interface between nodules and matrix.

4. CONCLUSIONS

Ductile cast iron plates have been manufactured with 9 different compositions in which Ni, Cr and Al have been used as alloying elements with the goal of improving the corrosion resistance of the resulting cast alloys. The three elements show changes in the microstructure of the alloys and also in their behaviour against atmospheric corrosion. The main conclusions obtained are the following:



FIGURE 11. Surface appearance of alloys (a) C1 y (b) C5, after the electrochemical corrosion tests.

- The addition of Ni and/or Cr promote the formation of pearlite in the matrix. Moreover, only the presence of Cr originates carbides that remain stable together with the pearlite after the annealing treatment. Fully ferritic matrices are obtained in the rest of the alloys after undergoing such thermal treatment.
- The atmospheric corrosion tests performed in this work revealed widespread corrosion on the surfaces of all materials tested, with no visually appreciable differences between the alloys used.
- The metallographic studies carried out on the plates exposed to the atmospheric conditions showed that the thicknesses of the oxide layers formed after 186 days of testing depends on the chemical composition of the prepared alloys. The lowest oxide layer thicknesses are obtained for the alloys with about 1.0 wt.% Cr and Ni and with 0.15 wt.% Al.
- Electrochemical corrosion studies carried out for four alloys in a 0.6 M NaCl solution indicate that they all show a similar corrosion rate characterised by diffusion control and an active anodic branch.

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REFERENCES

- AFS (1984). Reference microstructure for measurement of pearlite and ferrite content in ductile iron microstructures. AFS current information report. Quality Control Committee 12-E, Ductile Iron Division.
- Ali, M., Alshalal, I., Al Zubaidi, F.N., Yousif, A.R. (2020). Improvement of corrosion and erosion resistance properties for cast iron. *IOP Conf. Ser.: Mater. Sci. Eng.* 881, 012068. https://doi.org/10.1088/1757-899X/881/1/012068.
- Arenas, M.A., Niklas, A. Conde, A., Méndez, S., Sertucha, J., de Damborenea, J.J. (2014). Comportamiento frente a la corrosión de fundiciones con grafito laminar y esferoidal parcialmente modificadas con silicio en NaCl 0,03 M. Rev. Metal. 50 (4), e032. https://doi.org/10.3989/revmetalm.032.
- ASM Handbook (2017). Cast iron science and technology. Corrosion in cast Irons. (Vol 1A). in D. M. Stefanescu (Ed.) ASM International, Ohio, USA, pp. 502–510
- ASM Speciality Handbook (1996). Cast Irons. J.R. Davis, ASM International, Ohio, USA, pp. 437-447.
- Ebel, A., Brou, S.Y., Malard B., Lacaze, J., Monceau, D. /aissière, L. (2018). High-temperature oxidation of a high silicon SiMo spheroidal cast iron in air with in situ change in H₂O content. Mater. Sci. Forum 925, 353-360. https:// doi.org/10.4028/www.scientific.net/MSF.925.353
- Feret, L.R. (1931). Assoc. Internat. Pour I'Essai des Mat., 2 Group D, Zurich.
- Gulzar, A., Akhter, J.I., Ahmad, M., Ali, G., Mahmood, M. Ajmal, M. (2009). Microstructure evolution during surface alloying of ductile iron and austempered ductile iron by electron beam melting. *Appl. Surf. Sci.* 255 (20), 8527-8532. https://doi.org/10.1016/j.apsusc.2009.06.011. Hsu, C.H., Chen, M.L. (2010). Corrosion behavior of Ni alloyed
- and austempered ductile iron in 3.5% sodium chloride. Corros. Sci. 52 (9), 2945-2949. https://doi.org/10.1016/j. corsci.2010.05.006.
- Kim, B.H., Shin, J.S. Lee, S.M., Moon, B.M. (2007). Improvement

of tensile strength and corrosion resistance of high-silicon cast Irons by optimizing casting process parameters. J. Mater. Sci. 42, 109-117. https://doi.org/10.1007/s10853-006-1081-9.

- Lacaze, J., Larrañaga, P., Asenjo, I., Suárez, R., Sertucha, J. (2012). Influence of 1 wt-% addition of Ni on structural and mechanical properties of ferritic ductile irons. *Mater. Sci. Technol.* 28 (5), 603-608. https://doi. org/10.1179/1743284711Y.0000000100.
- Larrañaga, P., Sertucha, J. Suárez, R. (2006). Análisis del proceso de solidificación en fundiciones grafiticas esferoidales. Rev. Metal. 42 (4), 244-255. https://doi.org/10.3989/ revmetalm.2006.v42.i4.24
- Larrañaga, P., Sertucha, J. (2010). Estudio térmico y estructural del proceso de solidificación de fundiciones de hierro con grafito laminar. Rev. Metal. 46 (4), 370-380. https://doi. org/10.3989/revmetalm.0961.
- Lou, D.C., Akselsen, O.M., Onsøien, M.I., Solberg, J.K., Berget, J. (2006). Surface modification of steel and cast iron to improve corrosion resistance in molten aluminium. Surf. Coat. Technol. 200 (18-19), 5282–5288. https://doi. org/10.1016/j.surfcoat.2005.06.026.
- Medyński, D., Samociuk, B., Janus, A., Chęcmanowski, J. (2019). Effect of Cr, Mo and Al on microstructure, abrasive wear and corrosion resistance of Ni-Mn-Cu cast iron. Materials 12 (1), 3500. https://doi.org/10.3390/ma12213500
- Melchers, R.E. (2013). Long-term corrosion of cast irons and steel in marine and atmospheric environments. Corros. Sci. 68, 186-194. https://doi.org/10.1016/j.corsci.2012.11.014.
- Méndez, S., Arenas, M.A., Niklas, A., González, R., Conde, A., Sertucha, J., de Damborenea, J.J. (2019). Effect of silicon and graphite degeneration on high-temperature oxidation of ductile cast irons in open air. Oxid. Met. 91, 225-242. https://doi.org/10.1007/s11085-018-9875-0.
- Morcillo, M., de la Fuente, D., Díaz, J., Cano, H. (2011). Atmospheric corrosion of mild steel. *Rev. Metal.* 47 (5), 426-444. https://doi.org/10.3989/revmetalm.1125.
- Pourbaix, M., Pourbaix, A. (1989). Recent progress in atmospheric corrosion testing. *Corrosion* 45 (1), 71–83. https://doi.org/10.5006/1.3577890. Rajani, B., Kleiner, Y. (2003). Protecting ductile-iron water
- mains: what protection method works best for what soil condition?. J. Am. Water Work Assoc. 95 (11), 110-125. https://doi.org/10.1002/j.1551-8833.2003.tb10497.x
- Reynaud, A. (2008). Corrosion & cast irons. Ed. Editions techniques des industries de la fonderie, Sèvres, France, p. 11
- Sertucha, J., Suárez, R. (2005). Arenas de moldeo en verde. Ed. Azterlan, Durango, España, pp. 264-267.
- Sertucha, J., Larrañaga, P., Lacaze, J., Insausti, M. (2010). Experimental investigation on the effect of copper upon eutectoid transformation of as-cast and austenitized spheroidal graphite cast iron. Int. J. Met. 4, 51-58. https:// doi.org/10.1007/BF03355486.
- Sertucha, J., Lacaze, J., Serrallach, J., Suárez, R. Osuna, F. (2012). Effect of alloying on mechanical properties of as cast ferritic nodular cast irons. *Mater. Sci. Technol.* 28 (2), 184–191. https://doi.org/10.1179/1743284711Y.0000000014.
- Stawarz, M., Dojka, M. (2022). Corrosion resistance of selected cast iron grades under deposit mining conditions. Int. J. 16, 342-348. https://doi.org/10.1007/s40962-021-Met. 00607-6.
- Sun, Y., Hu, S., Xiao, Z., You, S., Zhao, J., Lv, Y. (2012). Effects of Ni on low-temperature impact toughness and corrosion Takamori, S., Osawa, Y., Halada, K. (2002). Aluminum-alloyed cast iron as a versatile alloy. *Mater. Trans.* 43 (3), 311-314.
- https://doi.org/10.2320/matertrans.43.311.
- Tiedje, N.S. (2010). Solidification, processing and properties of ductile cast iron. *Mater. Sci. Technol.* 26 (5), 505–514. https://doi.org/10.1179/026708310X12668415533649.
- Zhou, Y., Lu, Z., Zhan, M. (2007). An investigation of the erosion-corrosion characteristics of ductile cast iron. *Mater. Design* 28 (1), 260-265. https://doi.org/10.1016/j. matdes.2005.07.011.