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PRODUCTION OF LAMELLAR CAST IRON EN-GJL-150 FROM LOCAL MANGANESE-RICH PIG IRON BY MODIFICATION OF THE MELTING PROCESS

ABSTRACT

In the present study, a modified duplex melting process was set up so as to be able to produce an EN-GJL-150 gray cast iron from a local manganese-rich pig iron. A descriptive statistics showed an average Mn and Si content in raw material such that: Mn % = 2.457 ± 0.133 and Si % = 0.682 ± 0.088 . The demanganization process was run and monitored in a cascade of two industrial-scale furnaces: a rotary kiln and an electric arc furnace. The performed experiments indicated that: 1) the manganese content decreased from 2.45 % to 0.94 %, 2) the manganese oxidation obeys the first order kinetic model, 3) Brinell and Rockwell hardness's decreased by 38.83% and 27.81% respectively, and 4) the produced cast iron has a pearlitic microstructure with a small fraction of ferrite (1 to 5%) in the matrix and traces of cementite. All results showed that the produced castings comply with the standards in force for EN-GJL-150 cast irons, similar to gray cast iron ASTM A48 Class 20.

Keywords: Manganese-rich cast iron; demanganization; melting process; kinetics; micrography

INTRODUCTION

Cast iron offers high castability and good machining properties, as well as interesting mechanical properties [1-2]. Due to the economic benefits it offers, cast iron is used for many applications such as water pipes [3-5], machine building, in the automotive industry and in metal fabrication and processing [2]. Until today, cast iron still constitutes the majority ($\approx 70\%$) of metal castings [1, 6]. In addition, specific cast irons are the material of choice for seawater pump casings, rolling mill rolls and earthmoving machinery parts [2, 6-8].

Algeria, a country with considerable iron reserves, is one of some countries where metallurgists face the problem of a large content of manganese in pig iron of above 3%. As a

result, and for some time now, steelmakers have gave up using local iron ore, with a high manganese content, and have preferred to import, which has proven to be less expensive.

The literature suggests that Mn should be present in cast iron at low levels for its essential role in desulfurization [9-13]. Indeed, sulfur can exhibit many negative effects, including the promotion of degenerate graphite forms, intercellular carbides, increased chilling tendency and high hardness pearlite [11], and can reacts with iron to produce a low-melting phase (FeS) that may produce hot-shortness [11-13]. It is reported that Mn should be present around stoichiometric ratio ($\text{Mn:S} = 1.7:1$) to avoid the negative influence of sulfur [11-13]. In addition, at a low content, Mn also acts as a denitrifying element because the iron nitrides, due to the nitrogen present, disturb the graphitization by their action as carbide stabilizers [10]. On the other hand, at higher contents beyond 0.8%, manganese tends to oppose graphitization by increasing the stability of pearlite, whose hardness is relatively high [10] which will then influence the machinability of the castings. Furthermore, graphite, due to its relatively high specific heat compared to the other constituents of cast iron (austenite, cementite, pearlite, etc.), acts as a retarder of the cooling rate (due to its thermal inertia), which will improve the castability of the cast iron during the solidification as well as a better filling of the molds [9].

In addition to that, there are particular problems with pig iron that has manganese content above 1 %. The higher Mn content in hot metal during the oxidation process influences the formation of slag and causes serious problems for the technology [14-15]. Indeed, a large quantity of slag is obtained that decreases the yield and increases the splashing [15]. For this reason, the reaction between manganese and oxygen in hot metal is still being investigated specifically from the points of view of the reaction mechanism, the thermodynamics and the kinetics, and different conclusions were proposed [15-16]. However, the majority of investigations on manganese oxidation were performed on molten metal with low manganese content, below 1.00 % and very rarely when the manganese content is higher than 4 %, as the initial content.

The main objective of this research was to set up a melting process adapted so as to be able to use the local Algerian pig iron rich in manganese, produced by the Steel Complex of SA El-Hadjar (the largest steel plant of Algeria located in Annaba, 540 km east of Algiers), in substitution for casting irons hitherto imported, and this, to produce lamellar gray cast iron EN-GJL-150 (GG 150 or FT15D). So, to carry out this work we created an approach for lowering the manganese content, by combining the introduction of oxygen with a composition correction in two kinds of furnaces in duplex mode: a rotary kiln and an electric arc furnace, followed by processing of hot metal in a ladle. This provides a basis for investigations regarding high manganese iron ore treatment which may thus help to resolve some lingering misunderstandings and confusions about them. Specifically, the kinetics, the evolution of hardness and the microstructure were studied in this work.

MATERIALS AND METHODS

Demanganization process

In this study, we used as raw material pigs of 5 kg coming from the Steel Complex of El-hadjar (SA El-Hadjar) located in the department of Annaba, 540 km east of Algiers. Table 1 displays the elemental content of these pigs as supplied by the SA El-Hadjar.

Table 1. Elemental content of raw material supplied by SA El-Hadjar (Provider data)

Element	Carbon	Silicon	Manganese	Phosphorus	Sulfure
Mass content (%)	3.89-4.20	0.90-1.20	2.50-2.90	0.01	0.022

Thirty samples chosen at random from among these pigs were analyzed to determine their Manganese (Mn) and Silicon (Si) content, with the aim of making a statistical analysis. All the statistical calculations (descriptive statistics, histograms, Student-test, modeling) were performed by using the analysis design procedure of Statistica software (8th version).

Table 1 shows the manganese content of this local pig iron varying within a range of 2.5 to 2.9%; well above the maximum threshold for cast iron intended for foundries. The main objective of this study was to set up a melting process adapted so as to be able to use the local Algerian pig iron manganese-rich to produce lamellar gray cast iron EN-GJL-150 (Ft-15) in substitution for cast iron hitherto imported. Furthermore, according to the data in Table 1, the local cast iron of SA El-Hadjar is not only rich in manganese, but also poor in silicon. As a result, a correction of the content of the latter must be made during the melting process in order to meet the European standards of the EN-GJL-150 cast irons that we wish to develop in this work, and whose characteristics as well as the chemical composition are collated in Table 2.

Table 2. Properties of the lamellar cast iron EN-GJL-150

Denomination	European EN	DIN Germany	AFNOR France
	EN-GJL-150	GG-15	FT 15 D
Element / Mass content (%)	Carbon	Silicon	Manganese
	2.90-3.70	1.70-2.50	0.35-1.00
Mechanical properties	Tensile strength at break (MPa)	Brinell hardness	Elasticity modulus (GPa)
	150	125-205	78-103

The originality of this work was then to produce EN-GJL-150 lamellar cast iron from this local raw material by reducing its manganese content during a duplex melting process in two types of furnaces in cascade as well as in the treatment ladle as shown in Figure 1. We used for this purpose two industrial-scale furnaces in cascade: a rotary kiln with a maximum capacity of 5 tons and a 3-tons capacity electric arc furnace.

The initial charge treated consisted of 2.5 tons of pig iron, 90 kg of CaCO_3 and 40 kg of SiO_2 introduced first and spread on the floor of the rotary kiln. CaCO_3 has a fluxing action allowing reducing the concentration of impurities in cast iron giving rise to slag while Si acts as a graphitizer favoring the decomposition of cementite and the formation of graphite lamellae thus leading to a slowed down solidification, much sought after when casting thin parts. This comes from the fact that the specific heat of graphite is relatively high compared to the other constituents of cast iron (austenite, cementite, pearlite, etc.), which gives it greater thermal inertia. And in fact, when in a cast iron during solidification, graphite forms and

deposits, this has the effect - due to its thermal inertia and the heat it has stored - of reducing the cooling rate of castings, and therefore has a positive effect on the castability. The cast iron will thus cast better, and therefore has a greater ability to fill molds [9]. In addition, graphite has a lubricating action, reduces wear and improves machinability.

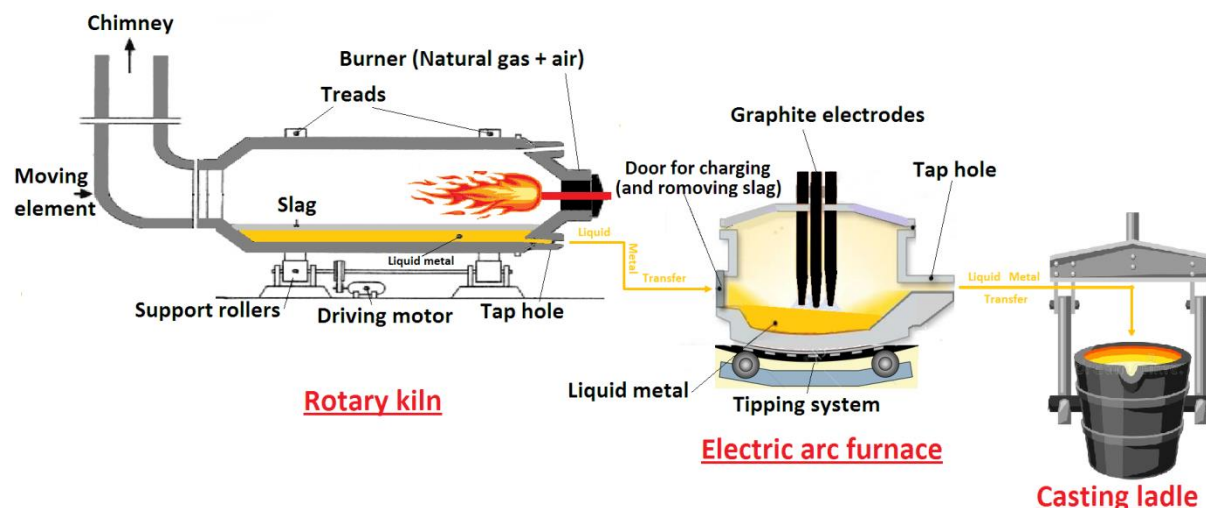


Fig. 1. Duplex melting process for the production of lamellar cast iron EN-GJL-150 from local manganese-rich raw material

The charge is brought to a temperature of 1300°C until total melting, for about 2 h; period during which regular scrapings were carried out on the surface in order to evacuate the slag. A first sampling was done at that time in order to analyze the manganese and silicon content. We then blew hot air from the heat exchanger supplied with the exhaust gases 6 times for a period of 2 hours at regular intervals of 15 minutes. Before each blowing of air, a surface scraping is done and a sampling carried out in order to monitor the evolution of the composition, the kinetics of the manganese oxidation as well as the hardness (Brinell 'BH' and Rockwell 'RCH').

The molten pig iron from the rotary kiln was then transferred to the electric arc furnace with a basic coating, the hearth of which was covered with ferric oxide (Fe_2O_3) in a proportion of 2.5% of the weight of the molten metal, acting as a vector of oxygen for the manganese oxidation. During this first refining period, which lasted 1 hour and during which the electric current was cut, 40 kg of silica were also added to the molten metal in order to improve the fluidity of the slag and facilitate its removal from the furnace. After this period of refining, the electric current was restored in order to superheat the metal and to proceed to the correction of its composition in order to meet the standards in force for cast iron EN-GJL-150, and this by adding 15 kg of carbon, 10 kg of phosphorus and 60 kg of FeSi75, acting as a reducer for the metals of their oxides. Sampling was carried out along with the slag evacuations approximately every 15 to 20 minutes in order to monitor the evolution of the composition, the kinetics of the manganese oxidation and the hardness (BH and RCH).

It is well known that the mechanical properties of cast irons strictly depend on their microstructures [7]. Moreover, the crystallization and graphitization of cast iron are very strongly influenced by its chemical composition [6, 17]. Thus, the control of the later as well as the mechanical properties and the microstructure were carried out on the final product at the outlet of the furnaces and in the treatment ladle after having added 3 kg of ferrosilicon FeSi75 for inoculation purposes. For this purpose, 2 groups of samples of 3 bars each have been prepared: at the outlet of the furnaces and after inoculation in the ladle. The test bars

with diameter 35 mm and length 300 mm were cast separately and side-by-side, at 1350°C in CO₂-hardened sand cores serving as a mold and having the following composition: 95% by weight of silica and 5% of sodium silicate. From these bars, standardized tensile specimens were machined according to ASTM E8 standards (205 mm in length, 28 mm in diameter with a groove in the middle with 20 mm diameter as shown in Figure 2) and discs for measuring the hardness (BH) were made.

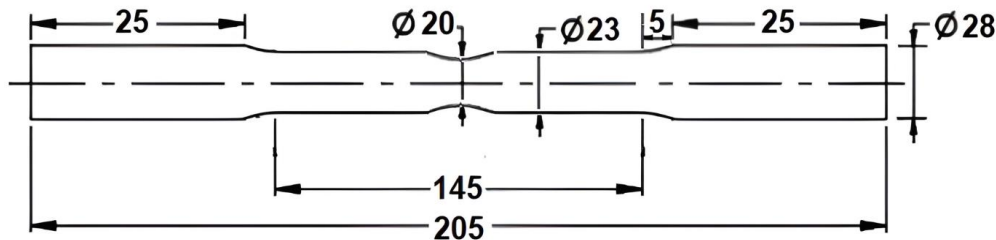


Fig. 2. Tensile test specimens (all the dimensions in mm)

Raw material analysis and characterization of the produced cast iron EN-GJL-150

chemical analysis

The evolution of the chemical composition of the molten pig iron throughout the treatment was monitored by regular sampling on which standardized specimens were produced according to the TGL 15477/03 standard.

The carbon and sulfur contents were determined by the volumetric method by measuring the volumes of CO₂ and SO₂ released respectively after combustion of the chips taken from the samples in an oxygen bath.

- The silicon, phosphorus and manganese contents were determined by analytical techniques with adding reagents. The silicon content was determined by gravimetry, by attacking a one gram sample with a mixture of 300 mL of HCl and 15 mL of H₂SO₄ for a few minutes, and then the solution was filtered and calcined at 1100°C for 30 minutes. The Si content was then calculated by the following Eq. (1):

$$\text{Si}\% = \frac{A \times 0.46744}{E} 100 \quad (1)$$

Where A and E are the weights (g) of the sample before and after calcination, respectively.

- The phosphorus content was determined by acid-base titration using a 5-20 mL volume of NaOH solution (0.2 M). The titration was carried out with a solution of H₂SO₄ (0.2 M), in the presence of phenolphthalein as a colored indicator. The P content was then calculated by the following Eq. (2):

$$\text{P}\% = \frac{(b-c) \times 0.00027}{E} 100 \quad (2)$$

Where b is the volume (mL) of NaOH solution used, c the volume (mL) of the H₂SO₄ solution poured in at equivalence and E is the weight (g) of the sample.

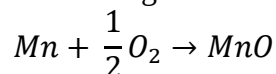
- The manganese content was determined by adding 50 ml of HNO₃ (0.2 M) to 0.3 g of the sample and heating until complete release of nitrous gases. Then, 25 mL of AgNO₃, 2 g of (NH₄)₂S₂O₈ and 25 mL of NaCl (0.2 M) were added to the mixture under vigorous stirring and then filtered with arsenic acid. The Mn content was then calculated by the following Eq. (3):

$$\text{Mn}\% = \frac{AA \times 0.000329}{E} 100 \quad (3)$$

Where AA is the amount (g) of arsenic acid used and E is the weight (g) of the sample.

Kinetic study of manganese oxidation

The oxidation of manganese contained in the molten pig iron inside the furnaces takes place by oxygen supply, according to the following balance equation:



The kinetics of this reaction was investigated by using the integral method which consists of comparing the measured concentration of manganese during the applied melting process, with the integral form of the rate law, as following:

$$\text{Rate expression: } R_{ox} = -\frac{d[\text{Mn}]}{dt} = k \cdot [\text{Mn}] \cdot [\text{O}_2] = k_{app} \cdot [\text{Mn}] \quad (4)$$

$$\text{Integrated form: } \ln([\text{Mn}]) = -k_{app} \cdot t + \ln([\text{Mn}]_0) \quad (5)$$

The graphic representation of Eq. (5) allows concluding as to the order of the oxidation reaction as well as its coefficient. In addition, to find out the adequacy of the applied model and how it fits the experimental data, a statistical analysis was performed to estimate the root-mean-square error (RMSE) and the Chi-square statistic (X^2) by using the following formulas [18]:

$$RMSE = \sqrt{\frac{1}{N} \cdot \sum_1^N (y_{exp} - y_{cal})^2} \quad (6)$$

$$X^2 = \sum_1^N \frac{(y_{exp} - y_{cal})^2}{y_{cal}} \quad (7)$$

Where N is the number of experiments while y_{exp} and y_{cal} are the experimental and calculated values respectively.

The smaller $RMSE$ and X^2 values the better is the fitting, meaning that the data from the used model are similar to the experimental data.

Mechanical tests

Hardness tests serve an important need in industry even though they are empirical, i.e. based on experiments and observation, rather than fundamental theory. Hardness is defined as the property of a material that enables it to resist plastic deformation, penetration, indentation, and scratching. Thereby, the resistance to wear by either friction or erosion (by steam, oil, and water) generally increases with hardness. In this work, the Brinell and Rockwell hardness tests were performed in compliance with NF EN 10003-1 and NF EN 10109-1 standard, respectively. A Brinell hardness tester was used at a constant applied load of 750 kgf, with a 10 mm ball of hardened steel as indenter. In parallel, a diamond cone having an included angle of 120° was used for the Rockwell hardness test RCH; a preload and a load of 10 and 150 kgf were applied consecutively.

Tensile testing were performed with an Instron test machine employing an average of three specimens for each sample with the respect to ASTM E8/E8M.

Microstructure analysis

The microscopic metallographic analysis was carried out on samples of cast iron leaving the electric arc furnace, with the aim of highlighting its various constituents. For this purpose, 5 bars of 310 mm in length with different diameters (5; 10; 20; 30 and 40 mm) were prepared

and cast at 1350°C in CO₂-hardened sand cores serving as a mold. From these bars, discs 5 cm long were cut and then polished; their surfaces underwent a pre-polishing with abrasive papers of decreasing grain size: 1000-600-180, then a finishing polishing with diamond paste, in order to eliminate any micro-scratches and streaks and to obtain a mirror surface, flat, perfectly smooth and reflective. These polished surfaces were then chemically attacked by a reagent composed of 5% HNO₃ and 95% C₂H₅OH, then analyzed by an inverted microscope model AXIOMAT IAC. The chemical attack was carried out at room temperature by immersion in the reagent, followed by washing with water and drying with compressed air. This attack reveals the structure of the cast iron and its constituent elements. The cooling of the samples not being homogeneous, i.e. depending on their dimensions, images were taken at the center and at the end of the surfaces of each sample.

RESULTS AND DISCUSSIONS

Statistical analysis on Mn and Si content in raw material

The histograms demonstrating the distribution of manganese and silicon contents in the thirty samples chosen at random among raw material provided by SA El-Hadjar are given in Figures 3 and 4, respectively. From these figures, it can be seen that the distribution of Mn content is normal while that of Si is multimodal, i.e. with several bumps in the data distribution.

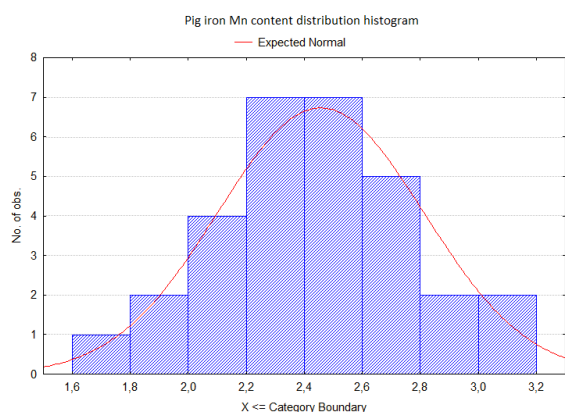


Fig. 3. Histogram representing the manganese content distribution in the pig iron

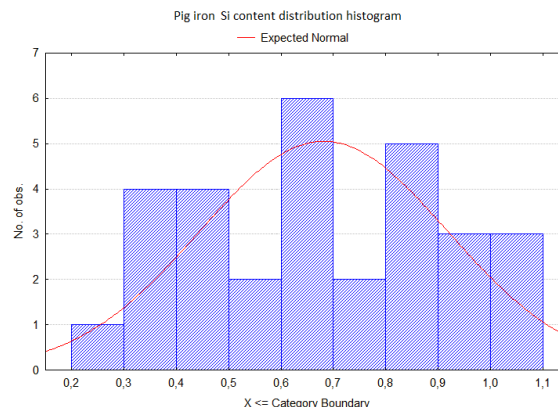


Fig. 4. Histogram representing the silicon content distribution in the pig iron

The results of the descriptive statistics of these data at confidence level of 95% are summarized in Table 3 where it can be seen that concentrations vary in the following ranges:

- Mn content: from 1.8 to 3.2% with a standard deviation of 0.356 and a confidence interval of the mean such that: $\overline{Mn\%} = 2.457 \pm 0.133$
- Si content: from 0.28 to 1.05% with a standard deviation of 0.237 and a confidence interval of the mean such that: $\overline{Si\%} = 0.682 \pm 0.088$.

Table 3. Statistical analysis of the distribution of manganese and silicon contents in pig iron

Variable	N° of samples	Min.	Max.	Mean	CL -95%	CL +95%	Std. Dev.	Variance	Coef. Var.
Mn content (%)	30	1.800	3.200	2.457	2.324	2.590	0.356	0.127	14.487
Si content (%)	30	0.280	1.050	0.682	0.594	0.770	0.237	0.056	34.771

Kinetic monitoring of the manganese oxidation

Table 4 below illustrates the evolution of the manganese content (Mn%) over time at the level of the two furnaces during the duplex melting process applied in the context of this work. From these results it can be seen that during the two hours of treatment at the level of the rotary kiln, where the hot air coming from the exchangers had been blown 6 times regularly per period of 15 minutes, it was not possible to lower the manganese content below 1.45%, which corresponds approximately to an oxidation ratio of 40.82%.

Table 4. Evolution of the manganese content during the duplex melting process

	Time (min)	Mn%	[Mn] (g/kg)
Rotary kiln	0	2.45	24.50
	30	2.25	22.50
	45	2.10	21.00
	60	2.05	20.50
	75	1.70	17.00
	90	1.61	16.10
	105	1.57	15.70
	120	1.50	15.00
	135	1.45	14.50
Electric arc furnace	0	1.45	14.50
	40	1.35	13.50
	55	1.30	13.00
	90	1.25	12.50
	105	1.18	11.80
	130	1.12	11.20
	160	1.09	10.90
	180	1.04	10.40
	200	0.97	9.70
	220	0.94	9.40

It should however be noted that the first blowing of air was carried out at 45 minutes after the complete melting of the alloy, and this, after having carried out a sampling from which the following composition of the molten metal was measured:

- Carbon: 3.42%, which corresponds to a loss of 15.45%;
- Silicon: 0.75%, indicating a loss of 28.57%;
- Manganese: 2.1%, this indicates an oxidation rate of 14.29%.

After 135 minutes of treatment in the rotary kiln, an elemental analysis was carried out and gave the following results:

- Carbon: 3.2%, i.e. a loss of 20.89% or approximately 21 kg;
- Silicon: 0.5%, meaning a loss of 52.38% or approximately 14 kg;
- Manganese: 1.45%, indicating an oxidation ratio of 40.82%.

The molten metal with this composition was then transferred to the electric arc furnace where the current was first cut for 1 hour, in order to allow a slow oxidation of the manganese, by the oxygen supplied by Fe_2O_3 . After that, the current was restored in order to superheat the molten iron and proceed to the correction of the carbon and silicon contents in order to comply with the standards in force for lamellar cast irons GN-GJL-150 (cf. Table 2). We then added 15 kg of carbon, 60 kg of FeSi75 and 10 kg of phosphorus to the molten pig iron.

After 220 minutes of treatment in the electric arc furnace, an elemental analysis was carried out and gave the following results:

- Carbon: 3.67%;
- Silicon: 2.29%;

- Manganese: 0.94%, indicating an oxidation ratio of 61.63%, through the 2 furnaces.
- Phosphorus: 0.5%;
- Sulfur: 0.013%.

The kinetic monitoring of the manganese oxidation was carried out by using the first order model (Eq. (4) & Eq. (5)) in order to estimate the manganese removal rate in each of the 2 furnaces used in duplex in this work. The graphic representation of Eq. (5) i.e. the linear plot of $\ln([Mn])$ against time allows one to obtain the apparent rate constant k_{app} as shown in Figure 5.

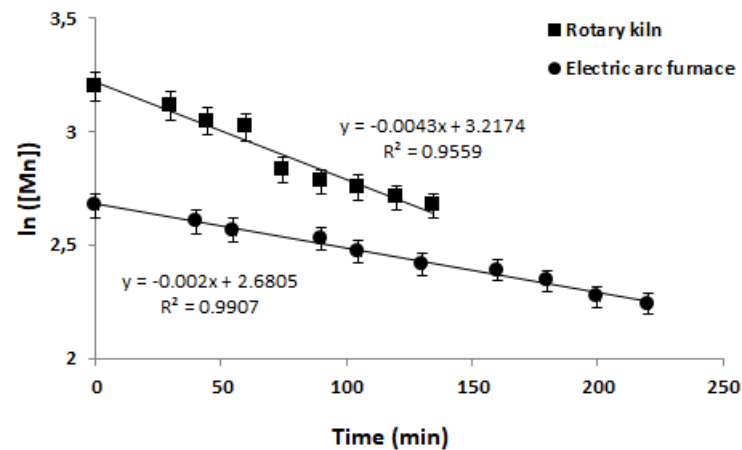


Fig. 5. Kinetics study of the demanganization during the duplex melting process: $\ln([Mn])$ vs. time

The shape of the straight lines in Figure 5 and the high values of the coefficients of determination (0.95 and 0.99) clearly show that the demanganization follows first-order kinetics. The values of the rate coefficients (0.0043 and 0.0020 min^{-1}) show on the other hand, that the manganese removal was 2 times faster in the rotary kiln than in the electric arc kiln. Indeed, the blowing of air is a process as brutal as effective which generates other losses by oxidation in parallel with the manganese: carbon and silicon.

Kinetic parameters are summarized in Table 5, as well as the determination coefficients (R^2), RMSE and X^2 values; the latter's clearly show the applicability of that kinetic model to predict the demanganization data through the two furnaces used in cascade.

Table 5. Kinetic parameters of the manganese oxidation in the rotary kiln and electric arc furnace

	Rotary Kiln	Electric arc furnace
Rate coefficient: $k \text{ (min}^{-1}\text{)}$	0.27	0.12
$R^2 \text{ (%)}$	95.34	99.07
RMSE	0.0374	0.0144
X^2	0.0038	0.0009

Monitoring of the evolution of Brinell and Rockwell hardness

Hardness is defined as the ability of a metal or metal alloy to resist plastic deformation, in a specific, localized location rather than in a general location. It is also defined as metal's resistance to indentation, scratching, or abrasion. Hardness is an important feature because the

level of hardness that a metal has directly relates to its ability to resist wear. Table 6 below gathers the Brinell and Rockwell hardness's measurements during the duplex melting process as a function of the manganese content in the molten pig iron. Table 6 gives also the confidence limits of the mean for each measurement at the 95% confidence level.

The data in Table 6 shows that hardness decreases with decreasing manganese content (Mn%) as expected and indicates that:

- The Brinell hardness decreases from 32.15 to 19.67, or 38.83%, when manganese content decreases from 2.5% to 0.94%
- The Rockwell hardness decreases from 207.33 to 149.67, or 27.81%, when manganese content decreases from 2.5% to 0.94%

Indeed, manganese is a carburogenic element, leading to the formation of carbides such as manganese carbide (Mn_3C) and carburized ferromanganese $(Fe,Mn)_3C$, which like all carbides, are compounds tending to be extremely hard, refractory and resistant to wear, corrosion and heat [10].

Furthermore, at low levels ($< 0.4\%$) manganese essentially has the role of desulphurizing and denitration [11-12]. But at higher contents, beyond 0.8% manganese tends to oppose graphitization by increasing the stability of pearlite, whose hardness is relatively high [10].

Table 6. Evolution of the hardness's (Brinell and Rockwell) according to the reduction of the manganese content through the two furnaces

	Mn%	Rockwell hardness				Brinell hardness			
		RCH1	RCH2	RCH3	Mean $\pm$ CL	BH1	BH2	BH3	Mean $\pm$ CL
Rotary kiln	2.25	31.5	33.45	31.5	32.1500 $\pm$ 2.7967	207	187	228	207.3333 $\pm$ 50.9299
	2.1	32	32.6	29	31.2000 $\pm$ 4.7912	190	207	198	198.3333 $\pm$ 21.1273
	2.05	29	25	33.5	29.1667 $\pm$ 10.5637	183	207	198	196.0000 $\pm$ 30.1186
	1.7	26	27	34	29.0000 $\pm$ 10.8281	166.8	207	198	190.6000 $\pm$ 52.4077
	1.5	27	27	32.32	28.7733 $\pm$ 7.6300	182.84	194	178	184.9467 $\pm$ 20.3833
Electric arc furnace	1.45	27.5	27.5	26.5	27.1667 $\pm$ 1.4342	178	194	167.52	179.8400 $\pm$ 33.1273
	1.35	24	27.5	25	25.5000 $\pm$ 4.4783	156.94	187	187	176.9800 $\pm$ 43.1126
	1.3	29	30.64	15	24.8800 $\pm$ 21.3525	178	194	148.2	173.4000 $\pm$ 57.7411
	1.25	21	25	27	24.3333 $\pm$ 7.5892	187	170	154.92	170.6400 $\pm$ 39.8694
	1.18	21	25	26	24.0000 $\pm$ 6.5724	161	170	155	162.0000 $\pm$ 18.7548
	1.12	28.8	18	21	22.6000 $\pm$ 13.8489	155	170	156	160.3333 $\pm$ 20.8332
	1.09	22	20	23	21.6667 $\pm$ 3.7946	156	161	150	155.6667 $\pm$ 13.6816
	1.04	21	20	20	20.3333 $\pm$ 1.4342	150	155	156	153.6667 $\pm$ 7.9854
	0.97	22.5	17	16	18.5000 $\pm$ 8.6945	148	161	148	152.3333 $\pm$ 18.6448
	0.94	21	20	18	19.6667 $\pm$ 3.7946	156	150	143	149.6667 $\pm$ 16.1628

Rockwell and Brinell hardness's related to the drop in manganese content are plotted in Figures 6 and 7, respectively. Actually, these data represent the calibration data set, which was used to estimate the parameters of the following empirical models (Eq. (8)) correlating hardness (either Brinell or Rockwell) to the manganese content.

$$H = a_0 + a_1 \cdot \ln (Mn\%) \quad (8)$$

Where H refers to Brinell or Rockwell hardness.

The parameter values in Eq. (8) were computed at the 95% confidence level, using 'Statistica' software; they are collated in Table 7.

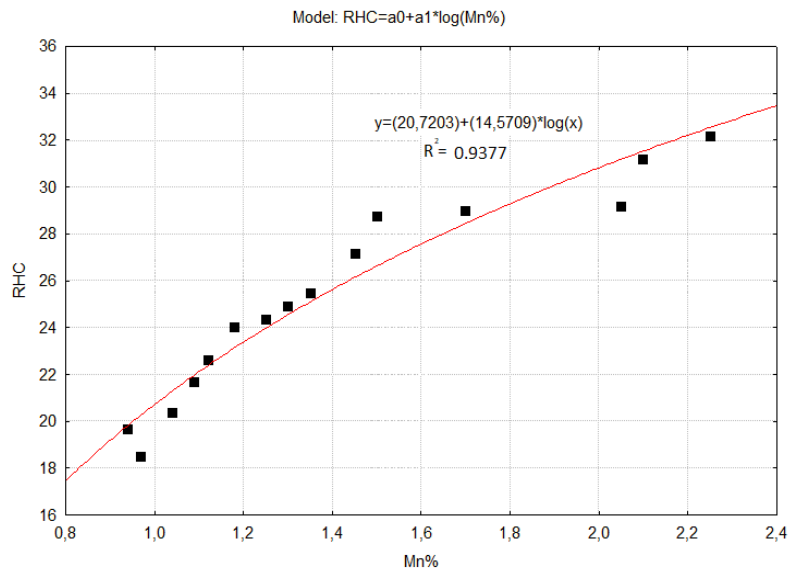


Fig. 6. Evolution of Rockwell hardness as a function of the drop in manganese content

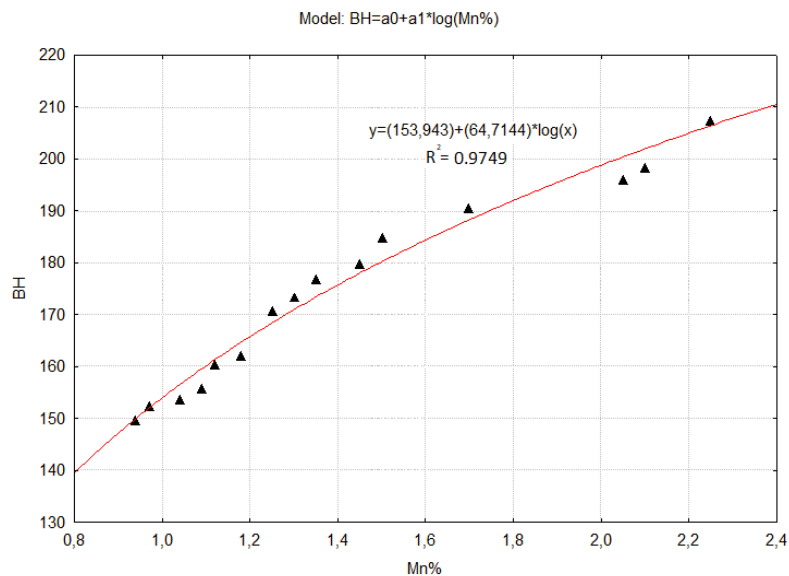


Fig. 7. Evolution of Brinell hardness as a function of the drop in manganese content

Table 7. Parameters of the model Eq. (8) correlating hardness to manganese content

Reponse: H	Coefficient	Estimate	Standard Error	t-value	Low conf. limit	Up conf. Limit
RCH	a_0	20.7203	0.4311	48.0624	19.7890	21.6517
	a_1	14.5709	1.0415	13.9901	12.3208	16.8210
BH	a_0	153.9429	1.1924	129.1012	151.3668	156.5189
	a_1	64.7144	2.8807	22.4645	58.4909	70.9378

It should be noted that although the two hardness tests have similarities, there are several important differences: 1) the Brinell hardness testing uses usually a 10 mm hardened steel ball, while the Rockwell test uses either a much smaller steel ball (< 4 mm), and 2) the Rockwell test measure the depth of the indentation, while the Brinell test measures the width of the indentation.

There are conversion tables between these 2 variables, but it's important to note that the conversion scales between them are not the same and should not be confused with one another.

In Figure 8 Brinell hardness is plotted against Rockwell hardness. A correlation given by Eq. (9) between these two variables was developed and its parameters were estimated at a 95% confidence interval, using the Statistica software.

$$BH = a_0 + a_1 \cdot RCH \quad (9)$$

The parameter values in Eq. (9) are gathered in Table 8.

Table 8. Parameters of the model Eq. (9) correlating Brinell hardness to Rockwell hardness

Coefficient	Estimate	Standard Error	t-value	Low conf. limit	Up conf. limit
a_0	66.1977	6.0414	10.9574	53.1461	79.2493
a_1	4.2719	0.2361	18.0966	3.7619	4.7819

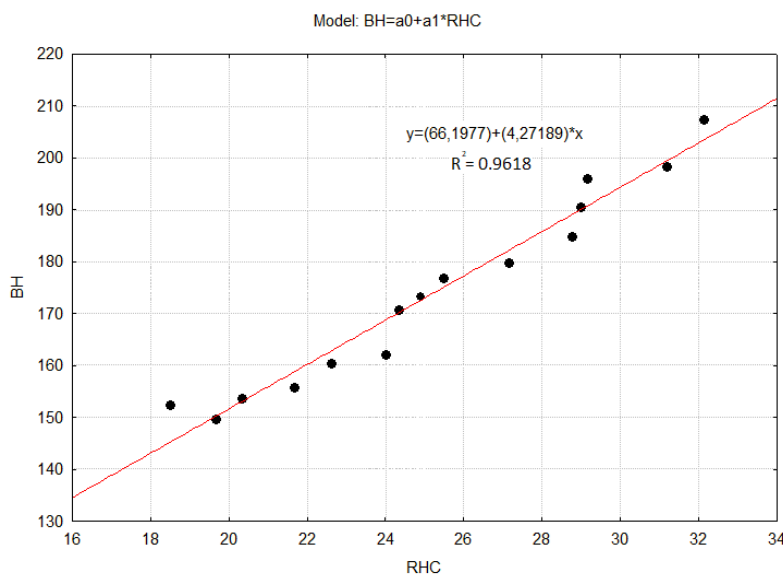


Fig. 8. Correlation between Brinell and Rockwell hardness's

Characterization and microstructure study of the produced EN-GJL-150

Table 9 gathers the chemical composition, tensile strength and Brinell hardness of the demanganized cast iron both in the out of the furnaces and in the ladle after inoculation. All of the results in this table show that the cast iron produced by the melting process adopted in this work complies with the standards in force for EN-GJL-150 cast irons listed in Table 2.

Table 9. Characterization of the produced EN-GJL-150 cast iron

Sampling	Reference	Element / Content (%)					Tensile strength (MPa)	Brinell hardness HB
		Carbon	Silicon	Manganese	Phosphorus	Sulfure		
at the outlet of the furnaces	OF-P1 ^(a)	3.81	2.21	0.95	0.07	0.032	162	207
	OF-P2 ^(a)	3.77	2.08	0.97	0.067	0.021	143	198
	OF-P3 ^(a)	3.74	2.24	0.94	0.057	0.015	147	198
	Mean	3.77	2.18	0.95	0.065	0.023	150.67	201
After the inoculation in the ladle	LI-P1 ^(b)	3.74	2.52	0.95	0.057	0.013	151	182
	LI-P2 ^(b)	3.63	2.53	0.95	0.054	0.016	150	187
	LI-P3 ^(b)	3.84	2.52	0.94	0.062	0.013	150	182
	Mean	3.74	2.52	0.95	0.058	0.014	150.33	183.7

^(a) Out of the furnaces - Product sample number; ^(b) After the inoculation in the ladle - Product sample number

On the other hand, it is well known that the mechanical properties of cast irons strictly depend on their microstructures [7]. Figure 9 illustrates the effect of the sample size (which induces non-homogeneous cooling) on the microstructure of the produced cast iron at the outlet of the furnaces.

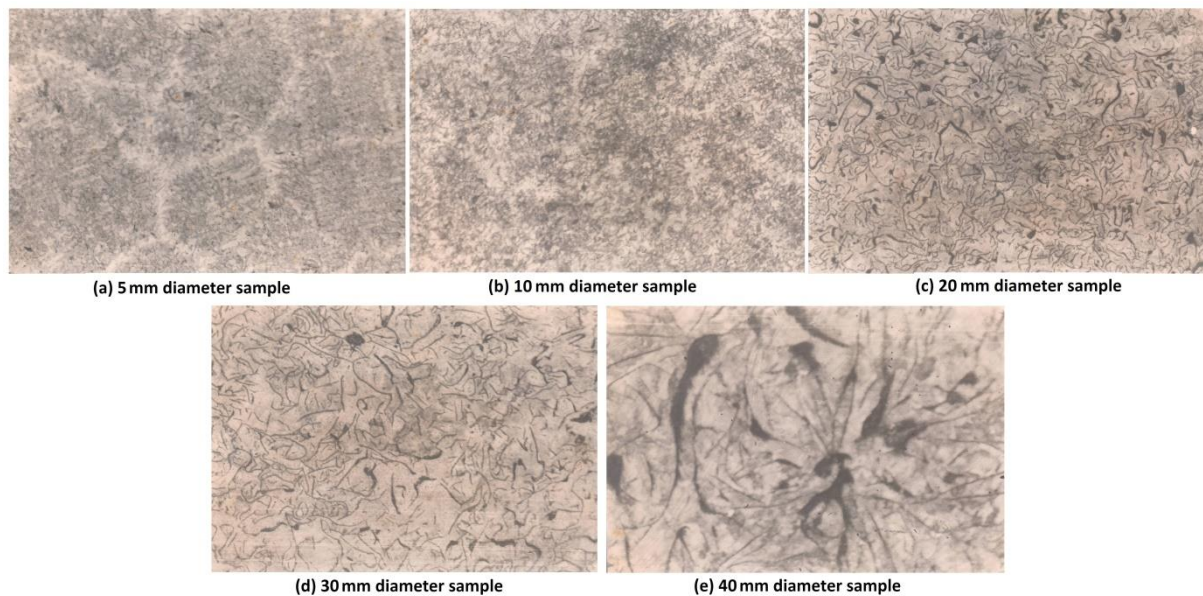


Fig. 9. Optical micrographs taken at the center of the samples and showing the microstructure of the produced EN-GJL-150 cast iron

To measure the length of the graphite lamellae, we used commercial image analysis software, as shown in the schematic pictured in the Figure 10 for hundreds of lamellae in each unetched sample.

From Figure 9, the following conclusions can be drawn:

- In Figure 9-a, the 5 mm diameter sample shows a fine intertidal structure with lamellae of lengths ranging from 10 to 20 μm .
- In Figure 9-b, the 10 mm diameter sample shows a fine intertidal distribution with lamellae of lengths ranging from 10 to 40 μm . Figure 9-b shows also a presence reaching 5% of graphite in the matrix.

- In Figure 9-c, the 20 mm diameter sample shows a pearlitic structure with a presence of graphite in the matrix ranging from 10 to 15%, ferrite from 1 to 2% and lamellae of lengths ranging from 40 to 250 μm in the shape of rosettes.
- In Figure 9-d, the 30 mm diameter sample shows a pearlitic structure with a presence of graphite in the matrix exceeding 15%, ferrite from 3 to 5% and lamellae of lengths ranging from 40 to 250 μm in the shape of rosettes.
- In Figure 9-e, the 40 mm diameter sample shows a pearlitic-ferritic structure with a presence of graphite in the matrix exceeding 15%, ferrite from 3 to 5% and lamellae of lengths ranging from 40 to 250 μm in the shape of rosettes.

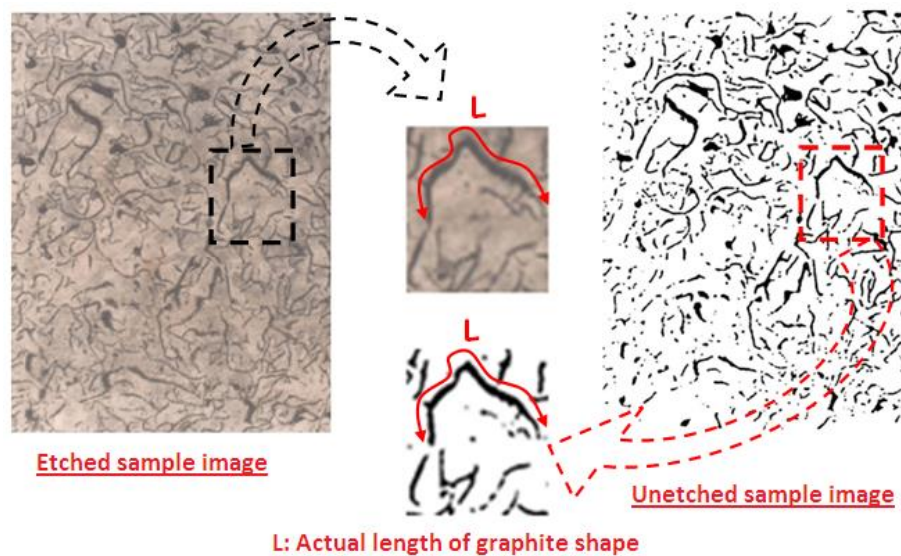


Fig. 10. Schematic showing the method of measuring the lengths of the graphite lamellae on unetched samples images

The micrographs in Figure 9 (a-b) for the smallest dimensions (5-10 mm) show a fine intertidal distribution of graphite with very fine lamellae of 10 to 15 μm located between the γ dendrites due to the fast cooling in contact with the walls of the mold. However, for the samples of larger dimensions (diameters 20, 30 and 40 mm), the micrographs in Figure 9 (c-d-e) show a distribution of graphite in the form of rosettes with lamellae of lengths ranging from 10 to 250 μm . This indicates that the cast iron produced here has a pearlitic microstructure with a small fraction of ferrite (1 to 5%) in the matrix and traces of cementite.

CONCLUSIONS

- The present study showed that local manganese-rich pig iron could be used to produce EN-GJL-150 gray cast iron hitherto imported.
- An industrial scale melting process has been studied and implemented so as to be able to reduce the Mn content and to fully comply with the standard in force for EN-GJL-150 gray cast iron.

- The descriptive statistics carried out on the raw material showed that its Mn content varied from 1.8 to 3.2% with an average such as: $Mn\%=2.457\pm0.133$, while the Si content varied from 0.28 to 1.05% with an average such that: $Si\%=0.682\pm0.088$.
- The melting process implemented in this study consisted in using two industrial-scale furnaces in duplex mode: a rotary kiln and an electric arc furnace, with the aim of reducing the Mn content on the one hand and correcting the chemical composition on the other hand.
- The performed experiments indicated that it was possible to reduce the manganese content in the hot metal from 2.45% to less than 0.95% at 1300°C.
- The monitoring of the manganese oxidation showed that it followed first-order kinetics with the following values of the rate coefficients: 0.0043 min^{-1} in the rotary kiln and 0.0020 min^{-1} in the electric arc furnace.
- The monitoring of the hardness during the melting process as a function of the decrease of Mn content showed that the Brinell hardness decreased from 207.33 to 149.67 (i.e. a decrease of 27.81%) and that the Rockwell hardness decreased from 32.15 to 19.67 (i.e. a decrease of 38.83%), when Mn content decreased from 2.45% to 0.94%.
- The optical micrography indicated that the cast iron at the outlet of the furnaces had a pearlitic microstructure with a small fraction of ferrite (1 to 5%) in the matrix and traces of cementite. In summary, the cast iron produced by the melting process implemented complies with the standards in force for EN-GJL-150 cast irons.

Conflict of interest statement

The authors declare that they have no conflict of interest.

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