

High-temperature oxidation of Si/SiMo ductile cast irons in aggressive combustion atmosphere – oxidized surface layer characteristics

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Abstract: The present work focuses on evaluating the oxidized layer formed on the surface of ductile iron specimens, specifically, a 5.25% Si iron and a 4.8% Si-2.3% Mo iron, exposed to a combustion gas atmosphere containing water vapor, as an effect of the heating temperature (400, 600, and 800 °C). These irons are characterized by slightly irregular spheroidal graphite, classified as Form V according to ISO 945-1:2008, with a roundness shape factor (RSF) of 0.62–0.71. Furthermore, they exhibit distinct matrix structures: the Si-iron features a predominantly ferritic matrix (85%–90% ferrite), while the SiMo-iron consists primarily of pearlite (<15% ferrite). At 400 °C, a discontinuous, thin, and compact single oxide layer (<5 µm thick) is observed. Then, at 600 °C, a multiscale structure with a total average thickness of 47–64 µm is formed. This structure consists of two sub-layers of comparable thickness: an inner sub-layer (internal scale) adjacent to the specimen matrix, and an outer sub-layer (external scale) at the surface. At 800 °C, the total oxide layer reaches an average thickness of 225–252 µm, approximately four times thicker than at 600 °C. At this temperature, the internal sub-layer becomes significantly dominant, accounting for 50%–70% of the total oxide layer thickness. Microstructural analysis reveals that at 600 °C, a compact void-free inner sub-layer is observed, whereas the external sub-layer contains small voids, primarily located within less than 10 µm beneath and along the surface. In contrast, at 800 °C, large voids are observed throughout the entire external sub-layer rather than being confined to the surface, while the inner sub-layer contains a high density of fine voids. Metal oxides formed through reactions with oxygen and water vapor are found to occupy the former graphite nodule sites, visible in the external sub-layer of the surface scale, while graphite nodules are still present within the inner sub-layer. Up to 600 °C, the increase in oxide layer thickness correlates positively with weight gain across all test variants. However, at the maximum temperature of 800 °C, the progression of oxidation is characterized primarily by an increase in layer thickness rather than a proportional weight gain.

Keywords: ductile cast iron; Si and SiMo alloying; FeSiCaMgRE treatment; inoculation; oxidation at high temperature; combustion gas atmosphere; water vapor; oxidized surface layer; surface layer thickness; weight gain

CLC numbers: TG143.5

Document code: A

Article ID: 1672-6421(2026)05-703-08

1 Introduction

Ductile (spheroidal graphite) cast iron became a commercial material in the 1950s. Since then, its production has continuously increased, and today,

its usage surpasses that of both steel and aluminium alloys^[1]. Ductile iron castings are practically used in all the industrial fields, with major applications in the automotive industry (50% and more)^[2].

Typically, the final chemical composition of ductile cast irons is characterized by higher levels of graphitizing elements such as carbon (C) at 3.2%–3.8% and silicon (Si) at 1.8%–3.0% (Fig. 1, Group A), along with low concentrations of detrimental phosphorous (P) (<0.05%) and sulphur (S) (<0.02%). Manganese (Mn) content is dependent on the metal matrix, typically ranging from 0.1% to 0.6%. Strict control of minor elements is necessary, especially those act as

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Received: 2026-03-19; Revised: 2026-06-24; Accepted: 2026-07-01

anti-spheroidizing agents or carbide-promoting elements.

Increasing the Si-content above 3.0% promotes the formation of a Si-solid solution strengthened ferrite (instead of pearlite) with superior strength properties, but with negative effects on ductility and toughness. These positive effects of silicon alloying resulted in ductile iron grades defined as “solid-solution strengthened ferritic spheroidal graphite cast irons” or “high-Si ductile irons” (Fig. 1, Group B). Generally, these ductile irons containing 3.2%–4.3% Si^[3] are mainly used in the automotive industry, usually replacing the unstable ferritic-pearlitic ductile iron grades (a variable ferrite/pearlite ratio creates difficulties not only in production, but especially in the machining process). Higher silicon content (usually 4%–6%) (Group C, Fig. 1) improves resistance to oxidation and corrosion at high temperatures, although at the expense of mechanical properties, which could be partly compensated at high temperatures through supplementary Mo alloying.

Typically, these ductile cast irons contain (2.5%–5.5%) Si and (0.2%–2.0%) Mo, such as SAE J2582:2004 grades. Silicon content exceeding 14% (usually up to 18%) offers high corrosion resistance; typical examples are the lamellar graphite cast irons defined by ASTM A 518: 2018 (Group D, Fig. 1).

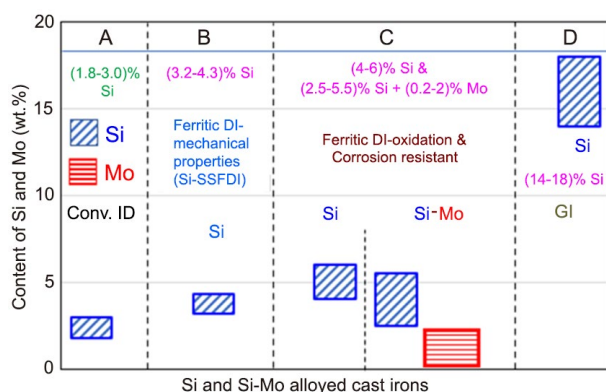


Fig. 1: Major groups of standard Si-alloyed cast irons: (A) ferritic to pearlitic ductile irons (conventional ductile irons), EN-1563:2018, ISO 1083:2018; (B) solid-solution strengthened ferritic ductile cast irons, EN-1563:2018, ISO 1083:2018; (C) Si (4%–6%) and Si-Mo [(2.5%–5.5%) Si+(0.2%–2.0%) Mo] alloyed ductile cast irons, oxidation and corrosion resistant, such as SAE J2582:2004 grades; (D) corrosion resistant high-Si (14%–18%) grey cast irons, ASTM A 518:2018

Ferritic ductile (spheroidal) graphite cast irons with high silicon content, encompassing various alloying systems such as Si, SiMo, SiMoCr, SiMoAl, SiMoCrAl, and SiNb (Group C, Fig. 1), are widely utilized for their superior resistance to oxidation and corrosion in air and combustion gases. These materials are particularly essential for exhaust systems in industrial equipment and automotive internal combustion engines.

A relatively large number of studies have evaluated the high-temperature oxidation process of ductile cast irons in gaseous atmospheres containing oxidation agents, e.g. oxygen, carbon dioxide, and water vapor, with particular emphasis on the influence of Si and Si-Mo alloying^[4-11].

Based on an extensive literature review, Çelik et al.^[4] pointed out that, in cast irons, silicon content is necessary to be increased to support the formation of Si-rich protective oxide layers. The presence of Si-rich oxides (Fe_2SiO_4 and SiO_2) in the oxide layer effectively inhibits the inward diffusion of oxygen and the outward diffusion of iron, thereby enhancing the oxidation resistance. As the silicon content increases, the amount of Si-rich protective oxide layer covering the surface increases and the oxidation rate decreases. A multilayered oxide scale forms on the surface of oxidized iron castings, comprising: (i) Fe-rich inner and outer oxide layers; (ii) an outer structure of Fe_2O_3 and Fe_3O_4 , resulting from the inward diffusion of oxygen; and (iii) a thin inner FeO layer, formed by the outward diffusion of iron. Furthermore, these oxide layers tend to thicken at high operation temperatures, accompanied by decarburization.

Automotive internal combustion engines continue to be a primary application field for iron castings, accommodating different fuel types and different hybrid powertrain configurations. A critical requirement in this field is that exhaust components, which are exposed to ambient air and combustion gases at elevated temperatures, must exhibit superior resistance to oxidation and corrosion. Generally, the combustion gas mainly contains nitrogen, carbon dioxide, and water vapor; a large amount of oxygen is also present in the combustion gas at high air/fuel ratios^[12, 13].

Some works have evaluated the high-temperature behavior of unalloyed and Si/SiMo alloyed ductile cast irons in gaseous atmospheres containing water vapor^[10-12, 14-19]. At both test temperatures (of 700 °C and 800 °C), water vapor was seen to promote internal oxidation of Si instead of its external oxidation for the 4.4% Si-0.5% Mo alloyed ductile iron. This leads to a higher oxidation rate at 700 °C and a higher decarburization rate at 800 °C^[12].

It was pointed out that water vapor accelerated nucleation of iron oxide nodules, increased oxidation kinetics, and led to porous iron oxide scales^[12, 15]. In H_2O -containing atmospheres, the oxidation rate increased rapidly after an incubation period of slow oxidation. Furthermore, with increasing H_2O contents in air- H_2O atmosphere, the incubation time decreased. Cross-sectional observations of oxide scale indicated that voids formed channels along the boundaries of columnar FeO crystals, suggesting transport of water molecules. Consequently, the Si-rich oxide layer changed into a $\text{FeO}+\text{Fe}_2\text{SiO}_4$ mixture due to penetration of water molecules. A combined process of perforating dissociation and transport of water molecules is attributed to the rapid growth of the inner $\text{FeO}+\text{Fe}_2\text{SiO}_4$ layer^[15].

The high-temperature experiments on the SiMo-ductile cast irons in air and a water vapor-containing combustion atmosphere typical for the exhaust manifolds, revealed a complex surface degradation process: the formation of a multilayered oxide scale and the development of internal porosity, which facilitates the decarburization of graphite nodules. The protection efficiency of formed amorphous silica

layers is limited by intensive decarburization at more than 700 °C. The final effects of the combined oxidation (weight gain) and decarburization (weight loss) depend on the heating temperature and the type of oxidizing atmospheres^[17, 18]. The supplementary alloying with Cr, Al, Nb, and Ni improved the resistance of the Si-Mo ductile iron to both oxidation and corrosion^[4, 6, 18-24].

Building upon previous studies^[10, 11] regarding specimen weight gain, this work evaluates the oxidized layers formed on ductile irons containing high Si (>5%) and Si-Mo (>4.5% Si, >2.0% Mo), respectively. The study focuses on the effects of heating temperature (400, 600, or 800 °C) in the most aggressive environment identified Atmosphere C (natural gas combustion with a 1.05 excess air coefficient), compared to Atmosphere B (0.55 excess air coefficient) and dry air (Atmosphere A). Although these alloying elements enhance oxidation and corrosion resistance, they are known to compromise the compactness of spheroidal graphite nodules^[25-27].

2 Background

The oxidation behavior of ductile cast irons containing 5.25% Si and 4.8% Si-2.3% Mo, treated with various inoculants (Ca, Ca/Ba, Ca/RE), was investigated^[10, 11]. The specimens were heated in an electric furnace equipped with SiC heating elements from 20 °C to 400, 600, or 800 °C, held for 8 h, and subsequently cooled to 20 °C within the furnace. Static oxidation tests were performed in dry air (Atmosphere A) and in combustion gas atmospheres generated by burning natural gas (97.6% CH₄, 0.8% C₂H₆, 0.4% C₃H₈, 1.2% N₂) under varying natural gas-to-air ratios, specifically Atmosphere B (excess air coefficient of 0.55) and Atmosphere C (excess air coefficient of 1.05). The cubic specimens (10 mm×10 mm×10 mm) for the oxidation tests were placed in a shallow alumina crucible to ensure that any spalled scale could be collected for subsequent mass measurements. The specimens and crucibles were weighed before and after oxidation to determine a total weight change. The oxidation behavior was expressed by the test samples' weight gain (wt.%) because of the oxidation process.

It was mentioned that high Si alloying grades led to a high oxidation resistance in aggressive atmospheres (low weight gain), with heating temperature as the major influencing factor (Fig. 2)^[10]: the higher the temperature, the higher the oxidation sensitivity, and the higher the contribution of the considered influencing factors.

Positive effects of inoculating elements increase with heating temperature, with Ca and Ca/Ba inoculation generally showing better performance. The weight gain increases from 0.001%–0.1% (400 °C) to 0.05%–0.70% (600 °C) and up to 0.10%–2.15% (800 °C)^[10].

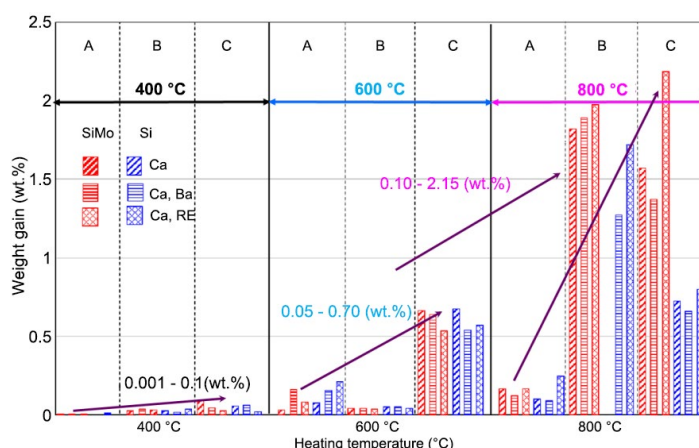


Fig. 2: Weight gain of inoculated (Ca, Ca/Ba, Ca/RE) Si/SiMo alloyed ductile irons at 400 °C, 600 °C, and 800 °C in Atmospheres A, B, and C^[10]

When heating at 400 °C, no specific influence is found for all the considered influencing factors. When heating at 600 °C, the atmosphere type appears to have a visible influence: a slightly higher oxidation rate in the dry air (Atmosphere A) compared to the combustion gas at a lower excess air coefficient (Atmosphere B), while the highest oxidation sensitivity occurs in the combustion atmosphere with a high excess air coefficient (Atmosphere C). At the highest temperature of 800 °C, all investigated factors appear to be important. Specifically, the ductile irons inoculated with Ca and RE-FeSi exhibit higher oxidation rates, whereas those inoculated with Ca and Ba-FeSi, combined with higher Si-alloying levels, demonstrate improved oxidation resistance. The presence of water vapor in an oxidizing atmosphere significantly influences the oxidation behavior of the high-Si and SiMo irons. This effect depends on both temperature and water vapor content: It is primarily driven by a high water content at 600 °C, but becomes independent of water vapor levels at 800 °C.

3 Experimental procedure

Experimental conditions were presented in detail in a previous study^[11]. The test ductile irons were produced by induction furnace melting, supplied to a tundish cover ladle treatment using FeSiCaMgRE for nodularization, followed by an in-mould inoculation: A pattern for four work positions included a central down sprue that supplies Mg-treated iron simultaneously to four separate reaction chambers for inoculation (adding 0.1wt.% Ca-FeSi, Ca and Ba-FeSi, and Ca and RE-FeSi alloys, respectively). Chill-wedge, plate (for spectrometer chemistry analysis), and round-bar (to supply 10 mm×10 mm×10 mm cubic specimens for oxidation tests) samples were gated from each inoculation chamber. A silica-sand moulding system bonded with furan resin and P-toluene sulphonic acid was used.

Previous studies^[10, 11] characterized oxidation behavior based on the weight gain (wt.%) of test samples, analyzing the effects of heating temperature, gas atmosphere, alloying system, and inoculation treatment. The present work extends this research by evaluating the characteristics of the surface oxide layer (specifically thickness and structure). These evaluations focus on samples heated at various temperatures, the most significant influencing factor identified,

within the most aggressive environment (Atmosphere C). The thickness of this layer was evaluated using ASTM B487: 2020: Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of Cross Section (optical microscope, 200:1)^[28]. Average values for 10 measurements were considered to express the layer thickness.

4 Results and discussion

The final chemical compositions (wt.%) of the two experimental ductile cast irons are characterized by similar levels of carbon (3.46 vs. 3.30), manganese (0.22 vs. 0.30), phosphorus (0.045 vs. 0.050), sulfur (0.01), and residual magnesium (0.045). The carbon equivalents are 5.05 and 4.75, respectively. The primary distinction lies in their alloying elements: high-Si iron contains 5.25% Si, whereas Si-Mo iron contains 4.8% Si and 2.3% Mo.

Figures 3 and 4 illustrate the specific graphite and metal

matrix characteristics of the experimental ductile cast irons solidified in a 25 mm thick section, representing non-thick-walled castings. The graphite phase consists primarily of Type-V, slightly irregular spheroidal graphite (ISO 945-1:2019)^[29]. This morphology is supported by the obtained roundness shape factors (RSF=0.62–0.71, Fig. 4), which fall at the lower limit of the generally defined range for Type V (RSF=0.6–0.8) and Type VI (RSF=0.8–1.0) in both Si alloyed and Si-Mo alloyed ductile cast irons. This shape factor is defined as the ratio of the graphite particle area (A_G) to the area of a circle with a diameter equal to the maximum F  ret diameter (F_{max}) of the same particle, as shown in Eq. (1):

$$RSF = \frac{4 \cdot A_G}{\pi \cdot F_{max}^2} \quad (1)$$

According to the international standard ISO 945-4:2019^[30], nodularity generally considers only graphite types V and VI, and is expressed (in %) as the ratio of the area of all

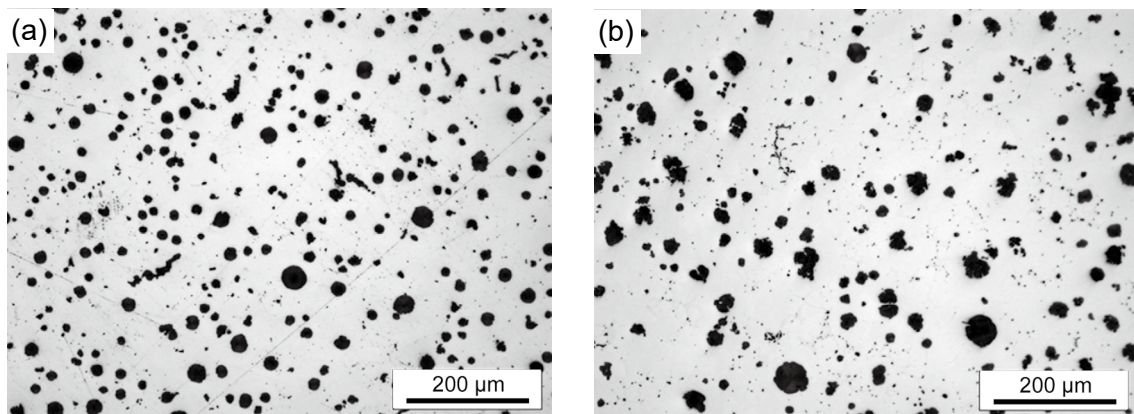


Fig. 3: Graphite morphologies in 5.25% Si (a) and 4.8% Si-2.3% Mo (b) ductile cast irons (un-etching)^[11]

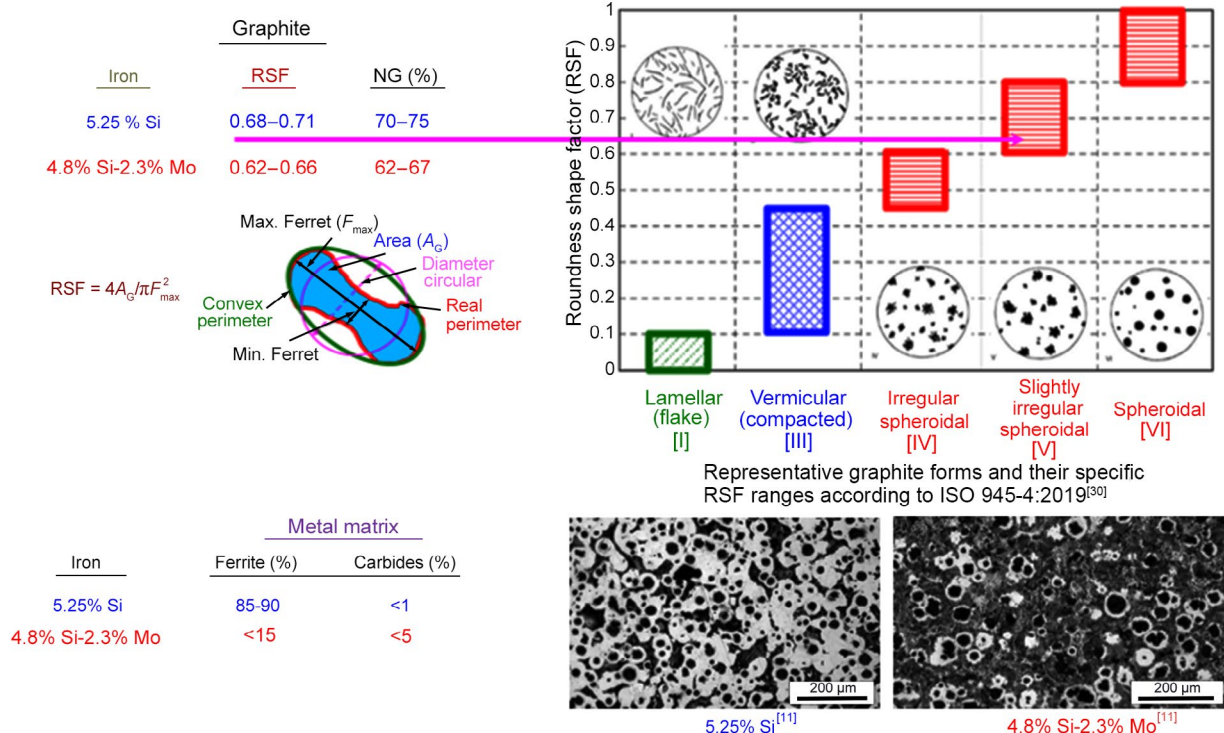


Fig. 4: Structure characteristics of RSF and graphite nodularity (NG)

graphite particles ($A_{\text{particles}}$) with roundness from 0.6 to 1.0 to the total area of all graphite particles (A_{tot}) that meet the size criteria (more than 10 μm and excluding the particles that intersect the border of the area of view). Equation (2) was used to calculate graphite nodularity (NG). Following the general guidelines of ISO 945-4:2019^[30], this calculation considers only graphite types V and VI. However, it accounts for the different compactness contributions of Types VI (higher compactness) and V [lower compactness. This distinction is particularly important under conditions with a very high proportion of Type V graphite, which is typical for high-Si alloys^[10, 11, 25-27, 31].

$$\text{NG} = \frac{\sum A_{\text{particles}} (\text{RSF} \geq 0.8) + 0.9 \cdot \sum A_{\text{particles}} (\text{RSF} = 0.6 - 0.8)}{\sum A_{\text{tot}}} \cdot 100\% \quad (2)$$

The graphite nodularity is visibly affected by the morphology of the graphite particles, as expressed by the RSF. Consistent with the microstructures shown in Fig. 4, the calculated graphite nodularity NG=70%–75% for 5.25% Si alloyed iron and 62%–67% for the iron alloyed with 4.8% Si and 2.3% Mo. The lower nodularity at higher alloying grades, for both Si and (especially) Si-Mo nodular graphite cast irons, is consistent with the data reported in other studies^[25, 27]. It was confirmed that silicon is an alloying

element that negatively affects the compactness of graphite nodules, particularly at contents exceeding 4%. This promotes the formation of Type V graphite, thereby reducing graphite nodularity. Furthermore, higher molybdenum content also exerts a detrimental effect on this parameter. Consequently, the combined presence of high silicon (4.8% Si) and high molybdenum (2.3% Mo) leads to an even lower nodularity.

The metal matrix of the 5.25% Si iron is predominantly ferritic (85%–90% ferrite, <1% carbides), whereas the Si-Mo iron exhibits a pearlitic structure (>80% pearlite, <15% ferrite, <5% carbides). In the 5.25% Si iron, the pearlite content is less than 15%, primarily due to the high Si content. The significantly higher pearlite fraction in the 4.8% Si-2.3% Mo iron can be attributed to its elevated Mo level, which is two to three times greater than that of standard grades according to SAE J2582 (2004)–Automotive ductile iron castings for high temperature applications. Although the applied inoculation is effective in preventing carbide formation, it proves insufficient in maintaining the desired degree of graphite compactness at high silicon contents and in controlling pearlite formation at high Mo levels in these materials.

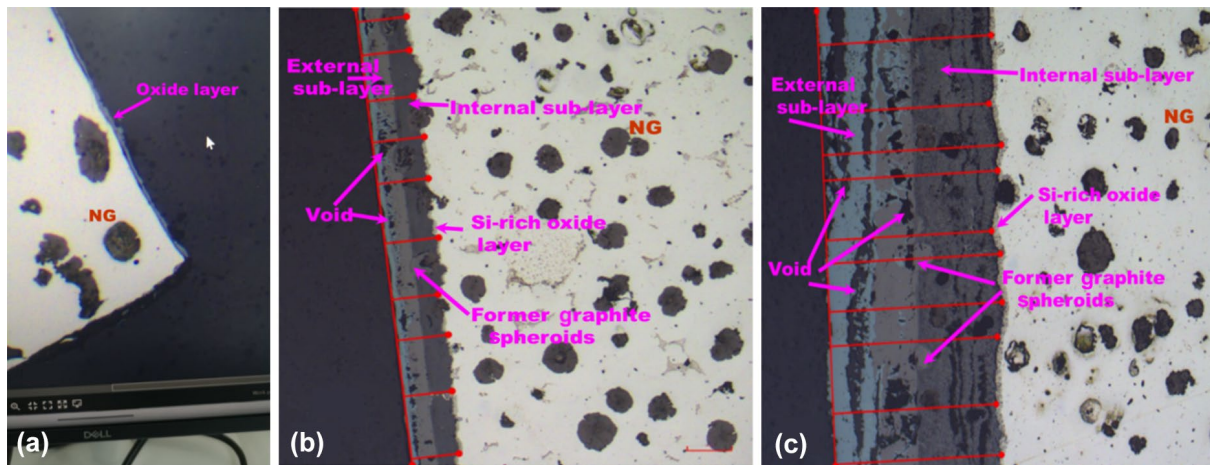


Fig. 5: Typical oxidized surface layer thickness and structure at various heating temperature: (a) 400 °C; (b) 600 °C; (c) 800 °C

Iron	600 °C			800 °C		
	Ca	Ca, Ba	Ca, RE	Ca	Ca, Ba	Ca, RE
5.25% Si						
4.8% Si-2.3% Mo						

Fig. 6: Typical oxidized surface layer thickness of Si and Si-Mo alloyed irons inoculated with various elements (Ca, Ca/Ba, Ca/RE) at 600 °C and 800 °C

The ductile cast iron samples subjected to Atmosphere C at 400–800 °C are characterized by the presence of an oxidized surface layer (Fig. 5). A discontinuous and thin surface layer (less than 5 μm) is observed at 400 °C [Fig. 5(a)], without a visible difference between the two test ductile cast irons. At 600 °C, the surface oxidized layer is visible for all the test

conditions [Figs. 5(b) and 6], at an average thickness in the range of 47–64 μm [Fig. 7(a)]. The increase of temperature from 600 °C to 800 °C leads to an increase of the oxidized layer thickness [Figs. 5(c) and 6] by more than 4 times (225–252 μm average) [Fig. 7(a)] and at higher standard deviation (6.6–11 versus 2.8–4.2) [Fig. 7(b)].

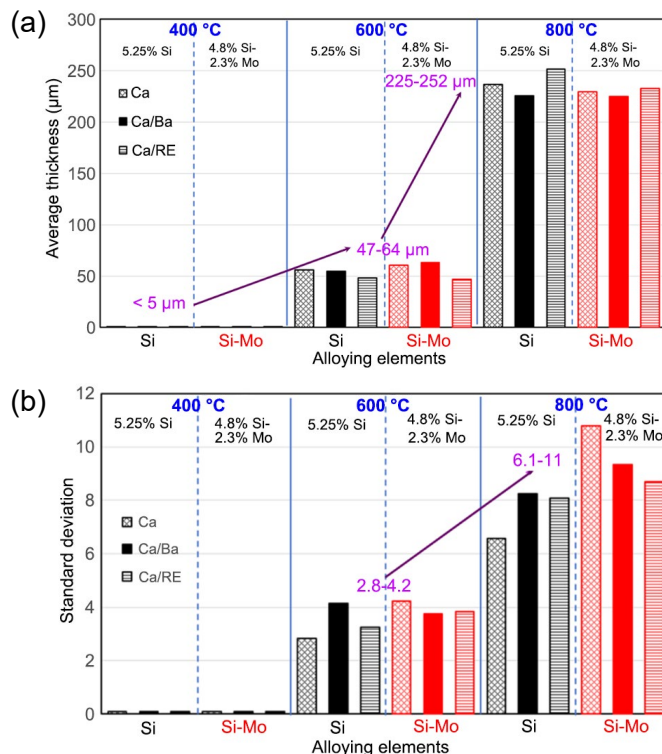


Fig. 7: Average thickness of surface oxidized layer (a) and its standard deviation (b)

The oxidized surface layer of ductile iron samples formed in gaseous atmosphere with high incidence of water vapor (resulted from natural gas burning) exhibits a complex multilayer-structure, more visible at higher heating temperatures, especially at 800 °C (Figs. 5, 6).

Basically, two distinct sub-layers are formed: an inner sub-layer (internal scale in contact with the specimen matrix) and an outer sub-layer (external scale on the specimen surface). The outer sub-layer accounts for approximately 50% of the total layer thickness at 600 °C and 30%–50% at 800 °C. The inner sub-layer exhibits a more jagged (uneven) morphology in the Si-Mo inoculated ductile iron compared to the Si ductile iron, particularly at 800 °C (Figs. 5, 6). This increased roughness is also associated with the lower compactness (Fig. 3) and reduced nodularity (Fig. 4) of the graphite particles in the Si-Mo inoculated ductile iron.

A critical feature of the formed surface oxide layer is the presence of voids with varying sizes and orientations within the two identified sub-layers. At 400 °C, the specimens are characterized by a continuous, thin, and compact surface layer free of voids. However, increasing the heating temperature to 600 °C leads to the formation of a bilayer structure consisting of a compact, void-free inner sub-layer and an outer sub-layer containing small voids. These voids are distributed across multiple locations, predominantly along the specimen surface and at depths of less than 10 μm .

Larger voids in the surface oxide sub-layer are characteristic of heating at 800 °C rather than 600 °C, and are more prevalent in the external scale than in the internal scale. At 800 °C, large voids are typically distributed throughout the entire volume of the external sub-layer and along the surface of the specimens. In contrast, the inner sub-layer of all specimens, regardless of the ductile iron alloying grade or inoculation treatment, contains a greater number of small voids.

The reaction of carbon (graphite) with oxygen, water vapor, and iron oxides produces gaseous carbon oxides. The percolation of these gases through the oxide scale results in carbon loss and the formation of metal oxides, which occupy the spaces previously occupied by graphite [Fig. 5(c)]. These oxide nodules are clearly visible in the external sub-layer of the surface oxide scale, whereas graphite nodules are retained in the inner sub-layer. Both graphite oxidation and the percolation of carbon oxides are facilitated by a discontinuous or porous oxide layer.

Recent studies have shown different mechanisms for these phenomena. It is assumed that H_2O enhances the diffusion or solubility of oxygen, or the diffusion of silicon in ferrite, thereby promoting the internal oxidation of silicon. Consequently, H_2O alters the oxidation mechanism, favoring internal oxidation over the formation of a continuous external SiO_2 scale that would otherwise act as a diffusion barrier. A peak in Si content is observed at the metal-oxide interface^[12],

a feature that is also evident in Fig. 5(c) of the present study. The Fe-1.5%Si alloy oxidized in different H₂O-containing atmospheres demonstrates that water vapor accelerates the nucleation of iron oxide nodules, increases oxidation kinetics and leads to porous iron oxide scales. The degree of corrosion in H₂O-containing atmospheres increases rapidly following an initial incubation period of slow oxidation^[15]. According to Ref. [12], scales are much thicker in humid air than in dry air for similar mass gains, at 800 °C.

Heating temperature is by far the most significant factor influencing the thickness of the oxidized surface layer, whereas the alloying system (Si vs. Si-Mo) and inoculating elements (Ca, Ca/Ba, Ca/RE) exhibit a comparatively minor effect (Figs. 6, 7). At 600 °C, the Si-Mo alloyed ductile irons exhibit a 5%–10% greater oxidized layer thickness and show higher standard deviations at both 600 °C and 800 °C.

Among the inoculation variants, the Ca/Ba inoculated Si-iron exhibits superior performance, particularly at 800 °C, which is consistent with the weight gain measurements^[10, 11] (Fig. 2). These results are consistent with data reported in previous studies^[25, 26, 28]. Ca/Ba inoculation system appears to be a better solution for improving graphite parameters, in terms of their compactness degree in high Si-ductile cast irons.

Both the thickness of the oxidized surface layer and the weight gain of the specimens increase with the increasing temperature (Fig. 7), as shown in Fig. 8. At 400 °C, a weight gain of less than 0.1wt.% corresponds to a discontinuous surface oxide layer thinner than 5 μm, with no significant differences observed among the tested alloying and inoculation parameters.

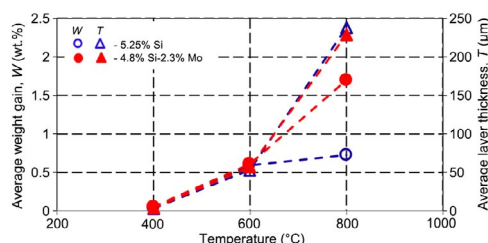


Fig. 8: Influence of temperature on average weight gain (*W*) and average thickness (*T*) of surface oxidized layer for 5.25% Si and 4.8% Si-2.3% Mo ductile cast irons in combustion gas containing water vapor

At 600 °C, the weight gain increases to (0.53–0.67)wt.%, accompanied by the formation of a continuous surface oxide layer 47–64 μm thick. This trend is consistent across all test variants. The maximum applied temperature of 800 °C further accelerates the oxidation of the ductile irons, albeit with varying effects: the Si-Mo irons exhibit a greater weight gain, while the oxide layer thickness remains comparable across variants, though with a narrower distribution for the Si-Mo irons.

5 Conclusions

This study investigated the effect of heating temperature (400, 600, and 800 °C) on the surface oxide layer of ductile irons with high Si (>5wt.%) and high Si-Mo (>4.5wt.% Si, >2.0wt.% Mo) contents, exposed to a water vapor-containing

combustion gas atmosphere at varying excess air/fuel ratios. Following conclusions can be obtained:

(1) The high-Si and high-SiMo ductile irons are characterized by slightly irregular spheroidal graphite (Type V, ISO 945-1:2015), with varying roundness shape factors (RSF) and graphite nodularity (NG): for the Si-iron, RSF=0.68–0.71 and NG=70%–75%; for the SiMo-iron, RSF=0.62–0.66 and NG= 2%–67%.

(2) The microstructure of the metallic matrix is strongly influenced by the alloy grade and the inoculation treatment: the Si-iron consists primarily of a ferritic matrix (85%–90%) without carbides, whereas the SiMo-iron is predominantly pearlitic, containing less than 15% ferrite and less than 5% carbides.

(3) A discontinuous, thin, and compact single layer (<5 μm) is observed at 400 °C. However, at 600 °C and 800 °C, a two-layered oxide structure appears. At 600 °C, the average thickness is 47–64 μm (standard deviation: 2.8–4.2 μm), whereas at 800 °C, it increases approximately fourfold to 225–252 μm (standard deviation: 6.6–11 μm). At 600 °C, the internal and external sub-layers are comparable in thickness. However, at 800 °C, the internal sub-layer accounts for 50%–70% of the total oxide layer thickness. Furthermore, the interface between the oxide layer and the matrix is more jagged in the SiMo-iron, which is attributed to the lower compactness and reduced graphite nodularity of its graphite particles.

(4) At 600 °C, a compact inner sub-layer free of voids is observed, whereas the outer sub-layer contains fine voids distributed across multiple locations, primarily along the specimen surface and at depths of less than 10 μm. At 800 °C, large voids are present throughout the entire volume of the outer sub-layer and along the surface, whereas the inner sub-layer contains a high density of fine voids, regardless of the alloy grade or inoculation treatment.

(5) Metal oxides, formed by reactions with oxygen and water vapor, occupy the sites formerly held by graphite nodules. These oxide nodules are clearly visible within the outer sub-layer of the surface oxide, whereas the graphite nodules remain intact in the inner sub-layer.

(6) Up to 600 °C, the increase in oxide layer thickness correlates with the weight gain across all test variants. However, heating at 800 °C accelerates the oxidation process differently: the weight gain is more pronounced in the Si-Mo irons, while the oxide layer thickness reaches a similar level but exhibits a narrower distribution.

Acknowledgment

This work was financially supported by the National Program for Research of the National Association of Technical Universities (Grant No. GNAC ARUT 2023), Romania.

Conflict of interest

Prof. Iulian Riposan is an EBM of *CHINA FOUNDRY*. He was not involved in the peer-review or handling of the manuscript.

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