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INFLUENCE OF CHEMICAL COMPOSITION ON THE HOT OXIDATION OF CARBON STEEL – A REVIEW

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Abstract: The hot forming of steels is associated with surface scales formed by layers of oxides whose oxidation kinetics and morphology are not fully understood, where there are several parameters that influence their formation. The chemical composition of carbon steel can influence the oxidation kinetics as well as the morphology of the oxide layers formed at high temperatures, which makes understanding these phenomena challenging. The fact is that each element behaves differently during steel oxidation. The alloying element Si, when present in the composition of steel, oxidizes to form silica, SiO₂. This oxide, in turn, at high temperatures, reacts with wustite, FeO, forming a complex oxide, fayalite, Fe₂SiO₄. The fayalite film has a protective characteristic, increasing the steel's resistance to oxidation and the adhesion of the oxide layers. Other alloying elements, in addition to Si, which have a greater tendency than iron to oxidize, and which form protective oxides, such as Al and Cr, can be added to the steel composition to promote certain resistance to oxidation, reducing the thickness of the layers of oxides. However, the formation of an alloying element oxide film will depend on its percentage in the steel composition. Alloy elements with low percentages in the steel composition tend not to form a continuous film, being precipitated in the wustite layer, close to the scale/substrate region, and in the steel, participating in internal oxidation. Low concentrations of alloying elements, even if they do not form continuous films, can influence the formation kinetics of other oxides. This review provides a comprehensive overview of the influence of alloying elements in hot oxidation regimes on the kinetics and mechanism of oxidation of carbon steels.

Keywords: hot oxidation, scale, iron oxides, alloying elements, carbon steel.

INTRODUCTION

The manufacturing process of carbon steel semi-products, in a steel mill, includes mechanical forming at high temperatures, such as hot rolling. The hot mechanical forming process consists of heating carbon steel to a temperature between 1000 and 1200 °C, with the aim of making it more malleable and thus facilitating its forming into the desired geometry (Cetlin and Helman, 2005; Zhong and Webler, 2024).

The problem is that when heated to these temperatures, steels suffer degradation with the formation of a layer of oxides on their surface called scale. Scale is the name given to the layer of oxides formed on the surface of carbon steel during a hot manufacturing process. It is made up of metal oxides present in the composition of steel, mostly iron oxides: wustite (FeO), magnetite (Fe₃O₄) and hematite (α-Fe₂O₃) (Martín, et al., 2012; Weihua, et al., 2004).

The formation of the oxide layer and its existence on the surface of steel generates changes in its dimensions, reduction of mechanical, chemical, physical properties and surface quality, which can lead to generalized corrosion and degradation of the material, if oxidation reactions are not carried out. are interrupted. For this reason, after the forming process, the scale must be removed, generating loss of material and costs for the company (Krzyzanowski, et al., 2010).

The composition and thickness of the oxides formed in the scale depends on the temperatures involved in the hot forming process, the exposure time at these temperatures, the oxidizing atmosphere, the chemical composition of the steel, the cooling rate, among others. Its thickness can vary from 130 μm to more than 2000 μm, whose average generation can exceed 1000 tons/month of metal loss in integrated plants (Basabe and Szpunar, 2008; Bhattacharya, et

al., 2006; Cunha, et al., 2006).

The financial loss and work that companies have to do to remove and dispose of scale is extremely considerable. It is estimated that the loss of steel in the form of scale is approximately 5% of the weight of the rolled product, and can represent up to 2% of the ton of raw steel produced, which leads to a loss of millions of tons of product per year. Furthermore, this waste is often inappropriately disposed of in landfills, not being given the correct destination, environmentally or even for reuse (Furmanski, 2016; Shatokha, et al., 2011).

The presence of alloying elements and impurities contained in steel can influence the oxidation kinetics as well as the scale morphology, which makes understanding these phenomena challenging. The fact is that each element behaves differently during steel oxidation (Birks, et al., 2006).

The present study was developed to analyze why and how the oxidation process occurs at high temperatures, analyzing the entire kinetics and mechanism of the processes, under variations in temperature and heating time, as well as the chemical composition of carbon steel, with the aim of better understand the complexities behind scale formation and how parameters modify it.

IRON OXIDATION

The oxygen present in the air reacts with Fe, by transferring electrons, causing the formation and growth of layers of iron oxides on the surface of the metal. The oxides formed can be α -Fe₂O₃ (hematite), Fe₃O₄ (magnetite) and FeO (wustite), as can be seen in Figure 1. All three types of iron oxides can be found together, under certain conditions, when iron is heated in air or oxygen. The growth of the layer will depend on how the ionic and electronic conduction phenomena occur within this same layer (Chabanier and Roth, 1982).

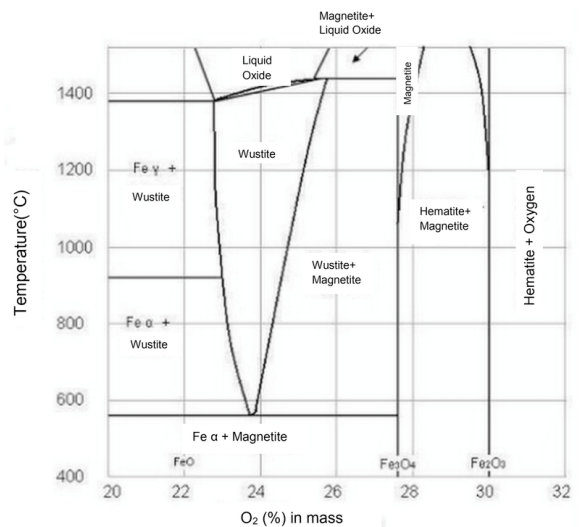


Figure 1: Iron-oxygen balance diagram (Bogdandy and Engell, 1971).

Hematite can be found in four polymorphic phases β , γ , ϵ , α -Fe₂O₃. However, the easiest to find are the γ - and α - phases. The γ -Fe₂O₃ phase has a cubic crystalline system at temperatures below 400 °C and, above, hematite appears in the form of α -Fe₂O₃ with a rhombohedral crystalline system. This is the most oxygen-rich oxide, having a chemical composition of 30.06%O–69.94%Fe (Danno, et al., 2013; Machala, et al., 2011).

Magnetite has a cubic crystal system with an inverted spine-type structure with a chemical composition of 27.64%O–72.36%Fe, by mass. Wustite, on the other hand, has a cubic crystalline system with a CFC-type structure with the iron ion arranged in the octahedral interstices between the oxygen ions. Its chemical composition varies between 23.1% and 25.6% oxygen by mass (Bogdandy and Engell, 1971).

Regarding pure iron, heated in oxygen to 1 atm, at temperatures below 575 °C, the predominance is the formation of magnetite, however, hematite is also formed. Wustite only forms from 575 °C, being observed at room temperature in a region of transformed wustite, decomposing into magnetite plus pure iron (Matlakhov, 2021).

Furthermore, it is possible to find wustite at temperatures below 575 °C, since this phase does not require high cooling rates to obtain its metastable form (Ramanathan, 1997).

Figure 2 shows a scheme of Fe oxidation. It can be seen that wustite (FeO) is formed next to pure Fe, hematite (Fe₂O₃) is in contact with the environment and magnetite (Fe₃O₄) is located between them. At temperatures above 800 °C, the total thickness of the iron oxide layer is formed by 95% wustite, 4.5% magnetite and 0.5% hematite (Ramanathan, 1997).

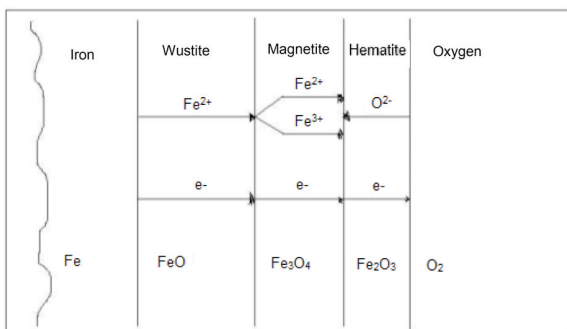


Figure 2: Schematic representation of iron oxidation (Ramanathan, 1997).

THE CAREPA

Scale is the name given to the carbon steel oxidation product generated during a hot manufacturing process, for example, rolling. It is formed at high production temperatures and is made up of metal oxides present in the composition of the steel, mostly iron oxides: wustite (FeO), magnetite (Fe₃O₄) and hematite (α-Fe₂O₃) (Martín, *et al.*, 2012; Weihua, *et al.*, 2004).

Carbon steel is basically an alloy formed by Fe (whose content can reach around 99%) and C (whose content, most commonly, can vary between 0.05 and 1%), with a small presence of residual elements arising from its process of manufacturing, such as Si, Mn, P and S (ABNT NBR NM 87, 2000; ASM HandBook, 1990).

Therefore, the oxidation process and formation of scale in carbon steels almost exclusively involves the oxidation of iron. Wustite iron oxide is the most abundant phase, followed by magnetite and hematite, finally, a small amount of oxides formed by other alloying elements present in steel (Umadevit, *et al.*, 2009).

Figure 3 shows the formation of different oxide layers in carbon steel. From the external face to the internal face, where the base metal is present, it is possible to observe the formation of layers of Fe₂O₃ (hematite), Fe₃O₄ (magnetite) and FeO (wustite), respectively. Below the wustite layer, there is a layer formed by oxides of some elements present in carbon steel, arising from its manufacturing process.

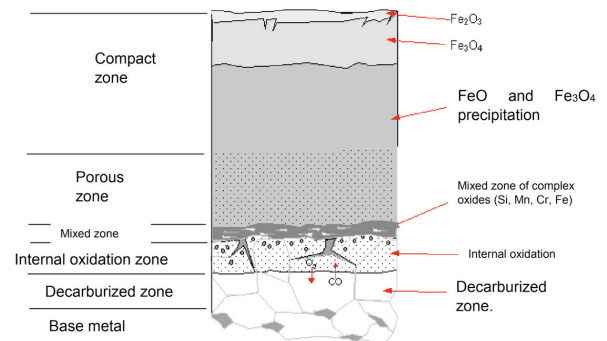
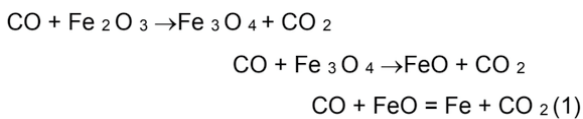


Figure 3 : Illustration of the carbon steel oxidation process (IRSID, 1983).

The scale has a porous zone region, located in the innermost layer. These voids can reach around 1 mm in thickness and their formation is related to the phenomena of oxygen and iron diffusion during cooling. Although the literature treats the region closest to the substrate, where a greater number of pores are present, as the internal porous layer, all layers of iron oxides formed at temperatures greater than 700 °C, they are porous. These pores facilitate the contamination of the oxidizing agent in the inner layers of the steel, causing internal oxidation (Basabe and Szpunar, 2008).

During the oxidation of steel, carbon reacts with oxygen in the air to form CO. This reaction creates a decarburized region on the substrate close to the contact surface with the formed oxides. Typically, this decarburization effect is observed at temperatures above 700 °C, especially in steels containing high carbon contents. The release of these gases can generate the formation of microcracks in the steel/scale region, facilitating air contact with the metal, increasing the oxidation rate (Chen and Yuen, 2003).

Normally, the CO gas produced can reduce the iron oxides in the scale and produce CO₂ through the reaction:



This reduction is related to the amount of oxygen removed from the iron oxide, leading to a decrease in the initial degree of oxidation. This causes many pores to be generated in the innermost oxide layer, due to the loss of mass caused by the reduction of CO, creating a region made up of pure Fe (Jie, *et al.*, 2008).

The composition and thickness of the oxides formed in the scale depend on the temperatures involved in the hot forming process, the exposure time at these temperatures, the oxidizing atmosphere, the type of steel, the cooling rate, among others. Its thickness can vary from 130 μm to more than 2000 μm, with an average generation that can easily exceed 1000 tons/month of metal loss in integrated plants. Plates, billets, blocks, plates, rebars and profiles are rolled at temperatures between 1000 and 1200 °C (Basabe and Szpunar, 2008; Bhattacharya, *et al.*, 2006; Cunha, *et al.*, 2006).

Scale grows very quickly, especially at high temperatures, and completely covers the steel. Generally, its increase in thickness in relation to the increase in temperature,

during oxidation, is related to the increase in the diffusion speed of oxygen and iron ions. The proportion of iron oxides in scale reflects the fact that the diffusion coefficient of iron in wustite is much higher than in magnetite, whereas in hematite the diffusion coefficients of iron and oxygen are very low (Chen and Yuen, 2003).

Hao, Sun and Wang (2020) evaluated the oxidation behavior of Fe-1%Cr-0.2%Si steel at high temperatures. The steel samples were subjected to heating in a furnace, in atmospheric air, at temperatures of 700, 800, 900, 1000 and 1100°C. Only after reaching the maximum temperatures, the samples were placed in the oven and heated isothermally for a period of 30 minutes, then cooled in air. Figure 4 shows the cross-sectional morphology of samples subjected to oxidation for 30 min at 700 to 1100 °C under a metallographic microscope. When the oxidation temperature is 700°C, the surface of the specimen begins to have a small amount of incompletely distributed iron oxide scales. When the temperature is greater than or equal to 800 °C, the surface of the specimen presents a complete layer of iron oxide scales with a specific thickness and covers the entire substrate. Especially under the oxidation temperatures of 900°C, 1000°C and 1100°C, the iron oxide scale formed by the specimen showed an apparent layered structure. It can be concluded that the oxidation kinetics becomes more intense only after 900 °C, where scale is formed with a layered structure, with the formation of oxides of various elements (Hao, *et al.* 2020).

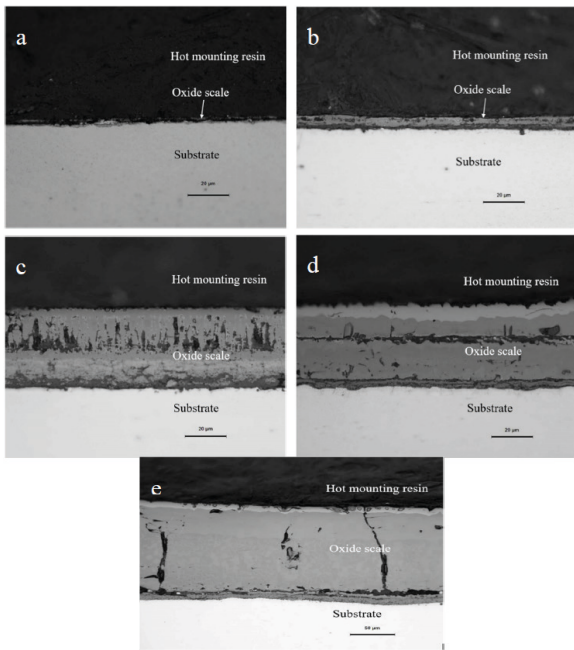


Figure 4 : Morphology of the oxide layer of Fe-1%Cr-0.2%Si steel in cross-section of specimens observed under a metallurgical microscope. (a) 700°C; (b) 800°C; (c) 900°C; (d) 1,000°C; (e) 1,100°C (Hao, et al. 2020).

A study carried out by Basabe and Szpunar (2008) aimed to characterize the mill scale of low carbon steel with chemical composition Fe-0.06%C-0.27%Mn-0.005%Si-0.006%Cu (% in Weight). The samples were heated from 1050 °C to 1250 °C, in an oven, under an oxidizing atmosphere with a mixture of O_2 - CO_2 - H_2O - N_2 , varying the oxidation time from 15 to 120 minutes. Subsequently, the samples were placed in a steel tube with argon flow and cooled to room temperature. Rapid cooling in an argon atmosphere was used to prevent further oxidation and minimize wustite decomposition. The results are presented in Figure 4 and Table 1.

Figure 5a shows the characterization of the sample heated to 1250 °C in an oven under an oxidizing atmosphere of 1% O_2 -15% CO_2 -10% H_2O -74% N_2 for 30 minutes. Figure 5b shows the characterization of the sample heated to 1250 °C under an atmosphere with a composition equal to 5% O_2 -15% CO_2 -10% H_2O -70% N_2 for 120 minutes.

for 120 minutes.

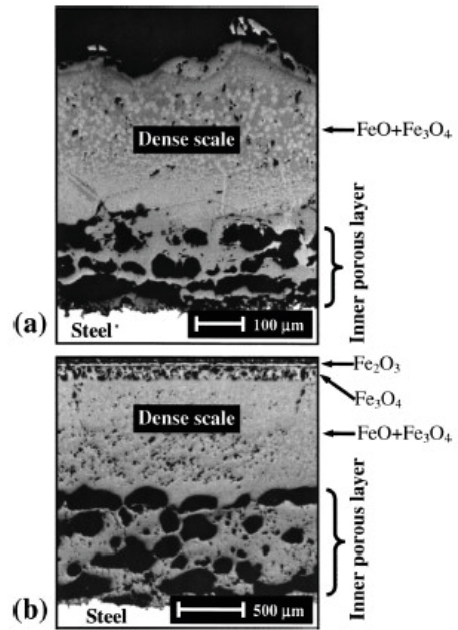


Figure 5 : Cross sections of low carbon steel scale (Fe-0.06%C-0.27%Mn-0.005%Si-0.006%Cu, % by weight) formed at 1250 °C in (a) 1 O_2 -15 CO_2 -10 H_2O - N_2 for 30 min, (b) 5 O_2 -15 CO_2 -10 H_2O - N_2 for 120 min (Basabe and Szpunar, 2008).

The results found by the researchers show that in the first condition, Figure 5a, the scale is formed by a layer of wustite (FeO) with some precipitation of magnetite (Fe_3O_4), caused by the decomposition of wustite through the cooling process. An internal porous layer can also be observed, close to the base metal. In the second condition, Figure 5b, with a more oxidizing atmosphere, with a greater amount of free oxygen, and a longer heating time, the three possible layers of iron oxides were formed in the scale, wustite (FeO), magnetite (Fe_3O_4) and hematite (α - Fe_2O_3). Precipitation of magnetite in the wustite layer and the porous layer region was also observed.

Table 1 shows the variation in scale morphology at different temperatures, composition of the oxidizing atmosphere and oxidation time. The researchers separated the results into two groups. In group one, the

classic three-layer scale is observed, which developed an internal porous layer with low or medium porosity. In the second group, three-layer scale was observed, which developed an internal porous layer with high porosity, and scale with only the wustite layer.

It is observed that with an increase in temperature and/or oxidation time and/or amount of free oxygen in the oxidizing atmosphere, there is an increase in the porosity percentage of the scale. It can also be observed that from 1050 °C to 1100 °C, under variation of all oxidation times and oxidizing atmospheres, the scale created consists of wustite (FeO), magnetite (Fe₃O₄) and hematite (α-Fe₂O₃). However, from 1150 °C onwards, the samples oxidized in the atmosphere with less free oxygen formed only the wustite layer, not being influenced by the variation in oxidation time up to 60 minutes. This is because from this temperature onwards, the increased diffusion of atoms caused by the increase in temperature favored the formation of only the wustite layer. After 120 minutes of oxidation in an atmosphere with less free oxygen, the scale created returns to the three forms of iron oxide. This transition occurs when the oxidation time is prolonged, increasing the thickness of the scale. The thicker scale reduces the diffusion of iron, facilitating the formation of magnetite (Fe₃O₄) and hematite (α-Fe₂O₃).

The cooling rate also directly influences the phases found in the scale as well as its thickness. At high cooling rates, the wustite layer retained below 575 °C increases considerably, while at low cooling rates the amount of wustite retained is much smaller, this is because there is greater decomposition of wustite into magnetite. On the other hand, low cooling rates tend to generate thicker scale (Bhattacharya, *et al.*, 2006).

The scale is poorly adherent to the metal surface, which causes detachment of part of

the layer formed, exposing the metal to further oxidation. This is because it has a different coefficient of expansion than steel, generating cracks on its surface during the natural heating and cooling cycles. In addition, cracks are also generated in the process of decomposition of wustite into magnetite during cooling and in the reaction of carbon with oxygen in the air forming CO. These cracks, in addition to the pores present in the iron oxide layers, allow water, oxygen and various contaminants to penetrate to the substrate. The presence of electrolytes generates a battery, oxidizing the steel and causing a reduction in oxygen on the scale. As oxidation progresses beneath the scale, it tends to expel it from the steel surface (Chen and Yuen, 2003; Basabe and Szpunar, 2008; Krzyzanowski, *et al.*, 2010).

Since scale does not protect the steel from atmospheric corrosion, it must be removed at the end of the forming process to avoid possible widespread corrosion (Krzyzanowski, *et al.*, 2010).

COMPLEX OXIDATION OF ALLOY ELEMENTS

The presence of alloying elements and impurities contained in steel can influence the oxidation kinetics as well as the scale morphology, which makes understanding these phenomena challenging. The fact is that each element behaves differently during steel oxidation (Birks, *et al.*, 2006).

Alloy elements that are less noble than iron and that form protective oxides, such as Si, Al and Cr, can be added to the steel composition to promote certain resistance to oxidation, reducing the thickness of the scale. The objective is to slow the growth of wustite through the formation of protective films that hinder the diffusion of Fe. However, the formation of an alloying element oxide film will depend on its percentage in the steel composition. Alloy elements with low

Temp. (°C)	Gas mixture	Time = 15 min			Time = 30 min			Time = 60 min			Time = 120 min		
		Mode	Structure	Porosity	Mode	Structure	Porosity	Mode	Structure	Porosity	Mode	Structure	Porosity
1050	1O ₂ -15CO ₂ -10H ₂ O-N ₂	1	T	L	1	T	M	2	T	H	2	T	H
1050	5O ₂ -15CO ₂ -10H ₂ O-N ₂	1	T	M	1	T	M	2	T	H	2	T	H
1100	1O ₂ -15CO ₂ -10H ₂ O-N ₂	1	T	M	1	T	M	2	T	H	2	T	H
1100	5O ₂ -15CO ₂ -10H ₂ O-N ₂	1	T	M	1	T	M	2	T	H	2	T	H
1150	1O ₂ -15CO ₂ -10H ₂ O-N ₂	2	C	M	2	C	M	2	C	H	2	T	H
1150	5O ₂ -15CO ₂ -10H ₂ O-N ₂	1	T	M	1	T	M	2	T	H	2	T	H
1200	1O ₂ -15CO ₂ -10H ₂ O-N ₂	2	C	H	2	C	H	2	C	H	2	T	E
1200	5O ₂ -15CO ₂ -10H ₂ O-N ₂	2	T	H	2	T	H	2	T	H	2	T	E
1250	1O ₂ -15CO ₂ -10H ₂ O-N ₂	2	C	H	2	C	H	2	C	H	2	T	E
1250	5O ₂ -15CO ₂ -10H ₂ O-N ₂	2	T	H	2	T	H	2	T	H	2	T	E

Table 1 : Variation in scale morphology at different temperatures, oxidizing atmosphere and oxidation time (Basabe and Szpunar, 2008).

Scale structure: T = three-layer scale; C = scale of one layer.

Scale porosity: L = low (porosity ≤ 5%); M = medium (5% < porosity ≤ 10%);

H = high (10% < porosity ≤ 20%); E = extra high (20% < porosity ≤ 30%).

percentages in the steel composition tend not to form a continuous film, being precipitated in the wustite layer, close to the scale/substrate region, and in the steel, participating in internal oxidation. Still, low concentrations of alloying elements, even if they do not form continuous films, can influence the formation kinetics of other oxides (Genève, *et al.*, 2006).

SILICON OXIDATION

The characteristic of the oxide/metal interface is influenced by silicon (Si), when present even in low concentrations, for example, values lower than 1% by weight, due to the formation of SiO₂. Oxygen reacts with Si, by transferring electrons, forming SiO₂. This oxide, in turn, at high temperatures, reacts with wustite, FeO, forming a complex oxide, fayalite, Fe₂SiO₄ (or 2FeO.SiO₂). Figure 6 presents the FeO-SiO₂ phase diagram, where it can be seen that fayalite forms from 800 °C onwards. Fayalite is a Si-rich iron oxide containing 70.57% FeO and 29.43% SiO₂ (Asrar and Thakur, 1995).

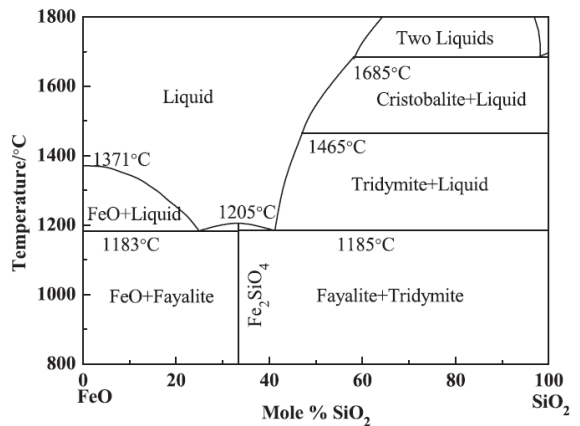


Figure 6 : FeO-SiO₂ phase diagram (Luo, *et al.*, 2016).

The fayalite film (Fe₂SiO₄) has a protective characteristic, so that it tends to form a “barrier” at the oxide/metal interface, making it difficult for Fe to diffuse through the scale to the external surface, thus reducing the kinetics of its growth and consequently its thickness (Yuan, *et al.*, 2016).

Another characteristic of the fayalite film is its strong adhesion to the metal substrate, influencing the greater adhesion of the entire scale, which makes it difficult to strip the scale after the hot rolling process. This occurs because the film has an irregular surface,

attaching itself firmly to the substrate and scale, as can be seen in Figure 7 (Fukagawa, et al., 1994).

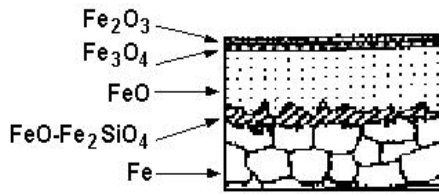


Figure 7 : Schematic structure of steel scale containing Si (Fukagawa, et al., 1994).

Fayalite has a relatively low melting point, around 1173 °C. Therefore, when Si-containing steels are oxidized above this temperature, a liquid phase of the eutectic FeO-Fe₂SiO₄ is formed at the oxide/metal interface, penetrating deeper into the scale as well as the steel substrate. During cooling, after oxidation, the liquid phase is solidified and binds strongly to the scale and steel substrate, causing even more adherence to the scale (Taniguchi, *et al.*, 2001).

Another theory is that the greater adhesion of the scale of Si-containing steels is obtained due to the smaller discrepancy between the lattice parameters of Fe₂SiO₄ in relation to steel, when compared to FeO/steel (Kizu, *et al.*, 2001).

The fact is that the higher the % of Si, the higher the % of Fe₂SiO₄ and the lower the % of FeO. Likewise, the higher the percentage of Fe₂SiO₄, the smaller the thickness of the scale and the greater its adhesion. The increase in temperature causes the difference in scale thickness to be greater, when compared to a steel with a lower % Si, as can be seen in Figure 8 (Chen and Yuen, 2003; Yuan, *et al.*, 2016).

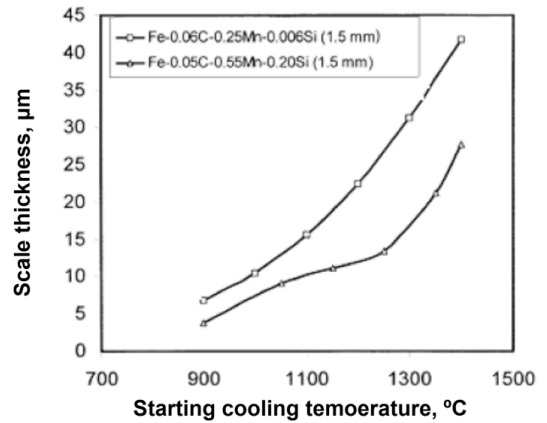


Figure 8 : Effect of Si content and heating temperature on the thickness of scale formed (Chen and Yuen, 2003).

Figure 9 shows the micrograph of low carbon steel oxidized at 1143 °C for 300 seconds, under varying Si content. Note the presence of layers of hematite, magnetite, wustite, containing a region with a large concentration of pores, the layer eutectic formed by wustite + fayalite and a reduction in scale thickness as the Si content increases. In Figure 10, with a higher magnification, it can be seen that the eutectic layer (wustite FeO + fayalite Fe₂SiO₄) it is also a porous layer, presenting several micropores (Taniguchi, *et al.*, 2001).

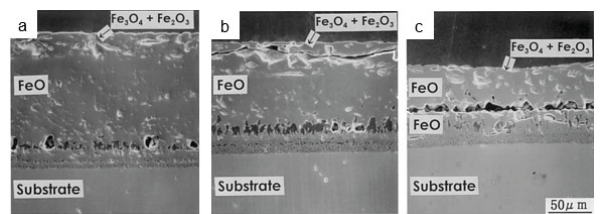


Figure 9 : Micrograph of low carbon steel oxidized at 1143 °C for 300 s of composition: (a) Fe-0.046%C-0.99%Mn-0.48%Si, (b) Fe-0.048%C-0, 99%Mn-0.98%Si, (c) Fe-0.049%C-0.99%Mn-1.49%Si (Taniguchi, et al., 2001).

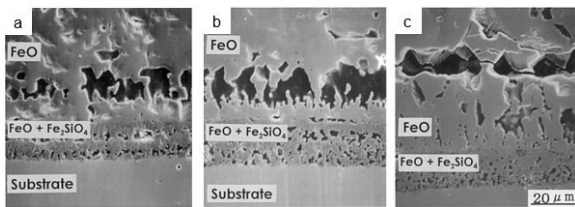


Figure 10 : Higher magnification micrographs of the scale/substrate interfaces of the specimens shown in Figure 9 (Taniguchi, et al., 2001).

Figure 11 shows the micrograph of the scale/substrate interfaces of low carbon steel oxidized at 1203 °C for 180 seconds, under varying Si content. After heating the samples above the melting point of fayalite, the morphology of the eutectic can be seen. FeO-Fe₂SiO₄ solidified. The layer is no longer porous and there is an increase in the size and depth of the eutectic as the Si content increases (Taniguchi, *et al.*, 2001).

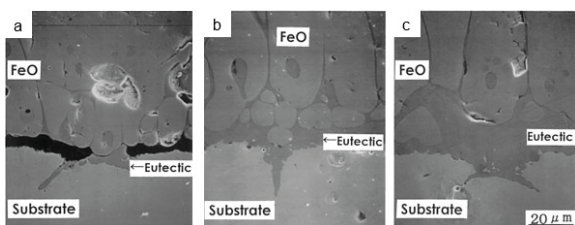


Figure 11 : Micrograph of the scale/substrate interfaces of low carbon steel oxidized at 1203 °C for 180 s of composition: (a) Fe-0.046%C-0.99%Mn-0.48%Si, (b) Fe-0.048 %C-0.99%Mn-0.98%Si, (c) Fe-0.049%C-0.99%Mn-1.49%Si (Taniguchi, et al., 2001).

The Pilling-Bedworth ratio (CPB), namely the ratio between the volume of oxide and the volume of metal consumed from Fe and Si oxides (FeO and SiO₂) is greater than 1 at temperatures above 1200 °C. This indicates that the volume of oxide is greater than that of the metal consumed, leading to a compressive stress on the oxide.

In other words, during the oxidation process, the oxidized part of the metal expands relative to the metal and compressive stress is produced on the oxide scale.

Furthermore, the compressive stress at the scale/substrate interface is greater than in the external position, leading to pressure differences at different points of the scale. In the case of fayalite, the Fe₂SiO₄ has a relatively low melting point, around 1173 °C, so the pressure difference in the liquid phase of Fe₂SiO₄ at a temperature of 1203 °C, for example, compels a part of Fe₂SiO₄ penetrating the inner layer of the substrate. The liquid phase Fe₂SiO₄ is distributed along the FeO grain boundary and solidifies upon cooling. Higher compressive stress due to more Fe₂SiO₄ in steels with higher silicon content results in a deeper penetration layer (Yuan, *et al.*, 2016).

ALUMINUM OXIDATION

When reacting with oxygen, aluminum precipitates at the substrate/scale interface to form alumina oxide Al₂O₃, an oxide that forms a protective film. Al₂O₃, in turn, can react with FeO to form the spinel-type complex oxide FeAl₂O₄, which has a similar effect to the Fe₂SiO₄ film, increasing the adhesion of the scale. These compounds participate in internal oxidation and accumulate at the scale/substrate interface (Chang, 1994; Genève, *et al.*, 2006).

In a study carried out by Tomaszewicz and Wallwork (1983), the influence of aluminum content on the oxidation process of pure iron-based binary alloys with 1.9 to 9.8% aluminum (% by mass) was evaluated. Oxidation studies were carried out in oxygen at 800 °C for 25 hours and the oxidation kinetics were evaluated by the continuous weighing process. Each specimen was individually attached to a short piece of platinum wire and then suspended on a thin fiber to the microbalance. This test makes it possible to evaluate instantaneous mass gain as time increases. As can be seen in Figure 12, the mass gain decreases as the aluminum content in the alloy increases (Tomaszewicz and Wallwork, 1983).

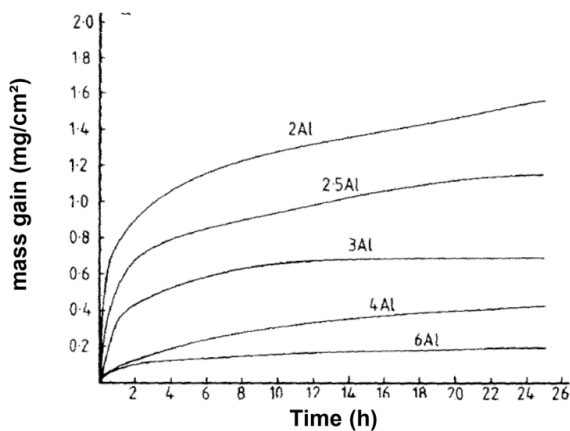


Figure 12 : Mass gain characteristics for the oxidation of a series of iron-aluminum binary alloys at 800 °C, as a function of Al content (% by mass) (Tomaszewicz and Wallwork, 1983).

CHROME OXIDATION

During the oxidation reaction, the alloying element Cr reacts with oxygen dissolved on the steel surface and precipitates in the form of the compound Cr_2O_3 , an oxide that forms a film with highly protective characteristics. At elevated temperatures, Cr_2O_3 , in turn, can react with FeO oxide to form the complex oxide $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, known as spinel FeCr_2O_4 . These compounds, Cr_2O_3 and FeCr_2O_4 , have a low solubility in wustite, FeO, and therefore accumulate in the oxide layer and in the internal oxidation region (Genève, *et al.*, 2008).

Figure 13 shows the metallographic cross section of the oxide layer in the Fe-10Cr-4Al alloy oxidized for 48 hours (16 cycles of 3 hours) at 1000 °C. In more internal layers, Sadique, *et al.*, (2000) observed the region of oxides in contact with the substrate, where they found a region that concentrates Fe, Cr and Al oxides. The region formed by the Fe-Cr-Al spinel increased the resistance to oxidation of the steel, however, the scale was defective, with pores and cracks, and the region of oxidation of alloy elements was seen to detach from the substrate., a factor that was intensified by the increase in heating time.

When this detachment occurs, the tendency to form imbalances in the oxide layers is enhanced, this means that a scale can exist in a higher oxidation state than would be possible when the scale is in contact with the alloy.

Although the oxidation kinetics observed by the authors was parabolic kinetics, they show that factors other than diffusive transport must be considered in an attempt to understand the oxidation of Fe-Cr alloys. Over time, the Cr_2O_3 incrustation ruptures and, as its growth progresses, the steel (Fe) begins to oxidize, being depleted in Cr, as Cr has already been depleted in the bulk alloy, close to the substrate. Therefore, the oxidation rate after rupture increases to high values, corresponding to greater formation of Fe_2O_3 - Fe_3O_4 (Sadique, *et al.*, 2000).

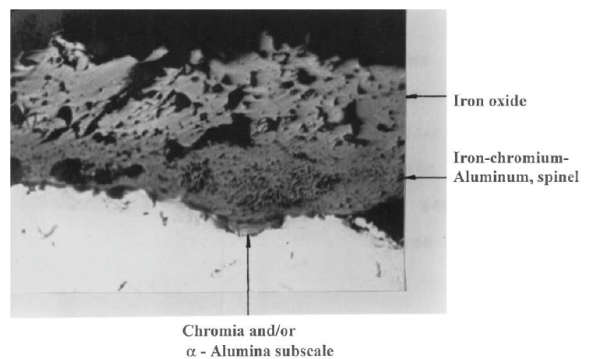


Figure 13 : Metallographic cross section of the oxide layer in Fe-10Cr-4Al oxidized for 48 hours (16 cycles of 3 hours) at 1,000 °C (Sadique, *et al.*, 2000).

NICKEL OXIDATION

A study carried out by Tatsuya, *et al.* (1997) evaluated the morphology of carbon steel scale, Figure 14, formed during oxidation in air, varying the chemical composition of Si and Ni in the alloy and the oxidation temperature, for a period of 60 minutes. As can be seen in Figure 14 (a, b, c, d), when the Ni content is 0.001% and Si 0.09% (by mass), the scale/steel interface is continuous. and regular, a fact justified by the formation of faialite. In Figure

14 (e, f, g, h), when the Ni content is 0.11% and Si 0.1% (by mass), the scale/steel interface became irregular. The irregularity of the scale/steel interface consists of the transgranular oxidation of austenite, caused by the presence of Ni in the steel.

This transgranular oxidation also causes an invasion of alloy element oxides into the austenite grain boundaries, meaning that the fayalite film no longer appears in a continuous and regular manner (Tatsuya, et al., 1997).

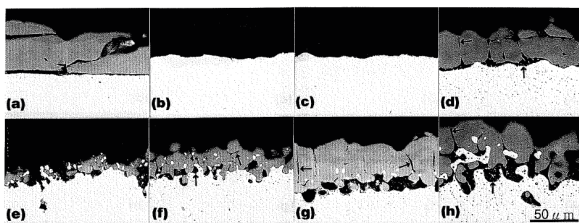


Figure 14 : Optical micrographs of the scale/steel interface in steels with 0.1% Si. The arrows in the figure indicate fayalite. Steel with 0.09% Si and 0.001% Ni heated to (a) 1,100°C, (b) 1,150°C, (c) 1,200°C and (d) 1,250°C. Steel with 0.1% Si and 0.11% Ni heated to (e) 1,100°C, (f) 1,150°C, (g) 1,200°C, and (h) 1,250°C (Tatsuya, et al., 1997).

Researchers Tatsuya, et al. (1997) also carried out an adhesion test that consisted of removing the primary scale through the use of a pressurized water jet on the samples, after leaving the oven. Residual scale is that which remains adherent to the metal substrate after the removal process, whereas primary scale is the part that is removed. They concluded that there was an increase in scale adhesion caused by the addition of small amounts of Ni, a fact that can be explained by the increase in the length of the scale/steel interface and its irregularity, causing the scale to adhere more strongly to the metallic substrate. On the other hand, the samples that presented a continuous and regular scale/steel interface showed greater adhesion than those that presented an irregular interface. This shows

that the influence of the continuous and flat layer of fayalite, in relation to the adhesion of the scale, is greater than the influence of the irregular scale/steel interface, generated by the transgranular corrosion of the austenite from the percentage of Ni (Tatsuya, et al., 1997).

MOLYBDENUM OXIDATION

In the study carried out by Zhang, et al. (2023) the researchers evaluated the effect of Mo on the oxidation behavior at 600 °C, through the discontinuous weighing method, varying the time from 20 to 100 hours, in the steel Fe-2.7%Cr-1.13% Ni-x%Mo (% by mass) for hot work, where steels with Mo percentages ranging from 0, 1, 2, 3 and 4% were analyzed.

Regarding mass gain, Figure 15, all steels showed parabolic oxidation kinetics. Increasing the Mo content up to 2% by mass proved to be favorable for increasing the oxidation resistance of the steel, however, when the Mo content becomes greater than or equal to 3% by mass, there is a decrease in resistance. to oxidation. First, Mo promoted the growth of Cr-rich layers by preventing the diffusion of O and Fe. Second, elemental Mo also improves the oxidation resistance of the test steel through its own oxides. Thirdly, Mo oxides, together with Cr-containing oxides, promote the formation of passivation films, such as CrMoO_4 oxide, thus improving their density. However, as at 600 °C MoO_3 , a volatile oxide, is produced, the second mechanism of action of Mo decreases with increasing temperature and Mo content, which, in turn, reduces this positive mechanism of action until producing a negative effect. In short, with the increase of Mo content, its synergistic mechanism plays an increasingly important role, while its own mechanism of action has a negative impact when the Mo content reaches or exceeds 3% by mass, mainly because Mo oxide produces MoO_3 oxide at 600 °C. This volatile oxide makes the oxide layer loose and

porous, making it impossible to form a dense passivation film and therefore causing low oxidation resistance. In addition to producing volatile oxides, it also tends to cause grain refinement (Zhang, et al., 2023).

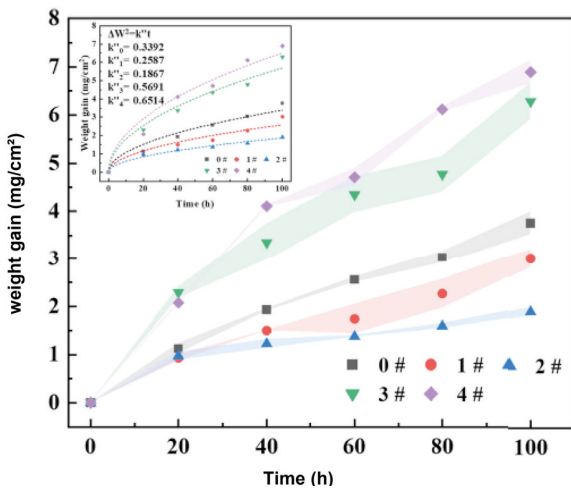


Figure 15 : Mass gain at 600 °C as a function of exposure time for the oxidation of Fe-2.7%Cr-1.13%Ni-x%Mo steels with different Mo contents (Zhang, et al., 2023).

Regarding the transverse structure/morphology of the scale, Figure 16, steels with Mo content of 0%, 3% and 4% (by mass) presented thicker oxide layers due to the higher degree of internal oxidation compared to steels with Mo content of 2% and 1% (by mass). Mo promoted the selective oxidation of Cr, causing the growth of Cr-rich oxide layers, Figure 16b and 16c, which in turn creates a more protective oxide layer. Despite being protective, these layers detached more significantly than the layers of the remaining three steels. In addition to the chromium oxide film having low adhesion to the substrate, this low adhesion was intensified by the generation of the volatile oxide MoO_3 . Figure 16d and 16e show that the increase in the Mo content to 3 and 4% (by mass), respectively, it generated scale with larger defects, which facilitated the diffusion of oxygen, increasing the thickness of the scale, when compared to

Figure 16a. As the Mo content increases, its ability to impede the diffusion of O and Fe becomes more pronounced, however, due to the increased production and volatilization of its own oxides, this weakens the density of the passivation layer and therefore Ultimately, it leads to more aggressive oxidation.

It can also be observed that the adhesion of the scale is greater when there is internal oxidation, generated by NiO (Zhang, et al., 2023).

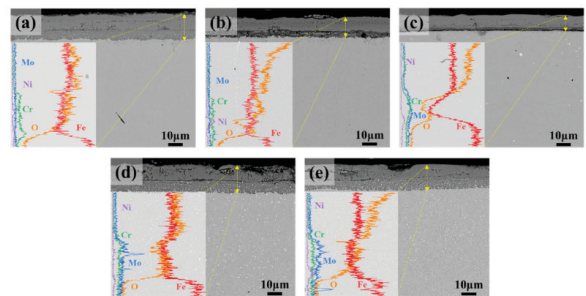


Figure 16 : SEM-EDS image of the cross-section of the oxide layer of the test steel after 20 hours of oxidation: (a) 0%Mo; (b) 1%Mo; (c) 2%Mo; (d) 3%Mo; (e) 4%Mo (Zhang, et al., 2023).

MANGANESE OXIDATION

The alloying element Mn has a greater chemical affinity for oxygen than Fe, however, like Fe, it does not form protective layers of oxides on the steel surface. However, during the oxidation reaction, Mn reacts with oxygen dissolved on the metal surface and precipitates in the form of MnO , participating in internal oxidation. This oxide forms a solid solution with wustite, tending to stabilize this phase, since its cations can replace the Fe atoms in the wustite network (Genève, et al., 2008).

Mn can also form spinels of the type $(\text{Fe-Mn-Ni})_2\text{O}_4$, $(\text{Fe-Cr-Mn})_2\text{O}_4$ in Fe-Ni-Cr alloy systems. The formation of these spinels can be expected in the innermost layers of the scale (Kao and Wan, 1988).

CARBON OXIDATION

As discussed in chapter 2.3 (scale), the oxidation of carbon forms a gas, CO and/or CO₂. This gas tends to escape from the metal surface and disappear into the atmosphere, as long as it does not encounter any obstacles, causing decarburization on the metal surface. Carbon is more oxidizable than iron, but does not participate in the phenomenon of internal oxidation (Jie, *et al.*, 2008).

Carbon and carbon oxides cannot diffuse through the iron oxide layers to reach the atmosphere. This happens because their solubilities in these oxides are insignificant, therefore, they require the presence of defects in these layers such as cracks and pores for their oxidation reactions to flow normally. The greater the number of existing defects, the greater the decarburization of the metal (Genève, *et al.*, 2006).

If a protective film is formed on the scale, which is adherent and free from defects due to the presence of an alloying element in the chemical composition of the steel, carbon tends to accumulate on the surface of the metal, as it will not be able to diffuse through the protective film. As the solubility of carbon in austenite is limited, when the carbon concentration on the metal surface becomes too high, carbon atoms precipitate and form iron carbides (Genève, *et al.*, 2008).

CONCLUSION

From the analysis of the literature in the present study, it is possible to infer the following conclusions:

- The oxide layers formed in the scale mainly contain iron oxides, namely: hematite, magnetite and wustite.
- The oxides of alloying elements tend to cluster close to the substrate, below the wustite layer.

- The formation of an alloying element oxide film will depend on its percentage in the steel composition. Alloy elements with low percentages in the steel composition tend not to form a continuous film, being precipitated in the wustite layer, close to the scale/substrate region, and in the steel, participating in internal oxidation. Still, low concentrations of alloying elements, even if they do not form continuous films, can influence the formation kinetics of other oxides.

- The alloying element Si oxidizes to form silica, SiO₂. This oxide, in turn, at high temperatures, reacts with wustite, FeO, forming a complex oxide, fayalite, Fe₂SiO₄. The fayalite film has a protective characteristic, meaning that it tends to form a “barrier” at the oxide/metal interface, making it difficult for Fe to diffuse through the scale to the external surface, thus reducing the kinetics of its growth and, consequently, its thickness. On the other hand, the fayalite film is very adherent to the metal substrate, influencing the greater adhesion of the entire scale, which makes it difficult to strip after the hot lamination process.

- Alloying elements such as Al and Cr, which have a greater tendency than iron to oxidize, and which form protective oxides, can be added to the steel composition to promote a certain resistance to oxidation, reducing the thickness of the scale.

- The alloying element Mn has a greater chemical affinity for oxygen than Fe, however, like Fe, it does not form protective layers of oxides on the metal surface. However, Mn reacts with oxygen dissolved on the metal surface and precipitates, in the metal layer close to the scale, in the form of MnO, participating

in internal oxidation. Its oxide, MnO, forms a solid solution with wustite, FeO, tending to stabilize this oxide at lower temperatures, since its cations can replace the Fe atoms in the wustite network.

- The alloying element such as Ni, austenite stabilizer, being oxidized, forms its oxide, NiO, at the boundaries of the austenite grains, causing transgranular oxidation and the formation of the irregular scale/substrate interface. Transgranular oxidation causes an invasion of alloy element oxides into the grain boundaries of austenite, causing

continuous and regular oxide films, such as fayalite, to appear irregular in shape.

- Mo, up to a certain percentage in the chemical composition of steel, tends to improve the oxidation resistance of the alloy, however, once a certain percentage is exceeded, this element already tends to reduce oxidation resistance. Furthermore, MoO₃ is a highly volatile oxide, which, like the oxides of C, CO and CO₂, generates pores and cracks in the scale, facilitating the diffusion of O, increasing oxidation and reducing its adhesion.

REFERENCES

- ABNT - Associação Brasileira de Normas Técnicas. Aço carbono e ligados para construção mecânica - Designação e composição química: ABNT NBR NM 87, São Paulo, 2000.
- ASM HandBook. *Properties and Selection: Irons, Steels, and High-Performance Alloys*. 10. ed. Asm Intl, 1990, v.1, 1063 p.
- Asrar, N., Thakur, C.P. Pickling silicon steels in mixed acid solutions. *Metal Finishing*, 1995, 93(2): 70-72.
- Basabe, V. V., Szpunar, J. A. Effect of O₂ in heating atmosphere on hydraulic descaling in hot rolling of low carbon steel. *ISIJ International*, 2008, 48(4): 467-474.
- Bhattacharya, R., Jha, G., Kundu, S., Shankar, R., Gope, N. Influence of cooling rate on the structure and formation of oxide scale in low carbon steel wire rods during hot rolling. *Surface and Coatings Technology*, 2006, 201(3): 526-532.
- Birks, N., Meier, G. H., Pettit, F. S. *Introduction to the high-temperature oxidation of metals*. 2. ed. New York: Cambridge University Press, 2006, 338 p.
- Bogdandy L. V., Engell H.J. *The reduction of iron ores: scientific basis and technology*. Berlin: Springer Berlin Heidelberg, 1971, 576 p.
- Cetlin, P. R., Helman, H. *Fundamentos da conformação: mecânica dos metais*. 2. ed. Artliber, 2005, 264p.
- Chabanier, J. E., Roth, J. L. Reflexions theoriques et efforts pratiques en vue de diminuer la perte de metal par oxidation au rechauffage dans le cas du laminage de brames. *Revue de Metallurgie*, Paris, 1982, 79(11): 917-924.
- Chang, Y. N. Roles of silicon and aluminium in pickling behaviour of low alloy hot rolled steel. *British Corrosion Journal*, 1994, 29(2): 136-139.
- Chen, R. Y., Yuen, W. Y. D. Review of the high-temperature oxidation of iron and carbon steels in air or oxygen. *Oxidation of Metals*, 2003, 59(5): 433-468.
- Cunha, A. F., Mol, M. P. G., Martins, M. E., Assis, P. S. Caracterização, beneficiamento e reciclagem de carepas geradas em processos siderúrgicos. *Revista Escola de Minas*, 2006, 59(1): 111-116.
- Danno, T., Nakatsuka, D., Kusano, Y., (...). Crystal structure of β-Fe₂O₃ and topotactic phase transformation to α-Fe₂O₃. *Crystal Growth and Design*, 2013, 13(2): 770-774.
- Fukagawa, T., Okada, H., Maehara, Y. Mechanism of red scale defect formation in Si-added hot-rolled steel sheets. *ISIJ International*, 1994, 34(11): 906-911.
- Furmanski, L. M. Estudo da utilização de carepa de laminação de aço em processo de obtenção de sulfato ferroso. Dissertação de Mestrado em Ciência e Engenharia de Materiais – Programa de Pós-Graduação em Ciência e Engenharia de Materiais, Universidade do Extremo Sul Catarinense. Criciúma, 2016, 115p.

- Genève, D., Rouxel, D., Pigeat, P., Weber, B., Confente, M. Surface composition modification of high-carbon low-alloy steels oxidized at high temperature in air. *Applied Surface Science*, 2008, 254(17): 5348–5358.
- Genève, D., Rouxel, D., Weber, B., Confente, M. Segregation across the metal/oxide interface occurring during oxidation at high temperatures of diluted iron based alloys. *Materials Science & Engineering A*, 2006, 435: 1-11.
- Hao, M.; Sun, B.; Wang, H. High-Temperature Oxidation Behavior of Fe–1Cr–0.2Si Steel. *Materials*, 2020, 13(3): 509-527.
- IRSID Le Décapage des Produits Plats. Oxydation du Fer et Caractéristiques de la Calamine. Textes des conférences données au cessed lors du séminaire d'octobre, Paris, 1983.
- Jie, S., Ren, W. D., Dong, H. Y., Bin, Q. H., Gao, W. Reduction of oxide scale on hot-rolled strip steels by carbon monoxide. *Materials Letters*, 2008, 62(20): 3500-3502.
- Kao, C. H., Wan, C. M. Effect of manganese on the oxidation of Fe-Mn-Al-C alloys. *Journal of Materials Science*, 1988, 23: 744-752.
- Kizu, T., Nagataki, T., Inazumi, T., Hosoya, Y. Effects of chemical composition and oxidation temperature on the adhesion of scale in plain carbon steels. *ISIJ International*, 2001, 41(12): 1494-1501.
- Krzyzanowski, M., Beynon, J. H., Farrugia, D. C. J. *Oxide scale behavior in high temperature metal processing*. Weinheim: John Wiley & Sons, 2010, 386p.
- Luo, Y., Zhu, D., Zhou, X., Shi, B., Zhang, F. Coproduction of DRI Powder and Semi-coke from Siderite Ore and Low Rank Coal by Excessive Coal-based Direct Reduction in Rotary Kiln. *ISIJ International*, 2016, 56 (1): 78–87.
- Machala, L., Tuček, J., Zbořil, R. Polymorphous Transformations of Nanometric Iron(III) Oxide: A Review. *Chemistry of Materials*, 2011, 23(14): 3255-3272.
- Martín, M. I., López, F. A., Torralba, J. M. Production of sponge iron powder by reduction of rolling mill scale. *Ironmaking and Steelmaking*, 2012, 39(3): 155-162.
- Matlakhov, A. N. *Corrosão e Proteção dos Materiais (organização de Matlakhova L. A.)*. São Paulo: Paco Editorial, 2021, 340p.
- Ramanathan, L.V. *Corrosão e seu controle*. 3. Ed. Sao Paulo: Hemus Editora Ltda, 1997, 344p.
- Sadique, S. E., Mollah, A. H., Islam, M. S., Ali, M. M., Megat, M. H. H., Basri, S. High-Temperature Oxidation Behavior of Iron–Chromium–Aluminum Alloys. *Oxidation of Metals*, 2000, 54(5/6): 385-400.
- Shatkhia, V. I., Gogenko, O. O., Kripak, S. M. Utilising of the oiled rolling mills scale in iron ore sintering process. *Resources, Conservation and Recycling*, 2011, 55(4): 435-440.
- Taniguchi, S., Yamamoto, K., Megumi, D., Shibata, T. Characteristics of scale/substrate interface area of Si-containing low-carbon steels at high temperatures. *Materials Science and Engineering: A*, 2001, 308(1): 250-257.
- Tatsuya A., Tetsuo S., Masayuki M. Influence Scale in of Ni Impurity in Steel Hydraulic Descaling on the Removability of Primary. *ISIJ International*: 1997, 37 (3): 272-277.
- Tomaszewicz, P., Wailwork, G. R. Observations of Nodule Growth During the Oxidation of Pure Binary Iron-Aluminum Alloys. *Oxidation of Metals*, 1983, 19(5/6): 165-185.
- Umadevit, T., Kumar, M. G. S., Mahapatra, P. C., Babu, T. M., Ranjan, M. Recycling of steel plant mill scale via iron ore pelletisation process. *Ironmaking and Steelmaking*, 2009, 36(6): 409-415.
- Yuan, Q., Xu, G., Zhou, M., He, B. The effect of the si content on the morphology and amount of Fe_2SiO_4 in low carbon steels. *Metals*, 2016, 6(4): 94-103.
- Weihua, S., Tieu, A. K., Zhengyi, J., Cheng, L. High temperature oxide scale characteristics of low carbon steel in hot rolling. *Journal of Materials Processing Technology*, 2004, 155: 1307-1312.
- Zhang, C., Zhang Y., Hu J., Wang Z., Xue J., Yu H., Zhang C., Wang X., Cai Q., Wang C., Jiang T., Wei S., Pan K. Effect of Mo on the high-temperature oxidation behavior of Cr-Ni-Mo hot-work die steels. *Corrosion Science*, 2023, 224: 1-13.
- Zhong, M., Webler, B. A. High temperature oxidation behaviors of steels at initial stages in air. *Corrosion Science*. 2024; 229; 111838