Mechanisms of Formation and Removal of the Primary Oxide in a Tunnel Furnace by the Descaling on a Compact Plant for Flat Products

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These works was made in a compact strip plant (CSP) and represent an effort to decrease the amount of coils of steel rejected by a cosmetic defect called primary oxide, the morphology of the scale and its characterization by optic and scanning electron microscope was presented. Different trials were made in order to find the mechanism and phenomena of how the primary oxide is formed. The different theories of how the scale is removed by a descaling system are described. The benefits obtained from this research are mentioned.

KEY WORDS: primary scale; tunnel furnace; descaling; fayalite.

1. Introduction

In a compact plant the slab from the casting enters into the tunnel furnace at temperatures to 1 050–1 150°C (Fig. 1), then enters in the descaling system in order to remove primary oxide generated in the tunnel furnace. The descaling (Fig. 1 and Fig. 2) is a device consisting of water jets at high pressure that remove the primary oxide before it enters to the mill (Fig. 1). The descaling of the compact plant consists of two pairs of water headers, low and high pressure 200 and 380 bars, these water pressures are very high if is compared with conventional mill (100–150) bar. Sometimes this oxide is not totally removed, being embedded by the mill, this cause a bad superficial appearance in the coils that is not suitable for some commercial applications.

2. Literature Review

2.1. Oxide Formation and Removal

A lot of studies on the oxidation of iron show that the dominant oxide at high temperature is wustite (FeO), on about 95%, 4% of magnetite (Fe3O4) and only 1% of hematite (Fe2O3). The wustite, which is the innermost oxide phase is formed near the metal surface and therefore is the richest in iron. Magnetite is an intermediate phase and is the main component at 500°C. Finally, the hematite, which is the outermost layer of oxide, has the highest oxygen content of about 30% by weight. Hematite can exist in two ways, such as α-Fe2O3, representing a rhombohedra structure and as γ-Fe2O3, representing a cubic structure.

A hematite has been found even at low temperature. Their presence is due to incomplete elimination of wustite.

Fig. 1. Schematic diagram of the compact plant (top) the descaling system (bottom) and the descaling header low and high pressure.

Fig. 2. Schematic diagram of impact, height and nozzle angle over the slab.
during rolling. **Figure 3** describes the mechanism where the particles of FeO are rolled break it significantly, separating from the matrix metal and exposed to the air. This implies a lower amount of iron atoms, while oxygen is abundant; resulting in acceleration in the reaction of wustite to magnetite and finally hematite. It is also common to observe the color of the hematite in silicon steels, are generally difficult to remove due to eutectic component (FeO/Fe2SiO4) formed in the interface and penetrates irregularly in both sides.5)

#### 2.2. Mechanical Removal of Primary Oxide by the Descaling

There are four theories related with this:

- **Cooling (thermal component):** The water hit the slab, cooling the oxide, this leads to a rapid contraction of the oxide and steel and finally is removed by water.
- **Phase change (pneumatic component):** Water penetrates into the cracks and changes from liquid to vapor generating a volumetric expansion breaking the scale.
- **The chisel effect (mechanical component):** The flat fan nozzles produce a very thin stream with high force, the combination of this on the surface of the slab remove scale.
- **The drag effect (hydraulic component):** The oxide is cleaned by the horizontal component of force when the water is applies.

The last theories provided some theoretical equations that help to predict the effective elimination of oxide by the descaling system.

These include: The water force, based on some mathematical simplifications, can be described as3):

\[
F = 0.236 \cdot G_a \sqrt{Q_a} \quad \text{(1)}
\]

\(G_a\) as the flow rate of water from the nozzle in (L/min), \(Q_a\) system pressure in bar and \(F\), force (N).

The water impact which is defined as4):

\[
j = K_b \frac{G_a \sqrt{Q_a}}{(H_j)^{1.5} \tan (\frac{\alpha_{\text{nozzle}}}{2})} \quad \text{(2)}
\]

where \(P\) is the full system pressure in bar, \(H_j\) is the distance from nozzle to oxide vertically measured (m), and \(\alpha_{\text{nozzle}}\) is the angle of the jet depending on the design of the nozzle (Fig. 2) and that \(x \leq K_b\) depend on the distance slab-nozzle, 1.34 and 0624 respectively in this case. Another important term is the amount of water (L/m²) which is expressed as5):

\[
U = \frac{G_a}{A_{\text{ch}} \cdot v_p} \quad \text{(3)}
\]

With \(\alpha_{\text{nozzle}}\) as the angle in the nozzle and \(H_j\) the vertical distance from the nozzle to the slab in mm (Fig. 2). Finally the term, fraction of water is considered the impact of water in the oxide as a large number of drops and only a small fraction of this is impacted in the oxide. This criterion establishes that the oxide will be removed when the water exceeds a certain critical velocity \(v_c\):

\[
v_c = a_0 \left(\frac{\xi}{19}\right)^{b} \quad \text{(5)}
\]

\(b\) takes the value of \(-0.37\), \(a_0\) depends on the steel and is taken for low carbon steels \(a_0 = 85\) and from silicon steels (0.15%) \(a_0 = 225\), and \(\xi\) represents the fraction of drops, this is calculated as:

\[
\xi = \frac{Q}{v_s \cdot XY} \quad \text{(6)}
\]

Where \(v_s\) is the speed of the slab in (m/s), \(Q\) is the volumetric flow rate in (m³/s), \(X\) is the width of the impact area and \(Y\) the thickness of the fan in meters.

### 3. Results

**Figure 4** is a series of coils seen in a pickling line with and without primary oxide; it shows the effects of impact force \(F\) (Eq. (1)) against the water quantity \(j\) (Eq. (2)), where \(F\) low With OP and \(F\) low Without OP means the water force (Eq. (1)) applied to the slab by the low pressure header (Fig. 1) and the presence of primary oxide in the coils as a pickling coils and \(j\) low (without OP) and \(j\) low (with OP) means the impact (Eq. (2)) applied by the low pressure header, is noted that when \(U\) is increases the amount of oxide observed decrease, in **Fig. 5** its shows a comparison of the fraction and the speed of water (Eqs. (5) and (6)) compared with a conventional mills in low carbon steel11) and in the top position the line for silicon steels (0.15% Si). Its shown theoretically and for the coils observed in the pickling line, that the primary oxide is more difficult to remove by the descaling of the CSP plants in low carbon steels and its shows top line the theoretical position for silicon steels (0.15% Si) in conventional mills.

#### 3.1. Characterization of Primary Oxide

In order to know the properties of the oxide, the mechanisms of their formation and their effective removal is essential to have a good characterization of it. Dimensional differences exist between the layer thickness and the adhesion between a primary and a secondary oxide the second is formed after lamination and can be easily removed with a chemical attack, whereas the primary oxide is embedded in the strip and is practically impossible to remove. A secondary oxide photomicrograph is shown in **Fig. 6**; the normal oxide thickness presents a continuous and uniform thickness.
ness from 5 to 40 μm, depending on the strip thickness as well as entry and finishing temperature.

In the interface between oxide and steel is a continuously thick with presence of a perpendicular crack in the rolling direction, which is caused by thermal stresses due to different coefficients of contraction between steel and oxide. In contrast, the primary oxide is embedded in the strip and is about ten times higher than the secondary oxide, the typical thickness are between 50 and 100 μm. A photomicrograph is shown in Fig. 7.

The morphology of primary oxide (Fig. 7) is a strongly embedded oxide on the steel surface. A top view of this is shown in Fig. 8, the oxide is elongated in the direction of rolling, and there are small zones of oxide in irregular shapes due to localized plastic deformation.

3.2. Study by Scanning Electron Microscopy of the Primary Oxide

A characterization by electron microscopy in zones of the oxide and outside was made (Fig. 9), it shows the oxide topography; zone A has oxide, while B is free of this. The topographies of both are totally different; in zone A was found typical elements of oxide and exogenous elements as Si, Ca and Al.

The sample (Fig. 9) was taken a series of spectrograms using the punctual technique, resulting in a variation of the chemical composition in the transition zone. The chemical composition of the zone B, (outside the oxide), consisted mainly of Fe, Mn, C and O. These elements are associated with the steel composition.
3.3. Time and Temperature Effect on the Slab into the Tunnel Furnace and the Presence of Primary Oxide Embedded in the Pickling Coils

With the aim of understanding the effect of time and temperature in the slab into the tunnel furnace (Fig. 1) vs. the occurrence of primary oxide in the coils, tests were performed with groups of slabs at different process conditions, these were inspected as coils in a pickling line, counting the amount of oxides embedded, the trials were made at three different temperatures (1 050, 1 085 and 1 150°C) and times of the slabs into the tunnel furnace between 10 to 22 min as an average.

At the same time with the data, was made a hypothesis test in order to see if the effect of time and temperature is affecting the amount of primary oxide embedded in the coils.9 As a result was found a significant difference in the amount of oxides embedded in the coils if the time and the temperature is increased (Figs. 10 and 11).9 For the trials in the tunnel furnace was possible to find a condition of “Safe Zone” for which the presence of primary scale on pickling coils is avoided (Figs. 12 and 13).

3.4. Primary Oxide Observed in the Bottom Side in Pickling Coils

Based on observations in the pickling line of two lots of coils, one with incrusted oxide in the bottom side at two different days, was conducted a review of the process variables that may cause the defects in the bottom side. From this analysis was found a strong influence the time and temperature in the tunnel furnace over the slabs when these slabs were made. Most of the time was consumed in transfer car (Fig. 1), where rolls and wheels are dry and the temperatures are above to 1 150°C. The oxide was aligned and located 20 mm on both sides of the coils observed.

This defect called “Tiger Strips”, is related to the concentration of silicon oxide and metal interface and is characteristic of steels with Silicon greater than 0.15%.3 One way to avoid these is to work at low temperatures, below 1 150°C which is near to the melting temperature of fayalite, being completely liquid to 1 171°C.

An analysis of the time and the temperature in the transfer zone (ferry zone) (Fig. 14) where the rolls temperature and the residence time of the slab is high; the slabs with embedded primary oxide in the bottom side is more severe, because the oscillation of the slab, damage the bottom surface. Undoubtedly, the mechanisms of the formation of incrusted oxide on the bottom side can occur by the presence of mold powder in the top side, but additionally the slab in the bottom side is in contact with the rolls of the furnace, this surface is damaged generating aligned oxide with the rolls.

Has been found, however, that this damage is not exclusive in dry rolls (transfer zone), also occurs in water-cooled

![Fig. 10. Amount of embedded oxides, depending on the temperature at two different times in the tunnel furnace, the points correspond to observations in the pickling line per each coils 12 coils analyzed.9](image)

![Fig. 11. Amount of embedded oxide depending on the time at three different temperatures 1 050, 1 085 and 1 150°C in the tunnel furnace, the points correspond to observations in the pickling line per each coil, 20 coils analyzed.9](image)

![Fig. 12. Relation between time and temperature of the slabs inside the tunnel furnace vs. observation of primary oxide in pickling coils where (Sin OP) means pickling coils observed without primary scale and (OP) means pickling coils observed with primary oxide.](image)

![Fig. 13. Actual process conditions in products with high quality surface requirements in order to prevent primary scale in the coils “Safe Zone”.](image)
rolls, due to the growth of oxide over the rolls (stick), eccentrics or motionless rolls. Thinking that some foreign elements from the roll wheels of tunnel furnace were cause of the defect, studies of the chemical composition of the scale adhered to the wheels was made.6) The chemical composition of samples were analyzed by EDXS microanalysis, as a result was detected only major elements as Fe and O. Studies of X-ray diffraction were carried out showed that only compounds present in the scale of the wheels were oxides as hematite, magnetite and wustite, no other elements was found.

4. Characterization

4.1. Slab Characterization Before Enter to the Tunnel Furnace

Based on the characterization of embedded oxide in the strip samples in pickling coils; was proceeded to cut piece of slabs before it entered to the furnace. These slabs were cut in cross-sections being analyzed by light and electron microscopy. A study on the slab surface was detected elements as silicon, calcium, magnesium and aluminum on the surface mainly. Figure 15 shows a SEM analysis. In the top surface of the slab was found the presence of silicon dispersed throughout the sample, carbon, aluminum calcium and magnesium very dispersed in the whole sample. Based on the presence of residual elements as silicon and calcium in the slab samples, a laboratory experiments was tested with mold powder, element used as a lubricant in the casting.

4.2. Laboratory Tests and Field Trials Adding Mold Powder to the Slab

One of the main sources of silicon and calcium is the mold powder used to lubricate the walls of the casting in order to prevent that the steel is sticking to the walls. A typical composition of this powder is 30–35% SiO₂, 31–33% CaO+MgO, 3–4% Al₂O₃, 11–15% Na₂O+K₂O, 6–8% of F and 3–5% C and others elements in less quantities. Trying to reproduce the chemical reaction between the slab and mold powder, several samples were subjected to different temperatures 900, 1000 and 1250°C in a laboratory furnace for 30 min.7,10) Figure 16 shows a general aspect of the microstructure in the interface between the mold powder and the steel. As a result a chemical reaction was observed, the spectrogram shows considerable enrichment of silicon and calcium as well as iron oxide (Fig. 17).

With the laboratory results of steel and mold powder reaction; was performed some tests in the tunnel furnace. The procedure for the tests was to systematically add mold powder at the end of some slabs, and then was observed in the inspection zone as a strip. A top view of the defect adding mold powder to the slab is shown in Fig. 18; this figure
shows a continuous patch in the center. The samples were characterized by light and electron microscopy; the results are shown in the top right (Fig. 18).

5. Discussion

5.1. Mechanism of Reaction between the Mold Powder and Slab

The chemical composition of mold powder are SiO$_2$ (CaO+MgO) and (Na$_2$O+K$_2$O), with less amount of MgO 2% and 0.5% less than K$_2$O. Systems SiO$_2$–CaO and SiO$_2$–Na$_2$O in the presence of H$_2$O vapor can produce elements with different properties, depending on the rate SiO$_2$ : CaO and SiO$_2$ :Na$_2$O, however, when the atmosphere also contains CO$_2$, the reaction between oxides can produce H$_2$CO$_3$ (carbonic acid), which catalyzes the reaction of silica gel colloidal throughout decomposition of the respective silicates, i.e.,

\[
2\text{CaSiO}_3(s) + 2\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \Leftrightarrow 2\text{CaCO}_3 + 2\text{SiO}_2 \quad \text{(7)}
\]

\[
2\text{NaSiO}_3(s) + 2\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \Leftrightarrow 2\text{NaCO}_3 + 2\text{SiO}_2 \quad \text{(8)}
\]

It is important to highlight here the balance established between CO, CO$_2$ and O$_2$ in the tunnel furnace atmosphere, that is:

\[
\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \Leftrightarrow \text{CO}_2(g) \quad \text{.................(9)}
\]

The presence of CO$_2$ is essential for the reactions of decomposition of the silicates, mention before (Eqs. (7) and (8)). Silica gel colloidal (SiO$_2$) has strong binding properties, because silicon bonds can be formed with the solid particles in which it is embedded.

The binding properties and the high resistance to compression of silica gel colloidal take its maximum at a certain critical value of the partial pressure of CO$_2$, in the atmosphere; at higher concentrations, the strength compressive decreases. The tunnel furnace atmosphere consists primarily of natural gas; they contain CO$_2$ and water vapor. A typical composition is 8.24% CO$_2$, H$_2$O 16.48%, 2.47% and 72.79% N$_2$O$_2$. The presence of O$_2$ and CO$_3$ in the atmosphere, necessarily mean the presence of CO because of the balance (Eq. (9)), so that CO is also present in the atmosphere. The presence of mold powder, rich in SiO$_2$, CaO and Na$_2$O and chemical composition of the atmosphere of the furnace, which is rich in CO$_2$ and H$_2$O, favors the decomposition of CaSiO$_3$, Na$_2$SiO$_3$ and the mold powder present in the mold.

When this compound is present in the oxide over the slab, and with high operating temperatures of the furnace, the silica gel hardens and acts as a binder between the FeO and metal. The time plays an important role, because the compressive strength is high, if the time is increased.

If the silica gel is in direct contact with steel, the chemical reaction is given as follows:

\[
2\text{Fe(s)} + 2\text{SiO}_2(\text{coloidal}) + \frac{1}{2}\text{O}_2(g) \Leftrightarrow 2\text{FeO} \cdot \text{SiO}_2 \quad \text{...(10)}
\]

In the more realistic situation that the silica gel colloidal is formed into the scale of FeO, the reaction is:

\[
4\text{FeO(s)} + 2\text{SiO}_2(\text{coloidal}) + \frac{1}{2}\text{O}_2(g) \Leftrightarrow 4\text{FeO} \cdot \text{SiO}_2 + \text{Fe}_3\text{O}_4 \quad \text{...(11)}
\]

In both reactions (Eqs. (10) and (11)) the product is iron silicate, which is combined with wustite known as fayalite (FeO/Fe$_2$SiO$_4$). As a result of this investigation, a reduction of primary oxide embedded in the coils was observed with an average of 1.05% of total production, to 0.2%, this represents an improvement of almost 80% (Fig. 20).

Moreover, was obtaining a better global condition, in the descaling and tunnel furnace principally, some things were improved. It changed the rollers of the furnace with problems on its wheels, (Fig. 1). The global temperature and time was decreased, was established an inspection routine of the condition of the rolls in the furnace, all actions contributed to decrease the primary oxide rolled in the coils.
6. Conclusions

(1) The combined effect of time and temperature in the tunnel furnace was a determining factor in the occurrence of primary oxide in the strip. On the bottom side, having the slab oscillation or when a roll is motionless the possibility of primary oxide in the bottom side is increased.

(2) The laboratory tests confirm the chemical reaction that happen in the furnace between the slab and mold powder, the adherence of the oxide is more severe.

(3) The electron microscopy reveal exogenous elements in the oxide embedded in the steel, such as Si and Ca, the principal factor of the strong adhesion of the primary oxide in the strip.

(4) The evidence of adding mold powder on the slab at the entrance of the furnace indicated that the powder was no removed by the descaling. However, it was not possible to reproduce the exact morphology of the oxide, there were only dark and gray spots, which by electron microscopy revealed the presence of mainly Si and Ca.

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