

Scale formation and surface quality of carbon steel at oxyfuel heating

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1. INTRODUCTION

Lower costs of steel production can be achieved not only via lower energy consumption, higher product quality and productivity but also by reduction of the mass loss of the material during heating. Oxidation of the steel during heating process is a source of substantial mass loss of steel. Scale formed on the surface of the heated steel is a source of a large problem in steel manufacturing industries. The aim of the study was to address the problem and describe the scale growth as well as the properties.

The time aspect is essential when reheating steel. At high temperature the steel oxidizes forming a scale that grows with time, decreasing the material yield. Of course there is major interest in finding ways to reduce this scale growth. Today's common practice to use air (air and fuel, hereafter denoted airfuel), as combustion oxidizer might not be favorable in the sense of minimizing the scale formation. Linde-gas has more than 90 oxyfuel (oxygen and fuel) installations around the world. The present investigation will compare conventional airfuel combustion with oxyfuel combustion technique.

When changing from air- to oxyfuel combustion technique in reheating furnaces its possible to;

- Improve material surface quality
- Completely remove scale more easily
- Increase process stability such as homogenous temperature distribution
- Decrease reheating time
- Reduce fuel consumption
- Use lower grade fuels
- Decrease the environmental impact when decreasing CO₂, CO, SO_x and NO_x emissions

2. MATERIAL AND EXPERIMENTAL PROCEDURE

Two commercial steel grades were used, Table 1 list their composition. Test pieces were cut from rolled material to 22 x 60 x 100mm dimension with a surface roughness of R_a=45µm. Oxidation experiments were performed as the table 2 show. The aim for the study was to go deeper into the oxyfuel combustion and to describe the oxidation growth rate and properties for all known reheating cases for batch type furnaces. Airfuel was studied in order to establish the difference to oxyfuel.

Table 1: Steel grade used in test. Steel 1 is low alloy steel and steel 2 is high carbon steel.

	EN Code	C	Cr	Si	Mn
Steel 1	102 09	0.04	-	0.01	0.2
Steel 2	100CR6	1.00	1.5	0.30	0.3

Table 2: Experimental parameters

Temperature (°C)	1150	1250	1300			
Time (min)	30	60	120	180	300	480
Oxyfuel Stoichiometry	5% CO	0% O ₂	2%O ₂	5%O ₂		
Airfuel Stoichiometry	-	0% O ₂	2%O ₂	-		

A 550 high, 400 wide and 1900mm deep furnace equipped with one flameless oxyfuel and one conventional air burner was used as experimental set-up. To achieve a low and constant flow rate of combustion gases, a 200mm high wall is placed in between the burner outlet and the test pieces. The thermal input was 30 to 100 kW using oxyfuel and 50 to 150 kW in airfuel. LPG with 95% propane was used as fuel. Temperature is measured with type S, Pt-Pt10%Rh thermo couples close to the steel sample. To analyze O₂, CO, CO₂ and NO_x a micro gas chromatograph was used together with a continuous logger. A typical gas analysis is shown in table 3.

Table 3: The wet flue gas analysis was maintained by a preset of the dry flue gases to 2% oxygen when firing propane as fuel.

	O ₂ -wet	CO ₂ -wet	H ₂ O	N ₂
Airfuel	1.7	10.8	13.7	73.8
Oxyfuel	0.9	43.7	55.4	-

The amount of scale and dimension change was measured in a light optical microscope (LOM). Chemical investigation was made in a scanning electron microscope (SEM) equipped with EDS. Wet chemical analysis was made on Steel 2 - flameless oxyfuel combustion samples. Selected pieces from Steel 2 were etched and investigated to visualize the decarburization of the steel. Thermo couples were drilled into the mass center to measure the test piece temperature. To stop further oxidation and avoid unwanted breakage of the scale, the specimens are taken to a water-cooled chamber that was purged with nitrogen gas. To measure the scale adhesion force to the metal a tool similar to a razor blade was used to scratch away the scale and the method is shown in figure 4b. A tensile stress test machine with a 100 kN force transducer was used.

3. RESULTS

3.1 COMPARISON OF COMBUSTION TECHNIQUES

Cold air combustion is known for its low efficiency. In the present case when using airfuel the thermal efficiency was about 40% at a furnace temperature of 1250°C. NO_x emission value where about 70 mg/MJ.

Due to a high concentration of oxygen in oxyfuel combustion, the thermal efficiency is about 80% at 1250°C. Due to the laboratory setup, heat was extracted to maintain a reasonable furnace pressure and to avoid air leakage. Extracting 50 kW of total 90 kW thermal input avoids air leakage and a reasonably high flue gas circulation was maintained. The NO_x value was below the limit of the instruments accuracy.

3.2 SCALE GROWTH IN LABORATORY SAMPLES

Scale consist of three oxides; FeO (wüstite), Fe₃O₄ (magnetite) and Fe₂O₃ (hematite). Wüstite has the highest growth velocity compared to magnetite and hematite. Magnetite is a spinel of wüstite and hematite. Cross sections from both materials and each combustion technique are shown in figure 1 (a - b). In both types of combustion technique the resulting oxide is porous and built up by different layers. Common to all is that close to the substrate FeO start to form at > 750°C. Next to this is a layer of Fe₃O₄ and at the top the stoichiometric oxide Fe₂O₃. In airfuel samples there is gap between magnetite and wüstite. The same type of gap occurs in oxyfuel samples but is located between steel and wüstite. Probably this is a result from the cooling and not from the scale formation in the furnace. The total oxide growth is 10% higher in Steel 1 compared to steel 2 due to lower diffusion rate in Steel 2 [1]. This means that Steel 1 is more sensitive to increasing temperatures. Micrographs from Steel 1 show that metal grain size growth increase with temperature but are not a function of the combustion oxidizer.

In oxyfuel atmosphere the scale growth is a function of time. Magnetite stand for about 50% of the oxide layer, a very small amount ≤ 5% is hematite the rest is wüstite. In airfuel combustion the magnetite (+hematite) layer where constant over time in contrast to the wüstite that grows with time. In both cases the scale formation is strongly temperature dependent. Porosity increase with temperature and at 1150°C about 25% of the total scale constitutes of pores, which increase to 30% at 1300°C. Pore size is greater in airfuel than in oxyfuel. The combustion stoichiometry had a lower influence on scale growth rate than expected. The simplified Wagner model for parabolic scale formation rate can be used to explain growth at a specific time and temperature:

$$x = \sqrt{k_{0, \text{dim}} \exp\left(-\frac{Q_{\text{reaction}}}{RT}\right)t} \quad \text{where } x[\text{m}], k[\text{m}^2/\text{sec}], Q/R[\text{K}], t[\text{s}] \text{ and } T \text{ in Kelvin.}$$

It was discovered that weight change as well as any scale dimension change also followed the Wagner parabolic behavior. Plotting log x²/t versus 1/T solves the Q value and k₀ is the intersection with the log x²/t

axis. Observe in figure 2, where scale thickness, t and dimension change, D (sample size before reheat – clean sample after reheat/2) is plotted versus temperatures that the dimension change is lower than scale thickness for constant time. This is a result of scale being very porous. If recalculating to a non-porous scale (30% less thickness) the scale thickness would still be higher due to the chemical reaction $Fe+O=FeO$. The relative factor (t/D) varies only with temperature. There is no difference regarding combustion oxidizers. The factor (t/D) for Steel 1 is constant and equals 2.6 (for all temperatures and both oxidizers). For Steel 2 it is 1.4 at 1150°C but 2.7 at 1300°C.

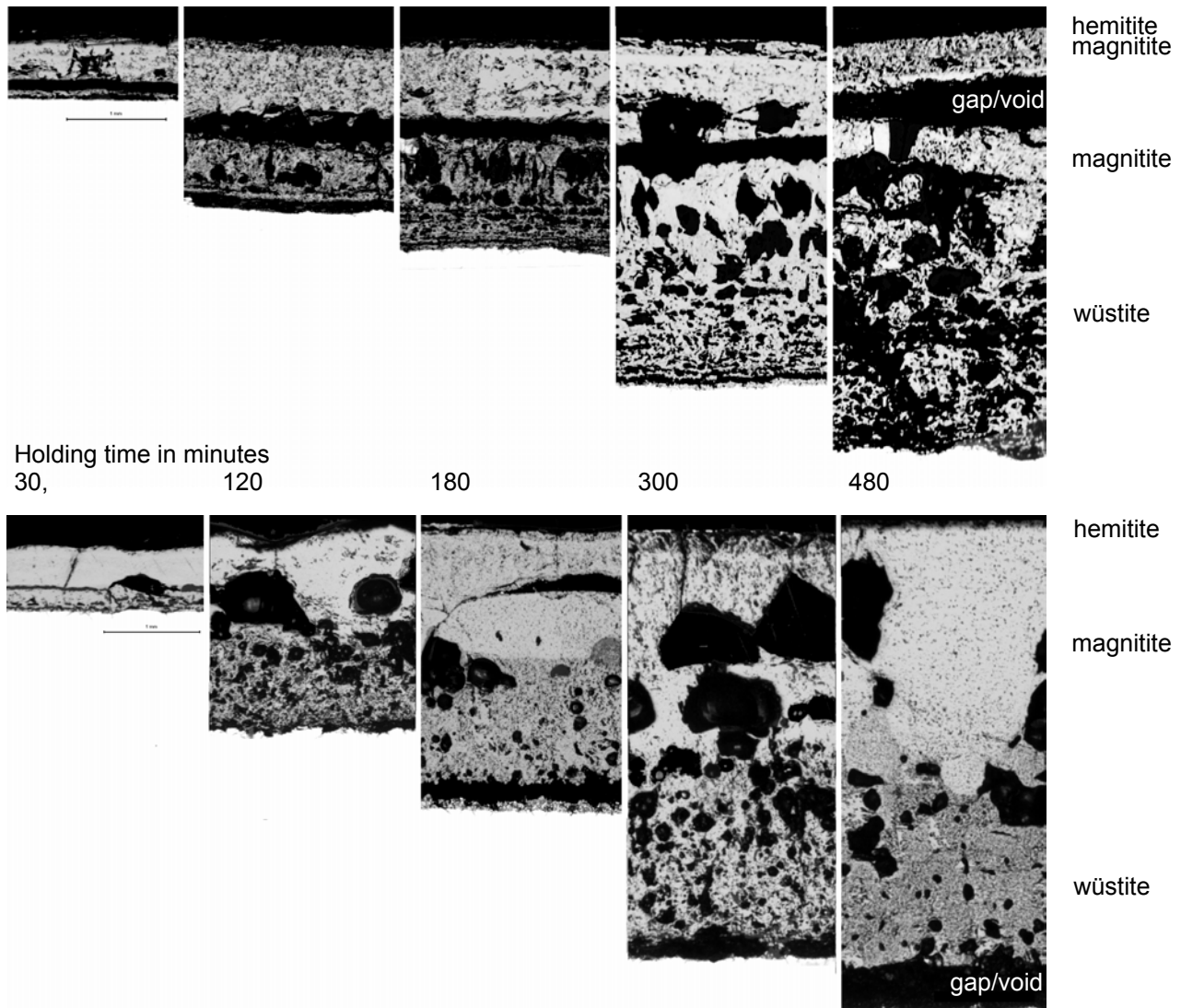


Figure 1. Scale cross-section of materials at 2 % excess oxygen at furnace temperature 1250°C at holding times 30, 120, 180, 300 and 480 minutes

a) Top- Steel 1 fired with airfuel, b) Bottom – Steel 1 fired with oxyfuel,

The gap (crack) in the airfuel case was located between magnetite and wüstite. In oxyfuel the gap was located between wüstite and steel and therefore was easier to completely remove the scale.

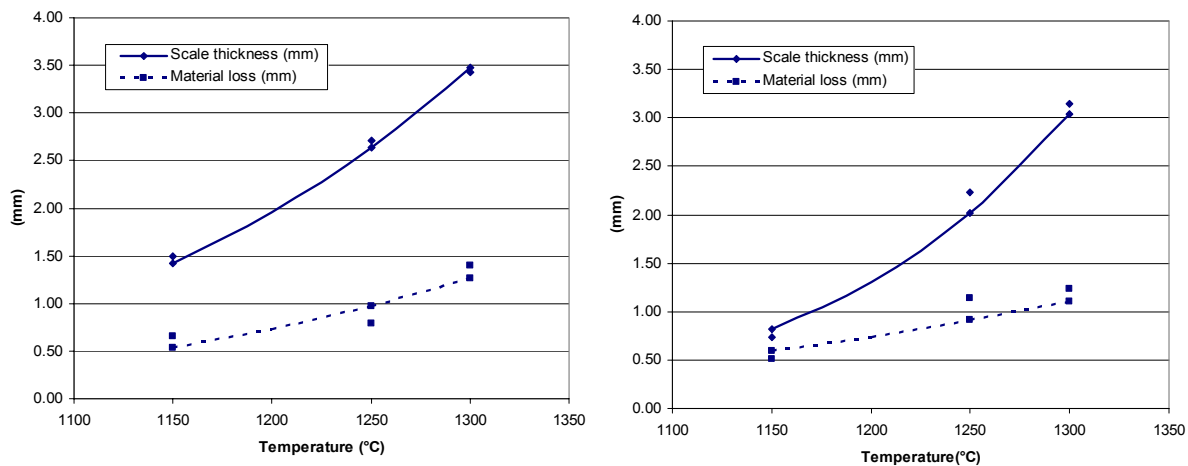


Figure 2a and 2b. Scale thickness and material loss for Steel 1(left: 2a) and Steel 2(right: 2b) at 2% excess oxygen at 120 minutes holding time when firing oxyfuel. The fractions of porous increase at higher temperatures for Steel 2 but the fractions of porous is more or less the same for Steel 1.

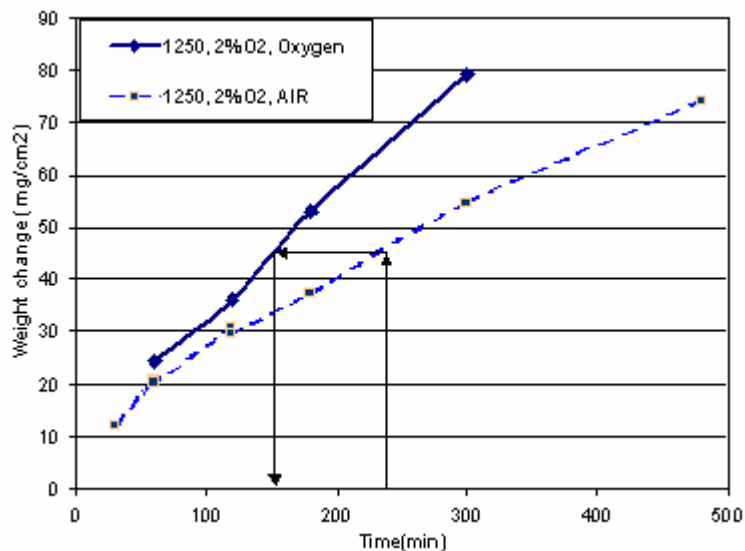


Figure 3. Weight change of carbon steel using oxyfuel and airfuel. Arrows show a reasonable time gain using oxyfuel for Steel 2.

3.3 SCALE GROWTH IN INDUSTRY

When comparing oxyfuel and airfuel cases in similar furnaces the following was found:

- same surface quality
- higher thermal efficiency
- higher productivity
- lower NOx
- less scale was formed
- less flue gases
- same dimension change when using oxyfuel

It was also found that the flameless oxyfuel has around 10-30% less scaled formed compared with conventional oxyfuel combustion. The scale had a slightly higher adhesion force than airfuel, but the scale comes off in one piece. The scale adhesion can be deduced to close to stoichiometric combustion. The time that was important in the laboratory has an important role in the industrial observation. It takes about 2 times longer to reach the goal temperatures in airfuel, and the result is a greater scale growth and a lower productivity.

3.4 Chemical analysis

The analysis of the SEM-EDS measurements show the expected results that chrome, silicon, and manganese oxidize and are located in the oxide layers close to the steel. Elements such as nickel and copper were not found in the scale. Oxygen must have diffused into the steel due to the fact that oxides besides Fe-oxides were found in the samples. Table 4 lists the results from wet chemical analysis of oxides formed in oxyfuel atmosphere. Elements such as chrome, silicon, manganese and alumina are present as oxides. Fe₃O₄ include also Fe₂O₃.

Table 4, Wet chemical analysis show that the iron oxide is dominant, but also Cr, Si, Mn and Al oxide is enriched in the scale.

Chemistry analysis	
FeO	64.4
Fe ₃ O ₄	35.1
Cr ₂ O ₃	1.6
SiO ₂	0.6
MnO	0.3
Al ₂ O ₃	0.2
Fe	0.1
NiO	0.1

Steel 2 shows a slightly lower decarburizing depth for oxy-fuel, table 5. Decarburization depths are defined by where the last ferrite is found in the etched steel matter.

Table 5, The numbers came from steel 2 after 120 minutes holding time for both combustion techniques. The decarburization in Steel 2 shows a slightly lower decarburizing depth for oxyfuel

Combustion oxidizer	Temperature °C	Decarburization depth mm
Airfuel	1150	0.25
	1250	0.40
	1300	0.45
Oxyfuel	1150	0.28
	1250	0.32
	1300	0.38

3.5 Scale adhesion

The excess oxygen concentration has an effect on scale growth and also on adhesion force. The excess oxygen concentration or combustion oxidizers do not affect the “raw steel skin”. Differences in topography of the scale are clear. At excess oxygen concentration of 10% or higher the surface layer was smooth as a millpond. With a low stoichiometry the top surface was rough. The magnetite oxide grain is shown in figure 4.

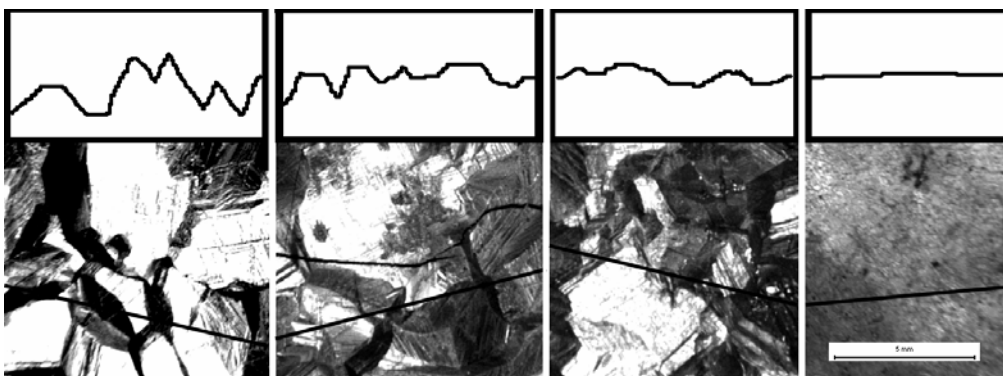


Figure 4, Scale topography at 1250 at 5% CO, stoichiometry, 2 respective 5 excess oxygen combustion.

As mentioned before the gap formed in between scale and steel surface in oxyfuel-processed samples, makes it very easy to be completely removed. Steel 1 has a more complex entanglement to the scale and therefore significant higher scale removal force. About 50% of all Steel 2 specimens had to low adhesion force and was therefore spontaneously cleaned during cool down procedure.

Table 6 lists the removal force variation with time and excess oxygen at oxyfuel combustion. At shorter times the force was low and vice versa for longer times. Test shows that removal force decrease with increasing excess oxygen. The adhesion force is independent of the amount of reducing atmosphere. A reducing atmosphere result in scale having greater entanglement to the substrate compared to an atmosphere with high excess oxygen concentration. Plots from removal force measurement, seen in figure 5 shows a notch at about 6mm from start position at which the scale detach completely from the substrate. Airfuel scale did not show the same pronounced notch and therefore no comparison between airfuel and oxyfuel has been made. (Our conclusion is that scale removal force was not measurable by this method in the airfuel case.)

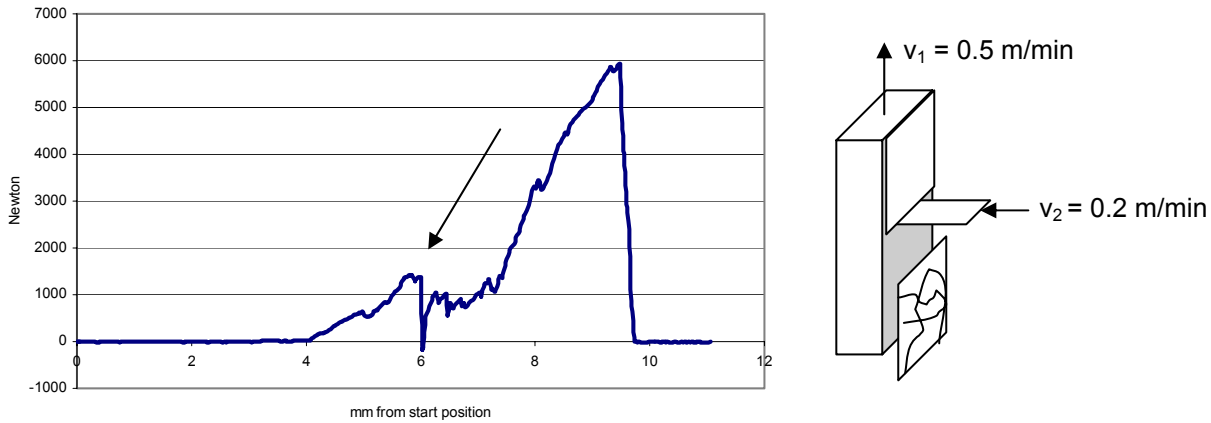


Figure 5a and 5b. Scale removal force for Steel 1 in oxyfuel combustion. Left figure the notch indicates when the scale falls of. The secondary peek is when the blade hit the steel surface. Right figure show the method that was used when scale removal, v_1 was the speed that was maintain by the tensile stress machine. Speed v_2 was the speed that the blade penetrates the scale at 90° angle.

Table 6, Scale removal force at different holding times and excess oxygen for Steel 1 when firing oxyfuel. Higher excess oxygen at shorter times gives an easier scale to remove.

Removing Force N	Time min	Removing Force N	Excess Oxygen
779	30	1392	(5% CO)
817	60	1318	0
1254	120	1249	2
1353	180	815	5

4. DISCUSSION

The result shows a clear relationship between the scale formation and both atmosphere and time. In an atmosphere with greater excess oxygen the free oxygen potential is higher at the oxide reaction and thus the oxide grow more rapidly compared to an oxygen poor atmosphere. In flameless oxidation the free oxygen is normally the same or less compared to airfuel due to the possibility to use a combustion ratio closer to stoichiometry, still getting a good fuel burn-out and a not to strong adhesion force to the steel.

Airfuel- compared to oxyfuel combustion in industry takes about 30% longer time to reheat steel, which is a result of the longer heat-up procedure. In laboratory this time was the same for both techniques and therefore variation in yield was found between airfuel and oxyfuel. In the industrial the scale growth was the same or lower.

They are two obvious differences between airfuel and oxyfuel scale cross-section in the present study. First, the pore size seams to be smaller but very well distributed in oxyfuel and has some large porous in the magnetite oxide. The pore distribution is most likely the same in airfuel, but the pores are larger in the wüstite. The total pore distribution is the same at both combustion techniques. Second, the gaps that are shown in figure 1a are mostly located between wüstite and magnetite. The gaps reflect a lower adhesion force in the scale layers and are a result of the steel shrinking more than the scale does (Wüstite shrink $14 \times 10^{-6} \text{ m}^\circ\text{C}$ and for iron $19 \times 10^{-6} \text{ m}^\circ\text{C}$ [2]). A gap is also present in oxyfuel but is located between steel and wüstite as figure 1b show.

To remove the scale in the present study, it was necessary to penetrate the top surface layers. For steel oxide the hardness value (Vickers at room temperature) is about 1000 for Fe_2O_3 , 320-500 for Fe_3O_4 and

270-350 for FeO [3]. That means that penetration through the top surface layer needs a higher removal force than for the other oxides.

5. CONCLUSION

The airfuel had less clean surface than for oxyfuel after removing the scale. Scale that was formed at high H₂O concentration gives a low adhered scale and a clean surface, which was supported by Griffiths [4]. The SEM-EDS and wet chemical analysis show the expected result that some of the alloying elements such as chrome, aluminum and silicon were found in the scale.

Industrial experiences show same or less amount of scale when converting furnaces to oxyfuel. The shorter heating times seem to compensate for the higher rate of scale formation. This study shows that when small samples are heated in the same way, oxyfuel creates a slightly thicker scale that is easier to remove. By comparing oxides at time X for airfuel and at time 0.7X for Oxyfuel it can be confirmed that the scale thickness is about the same. Time aspect is an important factor that needs to be shortened in order to increase productivity, decrease energy consumption and improving product quality in terms of decarburization and material losses in the production. The decarburization is the same or lower in oxyfuel.

The relationship between the laboratory results and the industrial cases needs to be investigated further. To get a complete understanding and more knowledge of the oxidation in industrial furnaces the heating procedure will be the next step to investigate deeper. More material types should also be included in the next study.

6. REFERENCE

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