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INFLUENCE OF SECONDARY REFINING TREATMENTS ON THE QUALITY OF HIGH-GRADE STEEL USED IN OIL AND GAS INDUSTRY

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ABSTRACT

Steel is the most important alloy used in oil and gas industry from production and processing to the distribution of refined products. In this research is analyzed the production technology of steel intended for long pipeline used in conveying gas and oil in the natural gas and oil industries. Data from 14 melts were analyzed. The basic oxygen furnace (BOF) is used for steelmaking. The secondary refining processes were conducted at the ladle furnace station by forming an active ladle slag and using the mixing of bath with argon. Steel degassing is conducted in RH vacuum degassing equipment. The variation of chemical composition, especially the content of carbon, oxygen, and hydrogen, was analyzed according to parameters of industrial technology.

KEYWORDS: steel, pipeline, oil and gas industry, secondary refining treatments

1. Introduction

High grade steels with special properties must be utilized in oil and gas industry [1, 2]. These steels are produced in the basic oxygen furnace (BOF) and then mill rolled. The thick sheets of steel are obtained in order to make pipes that work in adverse temperature conditions to transport oil and natural gas in oil and gas industry.

The cleanness assessment of high quality steels is provided through refining treatments developed in secondary steelmaking steps. These treatments are performed in ladle furnaces (LF) and in RH vacuum degassing units, pieces of equipment typically used in the mass production of high-purity steel in integrated steel mills plants. The most important functions of secondary refining are final desulphurization, degassing gas components such as oxygen, nitrogen, hydrogen, etc., removal of inclusions and final decarburization (for ultra-low carbon steel) [3-6].

In this research the refined treatments applied to molten steel before continuous casting were conducted in a ladle furnace. Moreover, the vacuum treatment is performed in a RH degassing station.

2. Experimental research

The chemical composition and mechanical properties of the steel suitable for long pipeline used in conveying gas and oil in the natural gas and oil industries in accordance with API SPEC 5L specification of standard [7] are given in Tables 1 and 2.

Table 1. *Chemical composition of X65 steel grade (wt.%)*

C	Si	Mn	P	S	Al	Ti	V	Mo	Nb	Ca	H_2 *	N_2 *
0.06 – 0.09	0.25 – 0.35	1.40 – 1.55	0.018	0.006	0.02 – 0.05	0.01 – 0.016	0.04 – 0.055	0.07 – 0.010	0.04 – 0.06	0.002	max. 3.0	max. 0.0070
* ppm												

The specific temperatures of X65 steel grade are the following: liquidus temperature 1521 °C; optimum tapping temperature 1546 °C; maximum casting temperature 1580 °C. The steel was made in a basic oxygen furnace (BOF). The primary raw materials were pre-desulfured liquid hot metal (S =

0.006%) and steel scrap in balance. A ladle furnace (LF) with the capacity of 180 t of steel was used for refining molten steel. Data from 14 melts were analyzed. In the LF the steel was reheated.

Table 2. *Mechanical properties of X65 steel grade*

R_c, [MPa]	$R_{p0.5}$, [MPa]	R_m, [MPa]	A, [%]	Charpy V - notch values at test temperature -51 °C, [J]
≥ 240	≥ 448	≥ 531	19 – 23	18

The temperature was properly adjusted depending on requirements. An active ladle slag with basic characteristics and physical properties adapted to the temperature close to the liquidus temperature of steel was used for liquid steel coverage during treatment. The literature recommends for carbon aluminum-killed steels the slag of the system CaO – Al_2O_3 – SiO_2: 45 – 60% CaO, <10% MgO, 25-40 Al_2O_3, <20% SiO_2, <0.5% (FeO+MnO) [8-10].

During treatment, argon is continuously stirred in liquid steel. So the metallurgical reactions such as deoxidation, desulphurization and removal of oxide-inclusions can be managed. All these steps have allowed to precisely adjust the final chemical composition and to obtain the quality required for the steel.

To remove hydrogen and nitrogen from molted steel, RH vacuum unit was used. Before degassing, the reactor was cleaned to remove crusts and then preheated to over 1000 °C. The ladle freeboard was of about 600 mm. To achieve a homogeneous bath temperature and composition, the steel in the ladle is stirred by means of argon gas bubbling. The volume of argon stirring gas varied in the range of 3.5 – 6.7 Nm^3/t. The recirculation of liquid steel started when a vacuum of 20-30 torr was reached. After 6-8 minutes when the 1 torr depression was reached, the addition of microalloying and deoxidizing materials has been initiated. The materials addition procedure lasted for 8-10 minutes. In the end, the molten steel temperature and the chemical composition were homogenized for a period of 5 minutes.

3. Results and discussion

The chemical composition of the steel after tapping from BOF and in LF is given in Table 3, respectively in Table 4. Adding alloy additives in the form of ferroalloys into steel is one of the most important stages of secondary metallurgy. During LF treatment the chemical composition was corrected by Ti, V, Nb Mo.

Table 3. *Chemical composition of steel after tapping from BOF (wt.%)*

No. melt	C	Mn	P	S	Si	Al	Mo
1	0,04	1.18	0.011	0.012	0.12	0.005	-
2	0.04	1.24	0.011	0.010	0.30	0.008	0.077
3	0.03	0.90	0.010	0.010	0.25	0.006	0.070
4	0.03	1.14	0.010	0.012	0.23	0.006	0.084
5	0.03	0.58	0.008	0.010	0.12	0.003	0.072
6	0.03	1.08	0.009	0.010	0.19	0.008	0.085
7	0.04	0.75	0.008	0.009	0.20	0.013	0.080
8	0.04	0.84	0.008	0.012	0.18	0.005	0.080
9	0.03	1.13	0.009	0.010	0.20	0.010	0.084
10	0.04	1.29	0.008	0.010	0.21	0.006	0.083
11	0.04	1.24	0.009	0.012	0.29	0.008	0.083
12	0.06	1.35	0.009	0.011	0.21	0.006	0.083
13	0.03	1.07	0.007	0.010	0.15	0.005	0.073
14	0.03	1.10	0.008	.008	0.17	0.006	0.074

Table 4. *Chemical composition of steel in the LF station, (wt.%)*

No. melt	Chemical composition (wt.%)										
	C	Si	Mn	P	S	Al	Ti	V	Mo	Nb	Ca
1	0.08	0.27	1.49	0.017	0.005	0.024	0.005	-	0.068	0.030	-
2	0.07	0.33	1.45	0.019	0.009	0.026	0.017	0.027	0.083	0.035	-
3	0.08	0.26	1.52	0.013	0.010	0.044	0.011	0.033	0.073	0.040	0.0008
4	0.07	0.33	1.45	0.017	0.009	0.054	0.019	0.032	0.085	0.040	-
5	0.05	0.26	1.43	0.010	0.010	0.054	0.015	0.027	0.074	0.035	-
6	0.05	0.33	1.50	0.017	0.008	0.044	0.010	0.032	0.090	0.039	0.0030
7	0.06	0.289	1.38	0.015	0.007	0.035	0.019	0.025	0.083	0.030	0.00018
8	0.07	0.25	1.50	0.017	0.012	0.020	-	0.025	0.080	0.033	0.0010
9	0.07	0.26	1.49	0.014	0.009	0.037	0.012	0.032	0.085	0.040	0.0005
10	0.07	0.25	1.50	0.011	0.008	0.036	0.012	0.032	0.083	0.036	0.0005
11	0.07	0.28	1.59	0.011	0.010	0.046	0.014	0.032	0.083	0.037	0.0005
12	0.07	0.26	1.50	0.011	0.009	0.050	0.013	0.032	0.083	0.042	0.0001
13	0.07	0.37	1.57	0.016	0.007	0.033	-	0.029	0.077	0.037	0.0004
14	0.08	0.33	1.44	0.013	0.007	0.021	0.019	0.024	0.075	0.034	0.0002

Table 5. *Aluminium and oxygen contents of steel after RH refining*

No.	Al [%]	Oxygen [ppm]
1	0.034	2.5
2	0.049	2.9
3	0.048	2.1
4	0.042	2.2
5	0.040	2.4
6	0.043	2.9
7	0.037	2.4
8	0.040	3.0
9	0.035	2.5
10	0.041	3.1
11	0.045	2.5
12	0.043	2.4
13	0.038	2.6
14	0.033	2.5

Table 6. *Hydrogen content during refining treatment, in ppm*

No.	Time of the test				
	In LF		In RH		
	Initial H content at tapping from BOF	Final H content at output from LF	Initial H content after feeding into RH station	Final H content at output from RH station	H content at continuous casting machine
1	6.2	6.5	6.5	1.4	1.4
2	6.7	7.0	7.0	1.7	1.7
3	7.1	7.3	7.3	2.3	2.3
4	7.0	7.4	7.4	2.4	2.4
5	6.6	6.9	6.9	1.9	1.9
6	10.1	10.6	10.6	3.5	3.5
7	6.8	7.1	7.1	2.2	2.2
8	6.7	7.0	7.0	2.3	2.3
9	6.4	6.8	6.8	1.7	1.7
10	6.9	7.0	7.0	2.1	2.1
11	6.3	6.6	6.6	2.0	2.0
12	6.2	6.5	6.5	1.7	1.7
13	6.7	6.9	6.9	2.1	2.1
14	6.5	6.8	6.8	1.8	1.8

The deoxidizing agents SiCa and Al have been added to the melt and blowed argon was used to stir liquid steel.

The ferroalloy purity has influence on the quality of steel. This is obvious as the ferroalloy additives are added at the final stage of steel melting. High total oxygen content in ferroalloys inevitably affects the purity of steel [11]. For oxygen removal a supplementary treatment is efficient. So, after refining, the molten steel was transported to RH vacuum degassing unit for secondary refining. Particles of Al were added in the RH station for the final deoxidation. So the oxygen content was reduced (Table 5).

The degassing under vacuum leads to a decrease in hydrogen content by 50 - 70% (Table 6).

The chemical composition of the steels after RH treatment is shown in Table 7.

Table 7. *Chemical composition of steel after RH refining process, (wt.%)*

No.	C	Si	Mn	P	S	Al	Ti	V
1	0.09	0.29	1.53	0.018	0.005	0.034	0.014	0.001
2	0.07	0.30	1.45	0.018	0.008	0.038	0.010	0.030
3	0.08	0.26	1.52	0.013	0.010	0.044	0.011	0.033
4	0.07	0.30	1.43	0.016	0.009	0.040	0.012	0.032
5	0.07	0.26	1.48	0.011	0.008	0.040	0.014	0.028
6	0.06	0.32	1.47	0.015	0.007	0.030	0.014	0.031
7	0.06	0.32	1.40	0.012	0.009	0.038	0.011	0.025
8	0.07	0.25	1.45	0.015	0.009	0.035	0.010	0.027
9	0.07	0.26	1.49	0.014	0.009	0.037	0.012	0.032
10	0.07	0.25	1.50	0.011	0.008	0.036	0.012	0.032
11	0.07	0.28	1.59	0.011	0.010	0.046	0.014	0.032
12	0.07	0.26	1.50	0.011	0.009	0.050	0.013	0.032
13	0.08	0.33	1.50	0.014	0.009	0.032	0.012	0.030
14	0.07	0.31	1.40	0.010	0.008	0.040	0.010	0.025

Table 7. *Chemical composition of steel after RH refining process, (wt.%) (continuation)*

No.	Cu	Ni	Cr	Mo	Nb	N	Ca
1	0.010	0.010	0.020	0.070	0.035	0.0054	0.0015
2	0.010	0.025	0.030	0.085	0.036	0.0075	0.001
3	0.015	0.010	0.020	0.070	0.040	0.0100	0.0001
4	0.005	0.005	0.030	0.085	0.039	0.0066	0.0001
5	0.010	0.010	0.015	0.076	0.037	0.0063	0.0007
6	0.010	0.010	0.010	0.085	0.034	0.0068	0.0001
7	0.010	0.010	0.010	0.080	0.032	0.0076	0.0020
8	0.005	0.005	0.015	0.080	0.33	0.0067	0.0001
9	0.005	0.005	0.010	0.085	0.040	0.0085	0.0005
10	0.005	0.005	0.015	0.085	0.036	0.0080	0.0005
11	0.005	0.005	0.015	0.083	0.037	0.0069	0.0005
12	0.010	0.010	0.010	0.083	0.042	0.0095	0.0001
13	0.010	0.010	0.015	0.074	0.035	0.0080	0.0001
14	0.010	0.010	0.010	0.075	0.033	0.0062	0.0001

The steel is discharged from the overheated converter. Ferroalloys and fluxes added to the steel in the LF and RH station affect its temperature.

Also the steel tapping and transport of ladle for further treatment lead to heat losses (Table 8 and Figure 1).

Table 8. *Temperature of the molten steel at different locations (°C)*

No.	after tapping from BOF	in the LF station	after RH refining
1	1617	1586	1570
2	1595	1565	1600
3	1638	1601	1573
4	1632	1603	1580
5	1619	1597	1572
6	1608	1620	1594
7	1579	1590	1569
8	1591	1620	1592
9	1619	1599	1571
10	1618	1633	1597
11	1575	1616	1584
12	1570	1601	1576
13	1610	1600	1578
14	1604	1595	1569

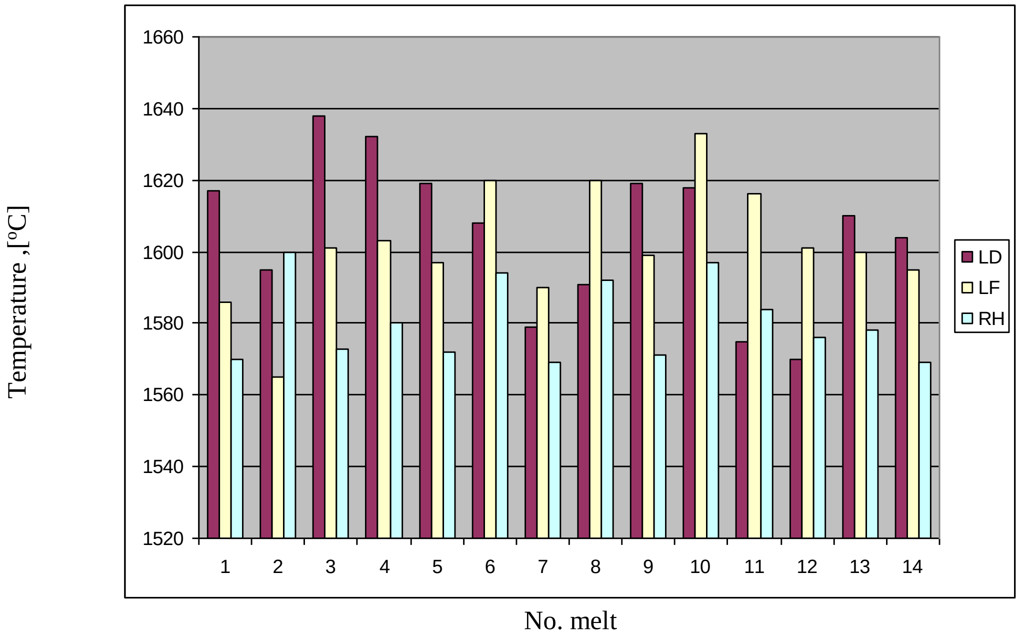

Fig. 1. *Temperature variation of molten steel during treatments*

At tapping from BOF, the carbon content of steel was below the values from standard specification (0.06 – 0.09%). The addition of a large amount of alloys in LF leads to an increase of carbon (Figure 2).

This allows for the additions of ferroalloys in the next stages of treatment without exceeding the prescribed final concentration.

Additional decarburization was carried out in the vacuum vessel.

The carbon is removed as carbon monoxide according to the reaction $[C] + [O] \rightarrow \{CO\}$.

So, oxygen and carbon contents are simultaneously reduced.

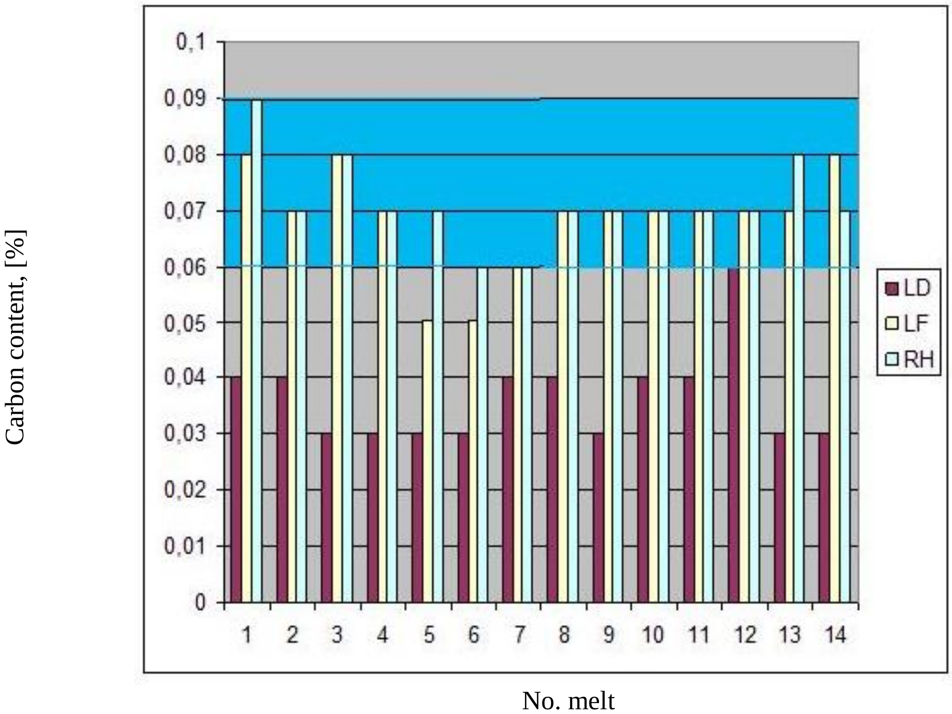

Fig. 2. *Carbon concentrations of steel X 65*

The hydrogen removal from liquid steel during vacuum degassing was possible (Figure 3).

In the end, the steel has got hydrogen content bellow the limit prescribed of 3.0 ppm. Only an exception was reported.

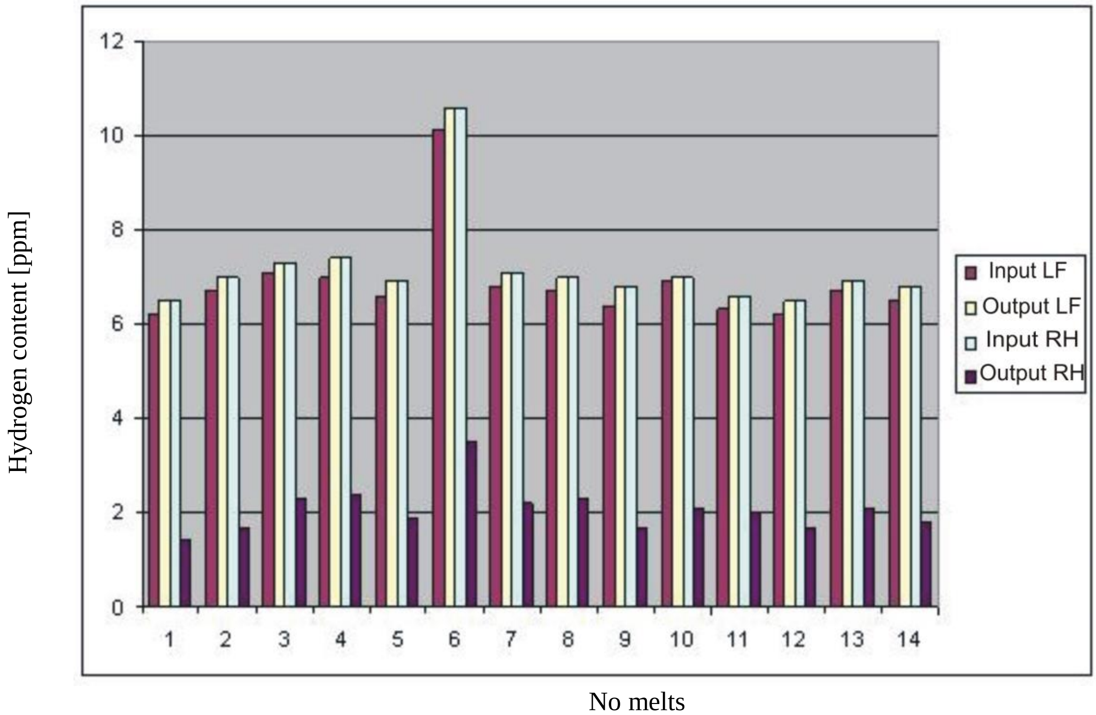

Fig. 3. *Hydrogen content in molten steel in accordance with refining treatments*

4. Conclusions

The requirements with respect to carbon, oxygen, hydrogen and sulfur (phosphorus) content of the final product make necessary the application of secondary refining treatments. In this case LF refining process and vacuum degassing in RH station were chosen.

The steelmaking technology (BOF steelmaking LF and RH treatments) is able to ensure appropriate temperature conditions for continuous castings. The final temperature of molten steel was in range of 1570 – 1600 ºC. Decarburization rate was satisfactory for the low carbon steel produced in a basic oxygen furnace and refined in a ladle furnace and an RH installation. The carbon content of steel obtained varied within the range of 0.06 – 0.09% required by standards.

The final concentration of oxygen shows that the improvement of metallurgical purity was guaranteed by vacuum treatment at the recirculating degassing system. This has ensured the decreasing of the total oxygen content in steel as in accordance with the application field (between 2.1 and 3.0 ppm). Also, this supplementary treatment proves to be effective for hydrogen removal. The hydrogen removal rates are calculated by relation $\frac{[H_i]-[H_f]}{[H_i]} \cdot 100 \ (\%)$, when $[H_i]$ is the initial hydrogen content of the steel measured after tapping from BOF and $[H_f]$ is the final hydrogen content of the steel measured after vacuum treatment. These values vary between 65.34 to 77.42 %. They indicate the efficiencies of recirculating systems for the removal of hydrogen from steel.

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