Research on the reduction of the hydrogen content in steels treated in vacuum

M Magaon, S Şerban and T Hepuţ
Politehnica University of Timisoara, Engineering and Management Department, 5 Revolution Street, Hunedoara, 331128, Romania
E-mail: miruna_magaon@yahoo.com

Abstract. This paper discusses the results of the research on the influence of the vacuuming technological factors on the hydrogen content in the steel produced in an electric furnace type EBT, treated outside the furnace in Ladle-Furnace (LF) and Vacuum Degassing (VD) facilities, and then continuously casted as semi round products designed for pipes manufacturing. Vacuuming main parameters were followed such as: the total duration of vacuuming, the duration of advanced vacuuming, the pressure in the vacuum facility, the vacuuming temperature drop during the treatment (considered independent parameters) and the amount of hydrogen removed from the metal bath during the vacuuming. The obtained data was processed in the MATLAB calculation program, using three types of equations, the results obtained being presented both in analytical and graphical form. The technological analysis of the correlation equations and the graphical representations allowed to establish the variation limits of the independent parameters in order to advance to reduce the steel hydrogen content.

1. Introduction

After the elaboration, casting and lamination processes, impurities remain in the steel structure such as hydrogen, nitrogen and oxygen, in addition to non-metallic inclusions and gases. It is well known that the presence of these gases has negative influence on the quality of steel, which is why their content should be reduced to values as low as possible (particularly hydrogen and oxygen).

Regarding hydrogen, it represents an impurity for steel products, its negative influence is manifested especially in steel because [1-4]:
- It’s one of the causes of sulphides in ingots and calmed steel castings;
- It contributes to the occurrence of the defect called “flakes” (very fine small cracks disposed as a rosette) in steels alloyed with chromium and nickel, which substantially reduces fatigue strength of steel parts;
- Decreases the elasticity and toughness of the steel;
- Affects the electrical and magnetic properties of steel.

To produce steel with low hydrogen content, a series of measures must be taken on the manufacturing flow such as [3], [5], [6]:
- the cargo used must be of good quality, without moisture, oils, calcined additions, freshly burnt limestone, etc;
- the use of chromium ferroalloys, molybdenum, calcined additions, freshly burnt nickel;
- the bubbling of liquid steel with inert gases (usually argon);
- the treatment of steel under vacuum;
2. Presentation of the experimental and data processing framework

In the research conducted, the possibilities to reduce the hydrogen content from steels designed for pipes manufacturing were investigated.

The researches were carried out at an electrical steelwork, equipped with an electric arc furnace type EBT (Electric Bottom Tapping) capacity 100t, LF (Ladle-Furnace) facility, VD (Vacuum Degassing) facility and a 5 wires continuous casting (ITC) facility. On the flow presented a total of 30 steel batches were followed, OLT45 type steel, circular rolled with a diameter of Ø180mm.

The 30 batches were monitored throughout the technological flow, stage by stage, as follows:

- Elaboration in the furnace: loads of good quality, without scrap with oil, moisture, rust under about 2%, freshly burnt limestone, iron ore (calcined when appropriate), adequately heated casting ladle;
- LF and VD treating facility: respecting the limits of variation of technological parameters (heating, bubbling), additions without moisture (for slag formation and alloying), mixing chemical and thermal by bubbling with argon followed by treatment in the vacuum facility without VD heat input, in the casting process the ladle and the distributor were heated adequately;
- The continuous casting compliance parameters: the casting speed correlated with the casting temperature, flow rate and pressure of cooling water in each cooling zone, the lubricating powders without moisture, the proper functioning of MTC.

The following parameters were:

- the hydrogen content before (initially) and after (final) vacuuming, \([H_i]\) [ppm], respectively \([H_f]\) [ppm], which are considered dependent parameters;
- the total duration of vacuuming, \(D_{v.t.}\) [min], independent parameter;
- the duration of advanced vacuuming, \(D_{v.a.}\) [min], independent parameter;
- the pressure in the vacuum facility, \(P_{V.D.}\) [mBar], independent parameter;
- the steel temperature at the entry and exit of the vacuum facility, \(T_i\) and \(T_f\), based on which is calculated the reduction of temperature, \(\Delta[T] = [T_i] - [T_f]\) [°C], independent parameter.

By processing the obtained data in the MATLAB calculation program, multiple correlation equations have resulted between the independent and dependent parameters, the results being presented both in analytical and graphical form. The hydrogen removal process is analyzed based on the obtained relations.

In order to obtain the correlation in MATLAB program I used three different equations type z - dependent parameter, \(x, y\) - independent parameters:

**EQUATION 1:**

\[
z = a(1) + a(2) \cdot x + a(3) \cdot x \cdot x^2 + a(4) \cdot x \cdot x^3 + a(5) \cdot y + a(6) \cdot y \cdot y^2 + a(7) \cdot y \cdot y^3 + a(8) \cdot y \cdot y^4 + a(9) \cdot y \cdot y^5
\]

**EQUATION 2:**

\[
z = a(1) + a(2) \cdot \log(x) + a(3) \cdot \log(x) \cdot x^2 + a(4) \cdot \log(x) \cdot x^3 + a(5) \cdot y + a(6) / (y \cdot y^2) + a(7) / (y \cdot y^3) + a(8) / (y \cdot y^4) + a(9) / (y \cdot y^5)
\]

**EQUATION 3:**

\[
z = a(1) \cdot x^2 + a(2) \cdot y \cdot x^2 + a(3) \cdot x \cdot x + a(4) \cdot x \cdot y + a(5) \cdot y + a(6)
\]

We have to mention that all correlations are significant both in terms of values for correlation coefficients, respectively in mathematical terms as well as for technological direction.

The results of data processing are presented in the next figures.
Equation 1
\[ z = a(1) + a(2) \cdot x + a(3) \cdot x^2 + a(4) \cdot x^3 + a(5) \cdot y + a(6) \cdot y^2 + a(7) \cdot y^3 + a(8) \cdot y^4 + a(9) \cdot y^5 \]
\[ D = 50143.37411; \quad H = -2291.32815; \quad R^2 = 0.69283; \quad r^2 = 0.68779 \]
\[ a_1 = -1145.66407; \quad a_2 = -10.94201; \quad a_3 = 0.361301; \quad a_4 = -0.003909; \quad a_5 = 426.291125; \quad a_6 = -57.08538; \quad a_7 = 3.77343; \quad a_8 = -0.12323; \quad a_9 = 0.00159 \]

Equation 2
\[ D = -53361734.97141; \quad H = 9129.39647; \quad R^2 = 0.45837; \quad r^2 = 0.67703 \]
\[ a_1 = 4564.69823; \quad a_2 = -2883.35866; \quad a_3 = 845.627604; \quad a_4 = -82.52299; \quad a_5 = -99622.18974; \quad a_6 = 3037813.21626; \quad a_7 = -45789786.20388; \quad a_8 = 341126005.604936; \quad a_9 = -1004504954.21221 \]
**Figure 3.** Correlation $[H] = f(D_{v}, D_{v.a.})$

Equation 3

$$R^2 = 0.59876$$

$$a_1 = 0.02052; \quad a_2 = 0.01238;$$

$$a_3 = -0.000285; \quad a_4 = -1.12525;$$

$$a_5 = -0.46862; \quad a_6 = 20.96577$$

**Figure 4.** Correlation $[H] = f(D_{v}, P_{v.})$

Equation 1

$$D = -21402.968209; \quad H = 1183.96614;$$

$$R^2 = 0.59917; \quad r^2 = 0.77406;$$

$$a_1 = 591.98307; \quad a_2 = -9.03863;$$

$$a_3 = 0.303679; \quad a_4 = -0.003351;$$

$$a_5 = -1006.38884; \quad a_6 = 0;$$

$$a_7 = 1270.083880; \quad a_8 = -1001.29237; \quad a_9 = 235.80519;$$
Figure 5. Correlation $[H] = f(D_v, P_v)$
Equation 2
$D = -34820868.25972$; $H = 7849.62416$; $R^2 = 0.59881$; $r^2 = 0.77382$;
$a_1 = 3924.81208$; $a_2 = -2191.59653$; $a_3 = 643.77787$; $a_4 = -62.92921$;
$a_5 = -6095.10921$; $a_6 = 7714.16717$; $a_7 = 0$; $a_8 = -6119.69409$; $a_9 = 3066.89523$;

Figure 6. Correlation $[H] = f(D_v, P_v)$
Equation 3
$D = 0.054954$; $H = 0.030394$; $R^2 = 0.82365$; $r^2 = 0.72162$;
$a_1 = 0.0151972$; $a_2 = 1.04289$; $a_3 = -0.09187$; $a_4 = -0.714028$;
$a_5 = 2.28989$; $a_6 = 7.88193$; $a_7 = 0$; $a_8 = -3066.89523$; $a_9 = 6119.69409$.
Figure 7. Correlation $[H] = f(D_v., D.T.)$

Equation 1

\[
D = 7791.336304; \quad H = -2473.444308; \\
R^2 = 0.554809; \quad r^2 = 0.74485; \\
a_1 = -1236.72215; \quad a_2 = -1.57499; \\
a_3 = 0.043454; \quad a_4 = -0.000357; \\
a_5 = 76.78162; \quad a_6 = -1.852201; \\
a_7 = 0.022024; \quad a_8 = -0.000129; \quad a_9 = 0;
\]

Figure 8. Correlation $[H] = f(D_v., D.T.)$

Equation 2

\[
D = -2931199.4192; \quad H = 1729.6901 \\
R^2 = 0.422522; \quad r^2 = 0.650017; \\
a_1 = 864.84508; \quad a_2 = -831.15991; \\
a_3 = 236.43427; \quad a_4 = -22.33452; \\
a_5 = 34960.30999; \quad a_6 = -4190887.606; \\
a_7 = 219058469.7883; \quad a_8 = -4223734695.9615; \quad a_9 = 0;
\]
Figure 9. Correlation \( [H] = f(Dv., D.T.) \)

Equation 3

\[ D = -2.16 \times 10^{-5}; \quad H = 0.03710; \]
\[ R_2 = 0.8235; \quad r_2 = 0.560541; \]
\[ a_1 = 0.01855; \quad a_2 = -0.0002895; \]
\[ a_3 = -0.000382; \quad a_4 = -1.01734; \]
\[ a_5 = 0.07069; \quad a_6 = 12.20237; \]

Figure 10. Correlation \( [H] = f(Dv.a., P_v.) \)

Equation 1

\[ D = -25804.29908; \quad H = 1100.9862; \]
\[ R_2 = 0.52185; \quad r_2 = 0.72239; \]
\[ a_1 = 550.4931; \quad a_2 = -11.71846; \]
\[ a_3 = 0.75717; \quad a_4 = -0.01601; \]
\[ a_5 = -958.55512; \quad a_6 = 0; \]
\[ a_7 = 1145.16551; \quad a_8 = -875.04711; \]
\[ a_9 = 199.2611; \]
Figure 11. Correlation $[H] = f(D_{v,a..}, P_v)$

Equation 2

$D = -4286170.14509, \quad H = 1105.60627,$

$R^2 = 0.78475, \quad r^2 = 0.72186,$

$a_1 = 552.80313, \quad a_2 = -1753.21723, \quad a_3 = 639.87045,$

$a_4 = -77.6772, \quad a_5 = 4189.74343, \quad a_6 = -5008.31045,$

$a_7 = 0, \quad a_8 = 3534.2579, \quad a_9 = -1671.75313.$

Figure 12. Correlation $[H] = f(D_{v,a..}, P_v)$

Equation 3

$D = -0.219832, \quad H = -0.008069,$

$R^2 = 0.74832, \quad r^2 = 0.65253,$

$a_1 = -0.004034, \quad a_2 = -4.26805, \quad a_3 = -0.53732,$

$a_4 = 0.85042, \quad a_5 = 22.19735, \quad a_6 = -21.62451.$
Figure 13. Correlation $[H] = f(D, v, a, D, T)$
Equation 1
$D = 17730.5808013$; $H = -2354.230908$;
$R^2 = 0.53083$; $r^2 = 0.72858$;
$a_1 = -1177.11545$; $a_2 = -3.76569$; $a_3 = 0.239211$;
$a_4 = -0.005036$; $a_5 = 73.00332$;
$a_6 = -1.754725$; $a_7 = 0.020788$;
$a_8 = -0.0001213$; $a_9 = 0$;

Figure 14. Correlation $[H] = f(D, v, a, D, T)$
Equation 2
$D = -96419.89852$; $H = 652.58094$;
$R^2 = 0.43949$; $r^2 = 0.66294$;
$a_1 = 326.29047$; $a_2 = -73.42107$;
$a_3 = 24.36214$; $a_4 = -2.69198$;
$a_5 = -117291.97043$; $a_6 = 21298262.972151$;
$a_7 = -1882891276.0254$; $a_8 = 81181908340.2696$;
$a_9 = -1368431890047.13$
Figure 15. Correlation \([H] = f(Dv.a.., D.T.)\)
Equation 3
\[ D = -2.35114133680876 \times 10^{-5} \]
\[ H = 0.006804; \]
\[ R^2 = 0.76341; \]
\[ r^2 = 0.58542; \]
\[ a_1 = 0.003402; \quad a_2 = 0.000174; \]
\[ a_3 = -0.00508; \quad a_4 = 0.266044; \]
\[ a_5 = 0.06884; \quad a_6 = -3.94954; \]

Figure 16. Correlation \([H] = f(Pv..., D.T.)\)
Equation 1
\[ D = -789108.88797; \]
\[ H = -894.018024; \]
\[ R^2 = 0.823008; \]
\[ r^2 = 0.907197; \]
\[ a_1 = -447.009012; \]
\[ a_2 = 392.34923; \quad a_3 = -295.92939; \]
\[ a_4 = 74.40428; \quad a_5 = 16.630155; \]
\[ a_6 = -0.39454; \quad a_7 = 0.00458; \]
\[ a_8 = -0.00002; \quad a_9 = 0. \]
Figure 17. Correlation \( [H] = f(P_v, D, T) \)

Equation 2

\[
D = -59073.73998; \quad H = -610.50587; \\
R^2 = 0.82664; \quad r^2 = 0.90919; \\
a1 = -305.2523; \quad a2 = 34.78972; \\
a3 = -128.82187; \quad a4 = 159.58653; \\
a5 = 113196.732; \quad a6 = -16493575.611; \\
a7 = 11767; \quad a8 = -41196729582.5623 \\
a9 = 567011467997.132
\]

Figure 18. Correlation \( [H] = f(P_v, D, T) \)

Equation 3

\[
D = 0.00704; \quad H = 7.350204; \\
R^2 = 0.78946; \quad r^2 = 0.75639; \\
a1 = -3.675102; \quad a2 = 0.000679; \\
a3 = 0.054216; \quad a4 = 6.8915; \\
a5 = 0.057437; \quad a6 = -7.11338;
\]
3. The technological analysis of the obtained results

The analysis of the graphical representations shows that the vacuuming parameters have significant influence on the final content of hydrogen and at the end of processing in the vacuuming facility.

It must also be emphasized that there is a very good correspondence between the values obtained for the dependent parameters at the same values of the independent parameters after these three equations (identical sometimes), which is a confirmation of the validity of the results obtained.

Within the comparative technological analysis for the 4 independent parameters the following values were chosen:

- the total duration of vacuuming: $D_{tv} = 30$ min.;
- the duration of advanced vacuuming: $D_{va} = 19$ min.;
- the pressure in the vacuum facility: $P_{VD} = 1,16$ mBar;
- the reduction of the temperature: $\Delta T = 76$ °C.

Consequently the technological analysis is presented for the 6 double correlations groups, each group comprising correlations after the three types of equations.

**Correlation 1:** $\lbrack H \rbrack = f( D_{tv}, D_{va})$ presented in figures 1, 2 and 3 with the spatial coordinate points A(30; 19; 0,9); B(30; 19; 1,0) and respectively C (30; 19; 1,1). The difference of 0,2 ppm [H] is admissible given the max. of 1,1 ppm [H]. Very good results are obtained for $D_{tv} = 25-31$ min and $D_{va} = 15-20$ min, resulting $\lbrack H \rbrack$ under 1,4 ppm.

**Correlation 2:** $\lbrack H \rbrack = f(D_{tv}, P_{VD})$ presented in figures 4, 5 and 6 with the spatial coordinate points A(30;1,16; 1,0); B(30; 1,16; 0,85) and respectively C(30;1,16; 1,0). The difference of 0,15 ppm [H] is admissible given the max. of 1,1 ppm [H]. Very good results are obtained for $D_{tv} = 25-31$ min and $P_{VD}$ under 1,35 mBar , resulting $\lbrack H \rbrack$ under 1,4 ppm.

**Correlation 3:** $\lbrack H \rbrack = f(D_{tv}, \Delta T)$ presented in figures 7, 8 and 9 with the spatial coordinate points A(30; 76; 1,0); B(30; 76; 1,0) and respectively C(30; 76; 1,2). The difference of 0,20 ppm [H] is admissible given the max. of 1,2 ppm [H]. Very good results are obtained for $D_{tv} = 25-31$ min and $\Delta T = 60 – 100$min, resulting $\lbrack H \rbrack$ under 1,4 ppm.

**Correlation 4:** $\lbrack H \rbrack = f(D_{va}, P_{VD})$ presented in figures 10, 11 and 12 with the spatial coordinate points A(19;1,16; 0,95); B(19; 1,16. 1,1) and respectively C(19; 1,16; 1,15). The difference of 0,20 ppm [H] is admissible given the max. of 1,15 ppm [H]. Very good results are obtained for $D_{va} = 15-20$ min and $P_{VD}$ under 1,35 mBar , resulting $\lbrack H \rbrack$ under 1,4 ppm.

**Correlation 5:** $\lbrack H \rbrack = f(D_{va}, \Delta T)$ presented in figures 13, 14 and 15 with the spatial coordinate points A(19;76; 1,0); B(19; 76. 1,0) and respectively C(19; 76; 1,25). The difference of 0,25 ppm [H] is admissible given the max. of 1,25 ppm [H], respectively equal values in points A and B. Very good results are obtained for $D_{va} = 15-20$ min and $\Delta T = 60 – 100$ °C, resulting $\lbrack H \rbrack$ under 1,4 ppm.

**Correlation 6:** $\lbrack H \rbrack = f(P_{VD}, \Delta T)$ presented in figures 16, 17 and 18 with the spatial coordinate points A(1,16;76; 0,75); B(1,16;76;0,95) and respectively C(1,16; 76; 1,1). The difference of 0,1 ppm [H] is admissible given the max. of 1,1 ppm [H]. Very good results are obtained for $P_{VD}$ under 1,35 mBar and $\Delta T = 60 – 100$ °C, resulting $\lbrack H \rbrack$ under 1,4ppm.

For all presented correlations can be choosed values for the independent parameters, respectively variation interval, so that for the final content of hydrogen (dependent parameter) to be obtained a value close to the desired one, or even the desired one.

4. Conclusions

By processing the data in the MATLAB calculation program, after these three types of equations and the technological analysis of the obtained results, one can conclude the following:

- the steel treatment in the vacuum facility without heat input determines a value for the hydrogen content in the liquid steel at the exit of the VD vacuum facility under 2,0 ppm (an extent of at least 90% of batches);
- the steel treatment in LF facility ensures, on the one hand, a good thermal and chemical homogeneity and, on the other hand, a refinery concerning the contents of gases and nonmetallic inclusions;
- as a result of the treatment in the LF facility a temperature drop can be determined during the treatment under vacuum up to 110 °C (less often over 90°C), which can ensure a value for the total duration of vacuuming up to 35 minutes and for the duration of advanced vacuuming (under 1.5 mBar) of 20 minutes;

- for ensuring the proper hydrogen content in the steel the following independent parameter variation limits are recommended:
  - the total duration of the treatment under vacuum: 25-31 minutes;
  - the duration of advanced vacuuming treatment: 15-20 minute;
  - the pressure in the vacuum facility: under 1.5 mBar;
  - the temperature drop during the treatment: $\Delta T = 60 - 100^\circ C$

References

[1] Nica G, Socalici A, Ardelean E and Hepuț T 2003 Technologies to improve the quality of steel, Mirton Publishing House, Timișoara, Romania

[2] Ștefănoiu R 2004 Research on the refining process of steels, inert gases, University Politehnica Bucharest, Romania, Doctoral Thesis

[3] Drăgoi F 2012 Research on reducing the gas content of the steel treated on the technological and EBT- TC, University Politehnica Timisoara, Romania, Doctoral Thesis

[4] Puțan A 2013 Research on steel refining elaborated on the flow: electric arc furnace-ladle furnace-continuous casting, University Politehnica Timisoara, Romania, Doctoral Thesis

[5] Ștefănoiu R and Geantă V 2005 The injection systems of inert gases used in the secondary metallurgy, Metalurgia 7 37-46

[6] Geantă V 2003 Processes and technologies for refining steel, PRINTECH Publishing House, Bucharest, Romania