Investigation on Different Melting Parameters Effect on Vacuum Oxygen Decarburization Process in Production of Low Carbon Stainless Steels

Hadi Mahmoodi[1]*

Phd student of metallurgy at Babol Noshirvani University of Technology
Email: hadimahmodi85@yahoo.com

Mehdi Qouchani[2]

Bachelor of Science in Materials Engineering.
Islamic Azad University of Sirjan ,Sirjan - Iran
Mehdi670430@gmail.com

Abstract - The central issue in stainless steelmaking is the difficulty of oxidizing carbon from molten steel without also oxidizing large proportions of expensive chromium. This can, however, be achieved by reducing the partial pressure of the gaseous product of carbon oxidation, carbon monoxide. Modern stainless steelmaking is dominated by duplex processes, which prepare a high carbon melt in an electrical arc furnace and then decarburize the melt in a converter, such as a 'vacuum oxygen decarburization' converter in which oxygen is blown onto the melt in an evacuated chamber. This study was done in EICO to investigate effect of initial condition on results of vacuum oxygen decarburization (VOD) process to produce low carbon steel. In this study different parameters such as initial analysis of melt, weight of melt, temperature of melt before delivery to vacuum vessel and oxygen gas blowing rate were employed. The calculated final metal composition and temperature are in reasonable agreement with the predictions.

KEY WORDS: stainless steel, vacuum oxygen decarburization, vacuum carbon deoxidation, secondary decarburization.

1. Introduction

The vacuum oxygen decarburization (VOD) process can be used to produce stainless steel. In stainless steel making, both chromium and carbon oxidizes when decarburization of melt is done[1-12]. The Ellingham-Richardsson diagram for oxidation of elements in pure state, indicates that oxidation of carbon in preference to chromium oxidation, can occur at temperatures greater than 1493 K [2]. Under all practical conditions, oxidation of carbon can takes place at temperatures above 2100 K in presence of chromium. VOD is considered to be an important vacuum process for production of stainless steels[1-12]. It is particularly suitable for special stainless steels that require the lowest carbon, nitrogen and hydrogen levels. In this process, the ladle is placed in vacuum chamber and there is a provision for oxygen lancing through vacuum tight gland and alloying additions. Basically, the method involves preferential oxidation of carbon over chromium leading to minimum chromium losses[4]. As carbon is oxidised to very low levels, its activity drops rapidly, which therefore leads to increase of the unwanted chromium oxidation possibility[2]. The need to oxidize carbon without also oxidizing a significant amount of chromium is the key technical challenge in stainless steelmaking.

In fig.1 VOD equipments is shown. VOD takes place in a bottom stirred ladle, which sits within an evacuated tank[2]. A very high capacity vacuum ejector system is required to cope with the high flow rates of carbon monoxide produced during the oxygen blowing period. Oxygen needed for decarburization is supplied by a single lance passing through the roof of the vacuum vessel. The VOD process has several advantages over other forms of stainless steelmaking. With the use of VOD plants the following aims can be achieved[1-12]:

➢ High productivity, i.e. high melting performance.
➢ Use of cost effective alloys, e.g. FeMn HC, FeCr HC, FeCr charge, FeNi, etc. with high carbon and silicon contents.
➢ High chromium recovery even at carbon content of < 0.03.
➢ Low nitrogen and hydrogen gas content.
➢ Carbon content as low as < 100 ppm.

The result of the decarburization process of high chromium alloyed steel grades depends on the chromium / carbon equilibrium, the temperature and the partial pressure P_{CO} of the resultant CO gas. Reducing the P_{CO} pressure at unchanged carbon content not only reduces the oxygen content dissolved in the heat at equilibrium, but also shifts the line of equilibrium of the chromium oxide phase. Hence it is possible to adjust lower carbon contents during the oxidation process of high chrome heats with reduced P_{CO} before chromium slagging occurs.

2.   The VOD process as operated at EICO

The VOD process consists of three stages. Actual processing conditions are a function of the initial metal conditions and the steel grade.

2.1. Oxygen blowing

In the first stage, oxygen is blown to decarburize the metal. Alloys and fluxes are added in advance. The oxygen flow rate is between 300 and 800 Nm3/h and the vacuum pressure is between 180 and 250 mbar. The initial steel temperature is about 1650 °C, and its initial composition in wt pct is [C] 0.50 to 1.10, [Si] 0.02 to 0.10, [Mn] 0.2 to 1.0, and [Cr] 11.0 to 26.0. Fluxes such as dolomite and lime and some alloys such as Fe-Si and Fe-Cr are added according to the steel composition and grade. The bottom stirring argon flow rate is 100 N lit/min.

2.2. Vacuum Carbon Deoxidation (VCD)

  In the VCD stage (about 10 minutes), the total pressure is reduced to less than 5 mbar. The metal is further decarburized as a result of the decreased pressure. No additional fluxes and alloys are added in this stage.

2.3. Reduction

  During the reduction stage, a reducing agent   is added to recover the chromium that has been oxidized during the blowing phase. Also, fluxes such as dolomite, lime, and etc. are added to control the slag composition and fluidity. Some alloys such as Fe-Si, Fe-Mn, Fe-Ni, and Al are added according to the steel compositions and steel grade.

3.   Determination of the necessary oxygen quantity

The necessary oxygen quantity which has to be blown is determined by:

➤   Oxygen necessary for oxidation of elements.
➤   Oxygen which is removed by vacuum pumps and is therefore lost for process.

With top blowing technology with water cooled or insulated oxygen lances the loss of oxygen can be considered to be 38% in average. Table 1 shows the oxygen quantity which is theoretically necessary for the oxidation of the various elements involved. Per ton of a VOD heat as a general rule, the following quantity of oxygen (Nm^3) can be estimated by equation (1);

$$[O]\ (Nm3) = (2.75\ +\ 15.1\ \times\ \%\Delta C\ +\ 12.9 \times\ \%\ \Delta Si\ +\ 8 \times \%\ \Delta Al\ ) \times heat\ weight\ (ton) \qquad (1)$$

With standard VOD conditions, the equation gives us approximately 15 Nm^3O_2/ton of melt depending on the heat composition and temperature at the beginning of blowing.

4.   Experimental

  In order to experimentally study of condition before VOD on final results, 8 heat numbers trial industrially in EAF – LF – VOD – VCD – VD route were conducted   at EICO. By end of chemical composition and temperature arrangement in LF stage, melt transferred to vacuum vessel. Pressure of vessel adjusted between 180 - 250 mbar then injection of oxygen by oxygen lance located at the 1100 mm distance from surface of melt started from 300 Nm^3/h to 700 Nm^3/h in final stage. When the oxygen supply is cut off, the vacuum pressure drops to < 5 mbar, so that boosters can be activated in order to reduce the pressure even further.

The CO exhaust volume now continues rising under the influence of the deep vacuum between   1 - 5 mbar. In the case of steel grades with < 0.02 % C, the purging gas rate of 50 N lit per minute is maintained. The VCD secondary decarburization process is not completed until the CO exhaust gas production decreases and the pat meter reading falls again. The VCD-step is carried out at a pressure between 5 and 1 mbar and takes places at a about 10 minutes time period. This secondary decarburization process is limited to 5 minutes in the case of nitrogen-alloyed steel grades. The conditions for the last step of the VOD treatment process, i.e.: reduction, desulphurization, heating and alloying are the following steps:

➤   Flooding the VOD system.
➤   Lifting the vacuum cover.
➤   Taking sample to check the C content.
➤   Measuring bath temperature.
➤   Calculating cooling scrap on exceeding of the set point of < 1750 °C; cooling scrap factor: - 20 °C/1 % addition.
➤   Preparing addition of solids: Al grains, FeSi dust and lime.

➢   After verification of the C value reached by respective sample, Al and FeSi is added.
➢   Adding the balance of the lime quantity according to the lime calculation.

Finally the vacuum must be interrupted for taking the respective sample and temperature measurement. When the result of the analysis is available, measures are taken to adjust the analysis, if necessary, and to perform the final alloying process. These measures include:

➢   Receipt of the analysis of the respective sample.
➢   Addition of alloying agents for alloys according to the respective sample.

If chemical analysis was adjusted and temperature was high enough, vacuum degassing process was done by reducing pressure of vessel to lower than 1 mbar for about 20 min to remove unwanted soluble gases of hydrogen, nitrogen and somewhat oxygen. Heat condition prior and after VOD treatment is shown in table 2.

5.   Results and discussions

Each parameters variation during VOD process and effective parameters on these verifications are presented here as following:

5.1. Changes in Carbon

Amount and how burning of carbon in the vacuum chamber is influenced by several parameters. Most important of these parameters can be primary carbon, the temperature of a liquid in vacuum and amount of injected oxygen. The effects of these parameters on the oxidation of carbon in the fig. 2, 3, 4 are given. According to the fig. 2, with the percentage of carbon input to the vacuum chamber, oxidation rate of melting increases. This results is consistent with the predictions of the theory. With the increase of percentage of primary carbon, carbon-oxygen reaction possibility increase due to an increase in collisions between atoms of carbon and oxygen in the melting, likely. Fig. 3 shows the relationship between changes in the carbon content of the melt and temperature. As the figure shows, with increase of temperature the molten sent to the vacuum chamber, the risk of carbon oxidation increases. High solubility of carbon in molten steel at high temperatures, the results justified. Fig. 4 is a relationship between the oxidation of carbon and oxygen. It is clear that by increasing the amount of oxygen blowing to melt, the possibility of carbon oxidation increases. In general, given the practical values obtained for the above meltings, the actual amount of oxygen required to perform VOD per ton of melt, on average and approximately can be estimated according to following equation:

$$[O](Nm3) = (14 \times \Delta C + 8 \times \Delta Si + 6 \times \Delta Al) \times \text{heat weight (ton)} + 50\,Nm3 \qquad (2)$$

5.2. Changes in silicon

According to Table 3, the silicon content during the VOD process is reduced to an average of about 40%. Since silicon elements is a high oxygen affinity one, therefore expecting to decrease during the process does not seem too far-fetched. However due performing process under vacuum condition, oxidation rate will be less of carbon.

5.3. Changes in manganese

According to table 3, the amount of manganese changes during the VOD process is reduced to an average of about 20%. Manganese like silicon has a relatively high affinity for oxygen but less than it. So there is also the possibility of oxidation of manganese. Experimental results obtained from melting processes confirms this claim.

5.4. Changes in phosphorous:

Based on Table 3 data, reduction the amount of phosphorus in VOD was about 7%. One of the key conditions required for phosphorus removal, is oxide condition. Because of providing this conditions in the vacuum chamber, phosphorus removal operations is partly done. Fig.11 also shows dependence of phosphorus removal on melt temperature. as figure shows, possibility of dephosphorization increases with temperature rises.

5.5. Changes in sulfur:

Unlike phosphorous, considering the oxide condition of VOD process, the possibility of reducing the sulfur content is very low. However, practical results confirms this claim. According to Table 3, Changes in average sulfur content is about 33% and rising.

5.6. Changes in chromium:

Although the basic philosophy VOD process is oxidation of carbon reduction with minimum loss of chromium, however, expectation of any chrome oxidation during process does not seem very fair. As is clear from table 3, we expected about 5% chromium oxidation in end of process.

5.7. Changes in temperature:

no significant temperature fluctuations during VOD process is clarified (+40 to -50 °C). Carbon burning reaction releases a significant amount of heat, while maintaining the melt within ladle under vacuum for at least 1 hour, leaded to a drop in the temperature of the melt that should be considered. The resultant effect of these two mechanisms leads to no significant change in temperature during the VOD process.

6. Conclusions

An experimental work was developed to investigate effects of different parameters on vacuum oxygen decarburization. The following conclusions were obtained by the analysis of industrial scale trial and the actual VOD process for stainless steel making.

i. with increase of temperature the molten sent to the vacuum chamber, carbon oxidation increases.
ii. with the percentage increase of carbon input to the vacuum chamber, oxidation rate of melting increases.
iii. the silicon content during the VOD process is reduced to an average of about 40%.
iv. Manganese like silicon has a relatively high affinity for oxygen but less than it.
v. reduction the amount of phosphorus in VOD was about 7%. possibility of dephosphorization increases with temperature rises.
vi. considering the oxide condition of VOD process, the possibility of reducing the sulfur content is very low. Changes in average sulfur content is about 33% and rising no significant change in temperature during the VOD process.

Acknowledgments

NOMENCLATURE:

C_i, C_f: carbon weight concentration before (i) and after VOD (f)

Si_i, Si_f: silicon weight concentration before (i) and after VOD (f)

Mn_i, Mn_f: manganese weight concentration before (i) and after VOD (f)

P_i, P_f: phosphorous weight concentration before (i) and after VOD (f)

S_i, S_f: sulfur weight concentration before (i) and after VOD (f)

Cr_i, Cr_f: chromium weight concentration before (i) and after VOD (f)

W_i (ton), W_f (ton): weight of heat before (i) and after VOD (f)

T_i (°C), T_f (°C): temperature of heat before (i) and after VOD (f)

W_i (ton), W_f (ton): weight of heat before (i) and after VOD (f)

t (min): time period of VOD treatment

O_2 (Nm³): Oxygen consumption

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Figure and table captions

Table I .theoretical quantity of oxygen necessary for the oxidation of elements.

Reaction	Oxygen quantity (Nm3 O2/ Kg element)
C + 1/2O2 = CO	0.933
Si + O2 = SiO2	0.800
2Al + 3/2O2 = Al2O3	0.622
2Cr + 3/2O2 = Cr2O3	0.323
Fe + 1/2O2 = FeO	0.200

Table II. Heat condition prior and after VOD treatment is shown in.

Melt No.	C_i	C_f	Si_i	Si_f	Mn_i	Mn_f	P_i	P_f	S_i	S_f	Cr_i	Cr_f	W_i (ton)	W_f (ton)	T_i (°C)	T_f (°C)	t (min)	O_2 (Nm³)
141004-03	0.96	0.03	0.13	0.10	0.89	0.66	0.031	0.034	0.014	0.017	24.07	24.1	47	45	1630	1670	170	700
121108-03	0.29	0.05	0.05	0.05	0.98	0.87	0.043	0.040	0.017	0.020	16.3	16.07	50	50	1650	1613	35	240
120704-01	1.21	0.07	0.05	0.03	0.36	0.30	0.028	0.027	0.026	0.044	14.87	15.04	43	40	1650	1643	85	520
120705-01	1.29	0.01	0.05	0.04	0.21	0.17	0.017	0.017	0.019	0.035	15.24	14.75	40	39	1660	1683	86	675
120530-02	1.19	0.06	0.11	0.05	0.83	0.70	0.034	0.034	0.022	0.036	17.9	18.43	---	---	1649	1613	87	715
120512-01	1.09	0.025	0.11	0.08	0.78	0.55	0.041	0.035	0.013	0.010	20.91	21.07	46.6	46	1660	1680	87	650
140623-02	0.46	0.01	0.08	0.04	0.26	0.26	0.033	0.028	0.023	0.030	12.71	13.73	51	50	1650	1730	87	500
140713-03	0.16	0.003	0.24	0.01	0.75	0.47	0.004	0.003	0.004	0.004	0.68	0.65	49	48	1670	1620	35	200

Table III. Changes in Carbon, Silicon, Chromium, Manganese, Phosphorous, Sulfur and Temperature.

| Melt no.	$\Delta C/C_i$(%)	$\Delta S_i/Si_i$(%)	$\Delta Cr/Cr_i$(%)	$\Delta Mn/Mn_i$(%)	ΔT	$\Delta P/P_i$(%)	$\Delta S/S_i$(%)
141004-03	-96.88	-23.08	-3.95	-25.84	40	9.68	21.43
121108-03	-82.76	0.00	-5.08	-11.22	-37	-6.98	17.65
120704-01	-94.21	-40.00	-5.09	-16.67	-7	-3.57	69.23
120705-01	-99.22	-20.00	-3.22	-19.05	23	0.00	84.21
120530-02	-94.96	-54.55	-0.38	-15.66	-36	0.00	63.64
120512-01	-97.71	-27.27	-3.97	-29.49	20	-14.63	-23.08
140623-02	-97.83	-50.00	-18.41	0.00	80	-15.15	30.43
140713-03	-98.13	-95.83	-4.41	-37.33	-50	-25.00	0.00
AVERAGE	-95.21	-38.84	-5.56	-19.41	4.13	-6.96	32.94
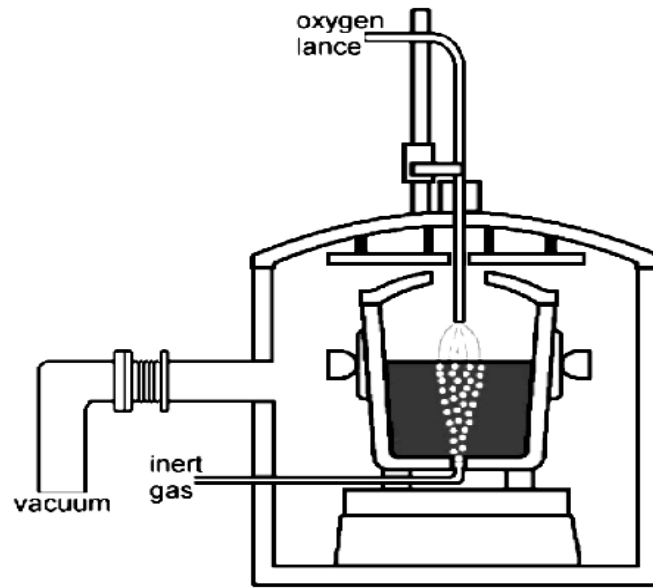
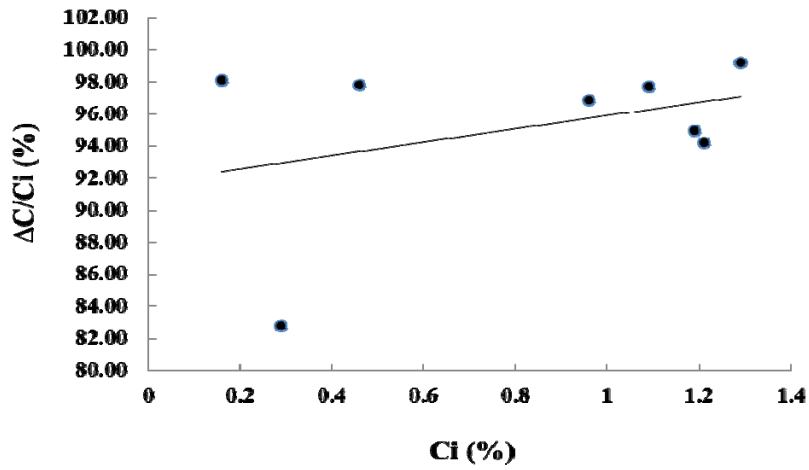Figure 1. Vacuum Oxygen Decarburisation (VOD) equipment.

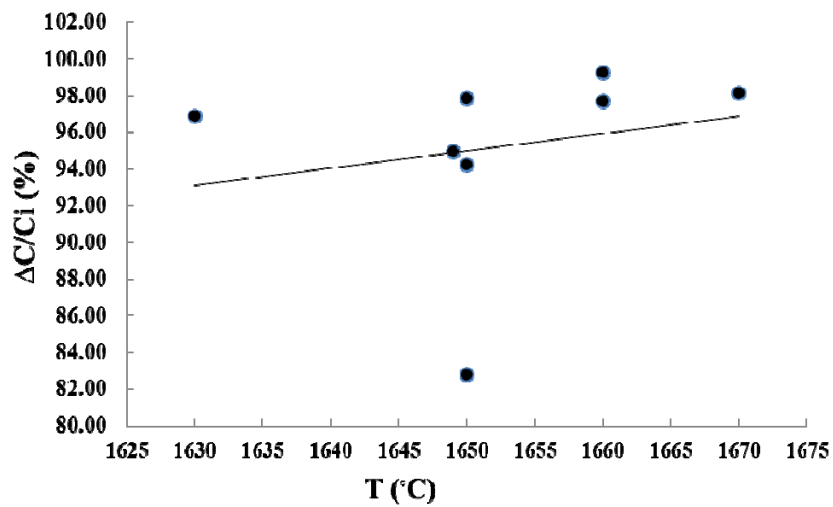Figure 2. changes in Carbon content droped with input carbon.

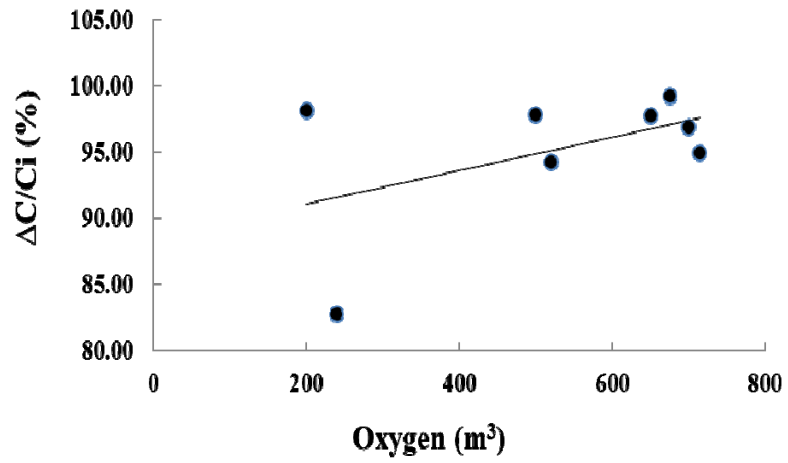Figure 3. changes in Carbon content droped with temperature.

Figure 4. changes in Carbon content droped with Oxygen.