Contribution to Deoxidation of Austenitic Steels in a Vacuum Induction Furnace with Carbon

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Abstract

Deoxidation of steel with carbon under reduced pressure is often used for increasing the steel purity. Suitable units for this purpose in foundries are vacuum induction furnaces. Possibilities of increasing the steel purity by deoxidation with carbon in the vacuum induction furnace were studied for the steel for the petrochemistry of specific composition 25Cr/35Ni. The charge composed of the return material only was melted in the air. During melting the charge oxidized and the oxidizing slag formed. Chemical composition of steel, morphology, chemical composition of inclusions in the steel and chemical composition of slag after vacuuming were studied on the basis of samples taken before and after vacuuming. Temperature and oxygen activity were measured before and after vacuuming. Globular inclusions with dominant content of silicon and manganese were observed in steel before and after vacuuming. Contents of total oxygen in steel didn't change significantly during vacuuming. On the basis of composition of inclusions and measured oxygen activity the activity of Cr_2O_3 in inclusions was calculated. A slag sample was taken after vacuuming and equilibrium oxygen activity in steel with regard to the Cr_2O_3 content in the slag was estimated from the slag composition. Equilibrium oxygen activity in relation to the Cr_2O_3 content in the slag was higher than equilibrium activity measured in the steel. For this reason it is not possible, under the studied conditions, to decrease oxygen content in steel during vacuuming.

Keywords: Vacuum induction furnace, Deoxidation with carbon, Steel for petrochemistry, Oxygen activity, Total oxygen

1. Introduction

A metallurgical unit composed of a vacuum induction furnace and a vacuumed crucible seems to be a prospective one for manufacture of exacting steel castings. In 2013 a vacuum induction furnace (VIF) with a vacuumed crucible of 100 kg melt weight has been installed in the university foundry of the Brno University of Technology. Experience with steel manufacture in this furnace indicate that the unit is suitable for:

- Manufacture of steel with higher concentration of elements with high oxygen activity. In particular its application for remelting of return material from these steels can be imagined.
- Reduction of nitrogen and hydrogen contents in vacuum.
- Production of high-alloy steels with carbon content under 0.020 % C.
- In manufacture of materials where deep deoxidation and low content of both active and total oxygen are required.
- Improving the quality of steels with content of alloying elements higher than 50 % and nickel-based superalloys.

Hitherto results are encouraging. A model of the kinetics of decarburization and a model of the change of nitrogen content

during vacuuming has already been published [1, 2]. The presented work deals with possibilities of reduction of oxidic inclusions, i.e. the reduction of total oxygen content in steel.

A method of melting the charge has a significant influence on the course of vacuuming. The charge can be melted in vacuum or in the air. Melting the charge in the air is more productive. For melting in vacuum it is necessary to treat the charge in such a way so that the entire weight of the charge can be loaded in the crucible before closing the furnace. The charge must be of such lumpiness that during melting it doesn't get „sticking" (forming no bridges). The influence of vacuuming of the charge melted in the air on deoxidation of steel with carbon is examined in the presented work.

During melting of the charge in the air the steel is oxidized and the slag is formed in which the ratio of individual elements is approximately the same as the ratio of elements in steel. Further on the slag reacts with metal and the less stable oxides are reduced by elements with higher affinity to oxygen which are dissolved in the steel. In contradistinction to unalloyed steels the aluminium isn't dominant for deoxidation of high-alloy steels. Aluminium content in high-alloy steels is usually lower than 0.050 % and aluminium oxidizes during melting of the charge to traces. As a result of the reaction of slag with steel the oxides of elements with low affinity to oxygen are reduced particularly with chromium and silicon. Steels alloyed with aluminium are an exception. Forming acid slag decreases the activity of alkaline oxides and even manganese oxides can occur in the slag in larger quantities. Then the oxides of the mentioned elements predominate in the slag. Composition of the mentioned slag also relates to the steel composition.

2. Objective of the work

The work is aimed at studying on experimental melts the deoxidation of steel with carbon in vacuum for the steel of specific composition 25 Cr/35 Ni with using the charge composed of the return material of high-alloy steels only.

3. Description of the experiment

The charge composed of the return material of high-alloy steel used in the petrochemistry was melted in the vacuum induction furnace in the air. Basic statistical characteristics of the set of experimental melts are given in tab. 1.

Table 1.
Statistical characteristics of the set of experimental melts

n=5	C	Si	Mn	Cr	Ni	Ti	Zr	Al
	%	%	%	%	%	ppm	ppm	ppm
average	0.46	1.64	0.86	24.73	34.70	195.0	45.3	160.0
s	0.01	0.06	0.01	0.21	0.18	98.5	2.2	14.1
min	0.45	1.56	0.85	24.43	34.52	110.0	43.0	150.0
max	0.47	1.68	0.87	24.88	34.94	290.0	48.0	180.0

Steel was further on alloyed with niobium which didn't participate in steel deoxidation. After melting the charge a sample for testing the chemical composition of steel was taken and temperature with oxygen activity were measured. Then the space above the bath was closed and the steel was vacuumed. Carbon boil started already under pressure of 600 hPa. During 30 minutes of vacuuming the pressure gradually decreased for all melts to 50 hPa. Temperature during vacuuming ranged within the interval of 1580 up to 1620 °C.

After 30 minutes of vacuuming the furnace was vented, temperature and oxygen activity were measured and a sample was taken for testing the chemical composition of steel and studying the morphology and chemical composition of inclusions. Inclusions were studied also on samples taken from the castings. Samples were prepared for testing by standard metallographic methods. Weight of castings was approximately 80kg.

Inclusions were analysed on a scanning microscope on JEOL JSM – 5510 equipped with an energy dispersive analyser of the company OXFORD Instruments. Metallographic samples for the analysis were prepared by a standard method.

4. Analysis of conditions of steel deoxidation in the vacuum induction furnace

Oxides (oxidic inclusions) dispersed in steel are reduced when the equilibrium oxygen activity in steel is lower than the equilibrium oxygen activity with oxides of the dominant deoxidation element. For the case when the dominant deoxidation element in steel is silicon the relationship between oxygen activity in steel and equilibrium oxygen activity with regard to silicon oxides can be described with the equation (1).

$$a_O < a_O^{Si} \tag{1}$$

a_O - oxygen activity in steel
a_O^{Si} - equilibrium oxygen activity in steel with a dominant deoxidation element (silicon)

Oxygen activity in steel is influenced by chemical composition of steel, temperature, the interaction between steel and its surroundings (especially with a lining and slag) and deoxidation action of carbon under reduced pressure. For each type of oxides there exists equilibrium oxygen activity. Assuming that the oxides are found in a standard condition as a pure substance the oxygen activity in steel can be calculated for the thermodynamic equilibrium.

Fig. 1. shows the equilibrium between oxygen activity in steel and the partial pressure of carbon monoxide in the atmosphere above the steel surface. The graph on fig. 1. further on shows the equilibrium oxygen activities of chosen oxides and partial pressure of CO at which the equilibrium is achieved. Calculations were carried out for the average composition of steel of experimental melts and the Rault activity of oxides equalled one.

In the case of aluminium and zirconium oxides the points on fig. 1. are informative only. The total Al and Zr contents determined on a quantometer were used for the calculation. Real

concentrations of Al and Zr dissolved in the steel will be lower than 0.010 %. In fig. 1. The equilibrium oxygen activities for activity of aluminium and zirconium equalled 100 ppm are informatively calculated.

It further on results from fig. 1. that with the given chemical composition of steel the silicon in particular will participate on deoxidation of steel. Forming oxides will reduce the activity of alkaline oxides and the elements forming alkaline oxides, especially manganese, will also participate in deoxidation of steel. Oxygen activity of steel under temperature of 1600 °C will therefore be less than 25 ppm.
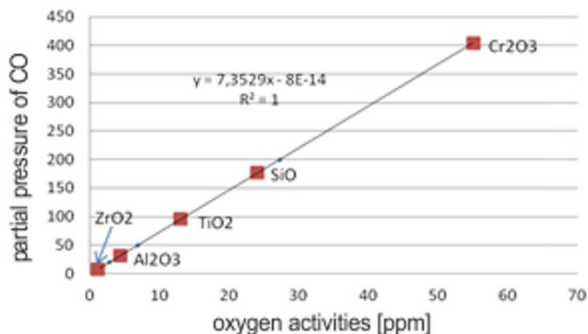

Fig. 1. Equilibrium oxygen activities with chosen oxides and partial pressure of CO; T = 1600 °C

5. Measured values

Oxygen activity depended on steel temperature. During statistical data processing the dependence on time and pressure during vacuuming hasn't been observed. Dependence of measured values of oxygen activity on temperature has been described by a statistically important equation (2).

$$a_O = 3 * 10^{-5} * e^{0.0082T} \qquad [ppm] \qquad (2)$$

For temperature of 1600 °C the oxygen activity of 15 ppm can be calculated from the equation (2). The measured oxygen activity is lower than the equilibrium oxygen activity with regard to silicon dioxide. Therefore the pure silicon dioxide will not be a product of deoxidation but a complex oxide in which the SiO_2 activity is lower than one.

After melting two types of oxidic inclusions were observed during metallographic study on the microscope. They were angular oxides which can be classified among the IIIrd type according to the classification of inclusions specified by Bůžek [3]. A typical inclusion is shown on fig. 2.
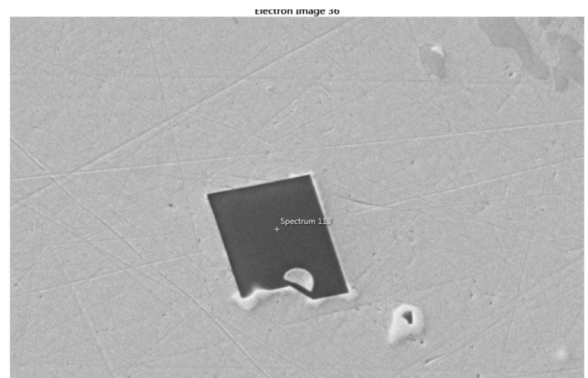

Fig. 2. Inclusion of aluminium oxide IIIrd type

Besides the inclusions of the IIIrd type the globular inclusions occurred on cut samples which cannot be exactly classified according to the classification of inclusions by Bůžek. Morphologically these inclusions belong between the type I and Ib. Typical globular observed inclusions are shown on fig. 3.
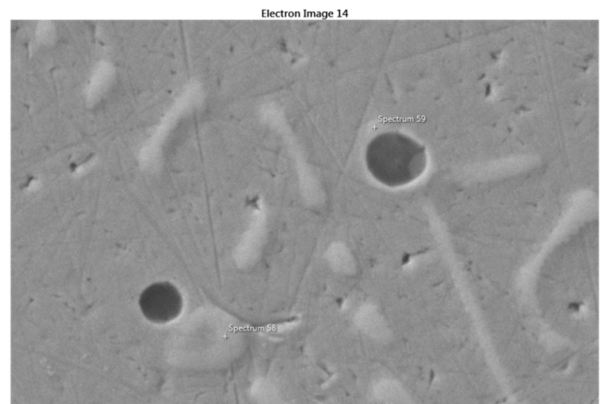

Fig. 3. Typical globular inclusions based on Si and Mn

Chemical compositions of inclusions of the IIIrd type corresponding to aluminium oxide on fig. 2. are in the atomic percentage in tab. 2.

Table 2.
Average composition of oxides of the IIIrd types of all studied melts

n = 8	O	Al	Si	S	Ti	Cr
	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	59.64	34.36	0.41	0.82	1.11	0.75
s	1.90	5.03	0.39	1.51	1.24	0.68
min	56.41	26.76	0.00	0.00	0.00	0.00
max	63.34	40.72	0.97	4.30	3.50	1.59
	Mn	Fe	Zr	Ni	Nb	Ca
	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	0.30	1.12	0.24	1.06	1.35	1.04
s	0.37	1.43	0.33	2.13	2.66	1.48
min	0.00	0.00	0.00	0.00	0.00	0.00
max	1.04	4.06	0.89	5.32	6.66	3.13

Chemical composition of inclusions given in tab. 2. corresponds almost stoichiometrically to aluminium oxide in which a part of aluminium is replaced with other elements. In concentration higher than 1 at. % the inclusions contain besides Si also Ti, Nb and Ca. Concentration of Cr, Fe and Ni in inclusions is apparently influenced by the matrix. After vacuuming on any cut sample no inclusions Al_2O_3 of the IIIrd type were observed.

During vacuuming of steel the chemical composition of inclusions changed. After melting the aluminium oxides were found in steel. After vacuuming no oxides of the Al_2O_3 type were already found in any sample. Basic statistical characteristics of the set of chemical composition of oxidic inclusions after melting are listed in tab. 3. Basic statistical characteristics of the set of chemical composition of inclusions after vacuuming are listed in tab. 4.

Table 3.
Basic statistical characteristics of chemical composition of globular oxides after melting

	O	Al	Si	S	Ti	Cr
n = 17	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	56.59	7.63	7.20	0.26	10.53	4.74
s	10.18	3.45	7.86	0.54	10.59	3.02
min	22.25	0.84	0.00	0.00	0.00	0.75
max	64.36	11.75	18.52	2.11	30.70	13.04
	Mn	Fe	Zr	Ni	Nb	Ca
	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	3.43	2.87	2.74	2.81	1.12	0.07
s	2.85	5.64	8.04	6.84	1.85	0.21
min	0.00	0.00	0.00	0.00	0.00	0.00
max	8.43	23.10	33.19	27.54	7.17	0.81

Table 4.
Basic statistical characteristics of chemical composition of globular oxides after vacuuming

	O	Al	Si	S	Ti	Cr
n = 17	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	58.71	7.27	16.46	1.17	2.41	2.84
s	6.12	1.43	4.03	2.73	4.02	2.57
min	37.54	3.83	6.47	0.00	0.00	0.92
max	62.68	9.42	22.41	13.47	19.11	14.23
	Mn	Fe	Zr	Ni	Nb	Ca
	[at %]	[at %]	[at %]	[at %]	[at %]	[at %]
average	7.84	1.49	0.00	0.80	1.00	0.00
s	2.76	3.15	0.02	2.10	2.93	0.00
min	3.30	0.00	0.00	0.00	0.00	0.00
max	18.82	16.10	0.10	10.45	14.28	0.00

It results from the comparison of the average composition of globular inclusions before and after vacuuming that the average content of aluminium in inclusions practically didn't change. The average content of silicon and manganese increased at the expense of the average content of titanium, chromium, iron and zirconium.

The content of total oxygen before vacuuming and after it and from castings has been also determined from all samples. Determined contents of total oxygen are given in tab. 5. Change

of the total oxygen content in steel during vacuuming has no importance from a practical point of view.

Table 5.
Contents of total oxygen [weight %]

before vacuuming	after vacuuming	from the casting
0.0172	0.0194	0.0166

Interpretation of measurement results
During all the time of vacuuming an intensive carbon boil took place in steel. But oxygen from oxides dispersed in steel didn't enter the reaction with carbon. Analysis of slag on the crucible surface formed during melting the charge in the air has shown a high content of reducible oxides, chromium and manganese ones in particular.

Oxygen activity which is in equilibrium with chromic oxide in the slag can be estimated on the basis of equation (3).

$$a_O^{incl} = a_O^{slag} * \frac{N_{Cr_2O_3}^{slag}}{N_{Cr_2O_3}^{incl}} \tag{3}$$

a_O^{incl} - oxygen activity in steel which is in equilibrium with activity of Cr_2O_3 in inclusions
a_O^{slag} - oxygen activity in steel which is in equilibrium with activity of Cr_2O_3 in slag
$N_{Cr_2O_3}^{incl}$ - mole fraction of Cr_2O_3 for the average concentration in inclusions [mol %]
$N_{Cr_2O_3}^{slag}$ – mole fraction of Cr_2O_3 for the average concentration in the slag [mol %]

Table 6.
Basic statistical characteristics of chemical composition of slags in weight %

	O	Mg	Al	Si	Ca	Ti
	[%]	[%]	[%]	[%]	[%]	[%]
average	35.52	1.81	10.61	12.41	0.29	3.78
s	2.37	1.13	4.10	1.38	0.11	1.66
min	32.32	0.23	4.57	10.41	0.11	1.31
max	40.52	3.98	16.28	15.38	0.56	6.55
	Cr	Mn	Fe	Cu	Zr	Nb
	[%]	[%]	[%]	[%]	[%]	[%]
average	18.27	13.62	0.73	0.29	1.63	0.62
s	2.18	3.19	0.21	0.07	0.89	0.20
min	13.34	9.35	0.43	0.15	0.92	0.24
max	21.83	22.09	1.08	0.40	4.37	0.93

For constant temperature of steel and the same value of the Rault activity coefficient $\gamma_{Cr_2O_3}$ the equilibrium oxygen activity in steel with regard to the activity of Cr_2O_3 in the slag at the end of vacuuming equals 25 ppm. A similar calculation of oxygen activity for the activity of MnO in the slag gives the value of oxygen activity in steel 26 ppm. Estimated oxygen activities in steel with regard to the Cr_2O_3 content in the slag are higher than the measured oxygen activity in steel and therefore the oxygen according to the equation (1) is transitioning from slag in steel.

Under these conditions the slag is a source of oxygen for the reaction with carbon. Under these conditions the carbon reduces oxygen contained in the slag and the reduction of oxides in steel doesn't occur. The total oxygen content in steel under these conditions remains unchanged.

Acknowledgements

References

[1] Šenberger, J., Pernica, V. & Pešek, J. (2015). *Slévárenství*, No 1/2.

[2] Šenberger, J., Pernica, V. & Pešek, J. (2015). *Slévárenství*, No 3/4, in print.

[3] Bůžek, Z. (1969). *Slévárenství*, No 10.