International Journal of ISSI, Vol.3 (2006), No. 2, pp. 22-28

Evaluation of Deoxidation Process in Medical Grade of 316L Stainless Steel

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Received June 3, 2006; Accepted April 30, 2007

Abstract

In the present work, deoxidation and refining of 316LVM steel (Low carbon Vacuum Melted) during the vacuum induction melting process was studied. This grade of stainless steel is one of the most important materials in medical applications. Vacuum deoxidation by carbon is the first stage of 316LVM stainless steel production process. In this stage, aluminum must be absent to avoid killing the C-O reaction. Deoxidation product in the VIM process is in gaseous state which is tapped by vacuum pump system. For this reason, vacuum deoxidation by carbon is the best method for refining 316LVM steel. Vacuum induction melting has no significant effects on reduction of sulfur and phosphorus. After deoxidation in vacuum by carbon, addition of Al+Ca/Si is the best way for reducing the oxygen and increasing the steel cleanness.

Keywords: VIM process, 316LVM stainless steel, Deoxidation, Calcium.

Introduction

Stainless steel began to be used in surgical applications in 1926 when Strauss patented the 18/8 stainless steel [1, 2)].

Owing to combination of its good mechanical properties, biocompatibility, ease of fabrication and economic aspects, stainless steel is one of the most frequently used biomaterials for internal fixation devices [3-5)].

Among these stainless steels, 316LVM medical grade is of great concern. LVM stands for low carbon content, which is produced by Vacuum Melting. Therefore, vacuum induction melting (VIM) and refining process are parts of production technology. The chemical and mechanical requirements of stainless steels for implant applications are stated in ISO 5832-1 and ASTM F138 and F 139 standards [6, 7)].

For surgical implants, corrosion resistance and high resistance to fatigue are important. The chemical composition of stainless steel provides these features. Non-metallic inclusions, i.e. oxides and sulphides, however, can act as initiation points for corrosion attacks and propagation of fatigue cracks by corrosive bodily fluids. In order to meet these requirements, the contents of carbon and oxygen have to be controlled [8, 9)].

During vacuum induction melting, two thermodynamic parameters (pressure and temperature) are controlled[10-12)].

In this paper, the role of vacuum induction melting as well as addition of deoxidizer elements such as aluminum, silicon and calcium in deoxidation of 316LVM stainless steel has been studied.

Experimental Procedures

Different stainless steel ingots with chemical composition indicated in Table 1 were prepared in a vacuum induction melting furnace. Pure iron, electrolytic nickel, low carbon ferro-chromium and molybdenum were used as raw materials. Alloying process was carried out under argon atmosphere. Spectrometer was used for chemical analysis of the metallic elements, and oxygen content was determined by the gas analyzer instrument (CHNOS).

Vacuum treatment was used as the first stage of deoxidation for all ingots. The chemical composition of the used ingots after almost 10min vacuum deoxidation is shown in Table 2. Addition of nickel, molybdenum, chromium, magnesium alloying elements and deoxidizer elements was performed in the argon gas atmosphere. Following the alloying process, in order to decrease the oxygen content, three parallel sets of experiments were designed. Ingots N1 and N2 were deoxidized with silicon, ingots N3 and N4 with aluminum and ingots N5 and N6 with aluminum plus calcium/silicon wire. Tables 3 and 4 show the experimental conditions and chemical composition of the produced ingots.

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Morphology and composition of inclusions were studied using scanning electron microscope (Cam Scan MV2300) equipped with EDS. In addition, shape, size and distribution of inclusions were determined with LEICA MW image analyzer program.

Results and discussion

By comparing the chemical composition of the ingots in Tables 1 and 2, it is found that vacuum induction melting has no significant effect on reduction of sulfur and phosphorus. Reduction of these impurities is accomplished by oxygen steel making process and using CaO base slags[11].

Chemical compositions of the ingots in Table 1 and 2 show that vacuum treatment not only results in deoxidation, but also causes carbon reduction; whereas other elements are almost unchanged. In the first stage of deoxidation process (vacuum treatment), oxygen reduced from 16 up to 55 percent and the remaining oxygen, was reduced up to 90 percent by adding aluminum and calcium/silicon elements.

Table 1. Chemical composition of the primary ingots (before vacuum deoxidation).

	C	S	P	Ni	Cr	Mo	Al	O(ppm)
N1	0.095	0.015	0.01	13.12	17.83	2.38	0	428
N2	0.091	0.018	0.01	13.83	17.55	2.45	0	395
N3	0.087	0.011	0.01	13.05	18.22	2.44	0.02	78
N4	0.09	0.015	0.01	14.11	18.16	2.39	0.03	81
N5	0.081	0.017	0.01	14.26	17.74	2.53	0	388
N6	0.085	0.013	0.01	13.94	17.68	2.48	0	435

Table 2. Chemical composition of the vacuum deoxidized ingots.

	C	S	P	Ni	Cr	Mo	Al	O(ppm)
N1	0.038	0.014	0.01	13.21	17.8	2.35	0	203
N2	0.022	0.017	0.01	13.74	17.54	2.41	0	195
N3	0.059	0.013	0.01	13.13	18.33	2.47	0.02	62
N4	0.063	0.015	0.01	14.2	18.3	2.43	0.03	68
N5	0.036	0.019	0.01	14.32	17.81	2.5	0	229
N6	0.031	0.012	0.01	13.88	17.59	2.41	0	276

Table 3. Deoxidation contents by vacuum and deoxidizer elements.
In the first set of specimens (N1, N2), deoxidation was accomplished by silicon element. In the second and third sets of samples (N3, N4 and N5, N6) aluminum and aluminum-calcium were added as deoxidizer elements.

	Deoxidation (%)			
	Vacuum (0.1 mbar)	Deoxidizer elements		
		Silicon	Aluminum	Aluminum+Calcium/Silicon
N1	52.5	60		
N2	55.6	63		
N3	20.5		79	
N4	16		78	
N5	41.2			95
N6	36.5			96.3

Table 4. Chemical composition of ingots after deoxidation with Si, Al, Al-Ca.

	C	S	P	Ni	Cr	Mo	Al	O(ppm)	Ca	Si	Deoxidizer elements
N1	0.033	0.012	0.01	13.15	17.88	2.35	0	80	0	0.63	*Deoxidized by Si*
N2	0.023	0.015	0.01	13.8	17.59	2.43	0	51	0	0.59	
N3	0.052	0.014	0.01	13.1	18.35	2.41	0.05	13	0	0.09	*Deoxidized by Al*
N4	0.055	0.014	0.01	14.22	18.35	2.44	0.04	15	0	0.11	
N5	0.038	0.01	0.01	14.29	17.73	2.56	0.06	12	0.013	0.71	*Deoxidized by Al.Ca/Si*
N6	0.035	0.007	0.01	13.81	17.76	2.43	0.05	10	0.011	0.69	

Table 5. Typical chemical composition of 316LVM steel.

C	Si	Cr	Ni	Al
0.03	0.5	17.5	13	0.01

Table 6. Interaction parameters of elements[13].

elements		Interaction parameters at 1873K	
i	**j**	e_i^j	r_i^j
Al	Al	0.043	
	C	0.091	
	Cr	0.012	
	O	-1.98	39.82
	Si	0.056	
O	Al	-1.17	-0.01
	C	-0.421	
	Cr	-0.031	
	O	-0.17	
	Si	-0.066	
Si	Al	0.058	
	C	0.18	
	Cr	-0.021	4.3×10^{-4}
	O	-0.119	
	Si	0.103	

Deoxidation in vacuum

Total oxygen in the melt can be presented by the following equation:

$$O_{Total} = O_{Dissolved} + O_{inclusions} \quad (1$$

If Henry's law is considered for dissolved oxygen in pure iron, the following equation will be obtained[11]:

$$O_2 \rightarrow 2[O]_{(wt\%inFe)} \quad \Delta G^{o}=-222140-11.74T \ (J) \quad (2$$

$$K = \frac{f_O^2[wt\%O]^2}{P_{O_2}} \quad (3$$

$$2\log[wt\%O] - \log P_{O_2} = 6.8 \qquad T=1873\ K \quad (4$$

Where K denotes equilibrium constant and f activity coefficient.

For 316LVM stainless steel with chemical composition indicated in Table 5 and interaction coefficients in Table 6, Eq. 5 will be obtained (T=1873 K):

$$\log p_{O_2} = 2\log[wt\%O] - 0.348[wt\%O] - 6.98 \quad (5$$

Figure 1 shows the curves related to eq.4 and 5. For example, if [wt%O] =300ppm, the equilibrium oxygen pressure for pure iron is 1.6×10^{-10} mbar and for stainless steel 10.6×10^{-11} mbar. In this research, the highest vacuum in empty chamber of furnace obtained was 10^{-4} mbar, which indicates that without reducing elements (for example, carbon), deoxidation by vacuum treatment will not be accomplished.

Deoxidation with Carbon in vacuum

In VIM process, removal of oxygen takes place through the formation of carbon monoxide [11]:

$$[C]_{(wt\%inFe)} + [O]_{(wt\%inFe)} \rightarrow CO_{(gas)} \quad (6$$

$$\Delta G^0 = 23000 - 38.98T \ (J)$$

$$K = \frac{P_{CO}}{a_c.a_o} \quad (7$$

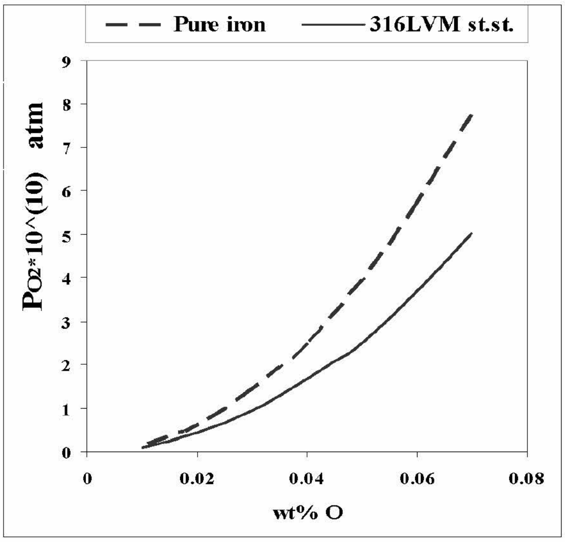

Fig. 1. Variation of oxygen pressure with different weight percent of oxygen.

Assuming no interaction coefficients for alloying elements, Eq.8 will be obtained for pure iron (T=1873 K).

In Figure 2, the variation of carbon and oxygen in 10^{-1} mbar pressure is shown.

$$\log P_{CO} = -0.297\,[wt\%O] + 0.09\,[wt\%C] + \log [wt\%O] + \log [wt\%C] + 2.86 \quad (8$$

The amount of carbon and oxygen in Tables 1 and 2 shows that deoxidation in vacuum occurs because of carbon-oxygen reaction.

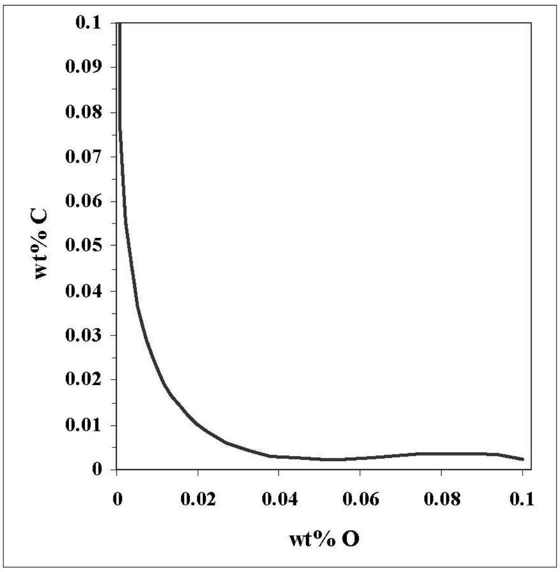

Fig. 2. Variation of oxygen and carbon in 10^{-1} mbar pressure.

If the interaction coefficients of aluminum, silicon, chromium and nickel are considered in Eq.6, Eq.9 will be obtained (at 1873K). In Figure 3, the variation of oxygen at different pressures of carbon monoxide for pure iron and 316LVM stainless steel is shown.

$$\log P_{CO} = -0.297\ [wt\%O] + 0.201\ [wt\%C] + \log [wt\%O] + \log [wt\%C] + 1.74 \qquad (9$$

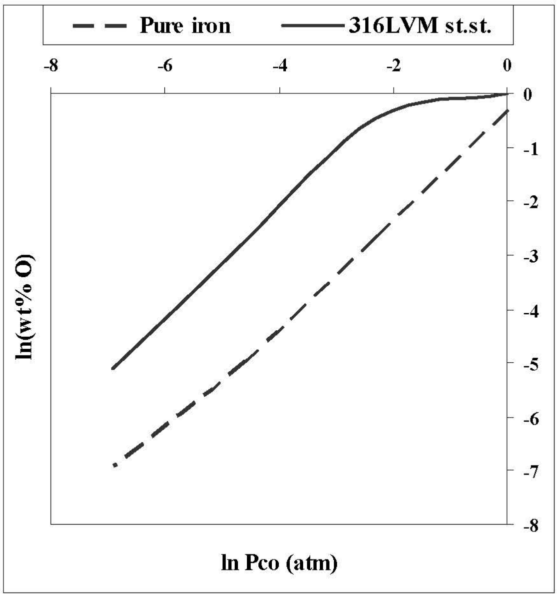

Fig. 3. Variation of oxygen at different pressures of carbon monoxide for pure iron and 316LVM stainless steel.

It is found that deoxidation in vacuum for 316LVM stainless steel is lower than that in pure iron. In fact, alloying elements such as aluminum, silicon and chromium reduce deoxidation in vacuum induction melting. In N3 and N4 ingots, 0.02 percent of aluminum reduces deoxidation under vacuum. The amount of aluminum and oxygen in Tables 1 and 2 shows the presence of aluminum in primary ingots, causing weaker deoxidizing treatment of "vacuum treatment".

Aluminum is the most important element for deoxidation in vacuum by carbon because it constitutes the Al_2O_3 inclusions. Alumina particles are stable at 1873K temperature (eq.10)[11] and reduction of these inclusions will not happen by carbon in vacuum.

$$(Al_2O_3)_{inc.} + 3[C]_{(wt\%inFe)} \longrightarrow 3CO_{(gas)} + 2[Al]_{(wt\%inFe)}$$

$$\Delta G^0_{1873\,K} = +246.2(kJ) \qquad (10$$

Deoxidation with deoxidizer elements

Table 7 shows type, average diameter, total inclusions area per sample area and number of inclusions for ten samples of each ingot. It is found that the number of inclusions in N3 and N4 samples that were deoxidized with aluminum is more than those in other ingots. N3 and N4 ingots have the finest inclusions among the others and have the largest ratio of "inclusions area/sample area" which is a measure of cleanness. N5 and N6 samples deoxidized by aluminum plus calcium/silicon wire have the largest inclusions and the best cleanness. Deoxidation mechanism and types of products are discussed below.

1. Silicon

Energy dispersive spectroscopy (EDS) of particles in N1 to N6 ingots after deoxidation in vacuum shows that inclusions are in chromium oxide form. In Figure 4 a chromium oxide inclusion with its EDS analysis is shown.

Deoxidation with silicon reduces the oxygen in chromium oxide (eq.11)[11]. Deoxidation products are SiO_2 inclusions that can be expressed by the following equations:

$$2(Cr_2O_3)_{inc.} + 3[Si]_{(wt\%inFe)} \longrightarrow 3(SiO_2)_{inc.} + 4[Cr]_{(wt\%inFe)}$$

$$\Delta G^0 = -174220 - 17.3T \quad (J) \qquad (11$$

$$[Si]_{(wt\%inFe)} + 2[O]_{(wt\%inFe)} \longrightarrow (SiO_2)_{inc.}$$

$$\Delta G^0 = -610800 + 242.32T \quad (J) \qquad (12$$

If the interaction coefficients of elements are considered, [wt%O] = 400 ppm and [wt%Si] = 0.5 ppm, the following equation for activity of silicon in the melt will be obtained from eq.12:

$$\log f_{Si}^{Cr} = -1.246 - 0.066[wt\%Cr] \qquad (13$$

In Fig.5, variation of f_{Si} at different wt%Cr is shown. In N1 and N2 ingots, final amount of oxygen is higher than that in the other ingots. It is observed that the deoxidizing power of silicon becomes weaker by the addition of chromium to the liquid iron.

Table 7. Specification of inclusions.

	number (0.5mm^2)	**Max. Diameter**(μm)	**Min. Diameter**(μm)	**Ave. Diameter**(μm)	**(inclusions area) /(sample area)**	**Type**
N1,N2 Si Deoxidized	38	17	9	12	12%	SiO_2
N3,N4 Al Deoxidized	142	13	2	4	33%	Al_2O_3
N5,N6 Al.Ca/Si Deoxidized	41	22	6	10	10%	$Al_2O_3.SiO_2$ $Al_2O_3.CaO$ $Al_2O_3.SiO_2.CaO$

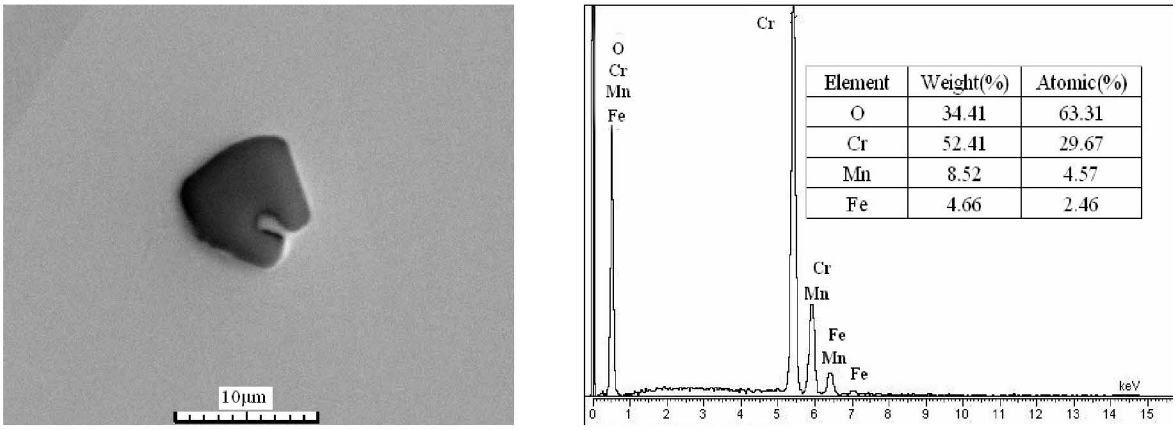

Fig. 4. Chromium oxide inclusion and its point analysis (EDS).

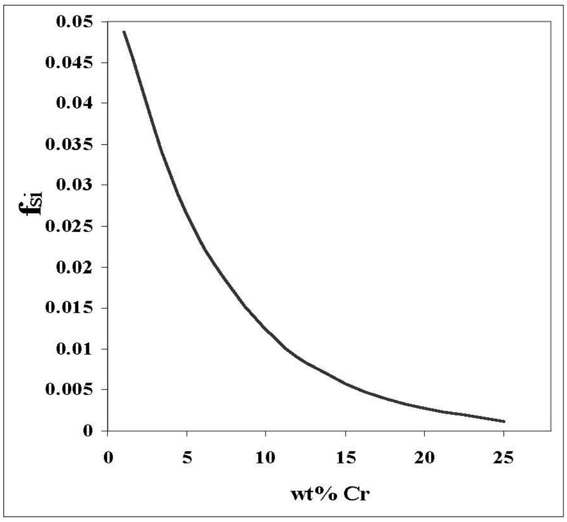

Fig. 5. Variation of f_{Si} with different amount of chromium.

2. Aluminum

Aluminum is the most important deoxidizer element in steels that can reduce the oxygen level to 10 ppm[11)]. After the addition of aluminum to the melt, deoxidation products are Al_2O_3 inclusions with 2323K melting point. Specifications of inclusions in Table 7 showed that alumina solid particles are the smallest inclusions that can remain in the structure during the solidification process. Formation of Al_2O_3 inclusions can be expressed by equations 14 and 15 (1873 K):

$$2[Al]_{(wt\%inFe)}+3[O]_{(wt\%inFe)} \rightarrow (Al_2O_3)_{inc.} \qquad (14$$

The amount of oxygen in Table 4 and specifications of inclusions in Table 7 show that by deoxidizing with aluminum, oxygen is reduced to 15ppm and cleanness is reduced as well. In Figure 6, an alumina inclusion and its point analysis are shown.

$$2[Al]_{(wt\%inFe)} + (Cr_2O_3)_{inc.} \longrightarrow (Al_2O_3)_{inc.} + 2[Cr]_{(wt\%inFe)} \quad (15$$

3. Calcium

N5 and N6 ingots were deoxidized by calcium after pre-deoxidation by aluminum. After the addition of aluminum and calcium/silicon wire for deoxidation, products were found to be complex inclusions with complicated composition in Al-Si-Ca system.

$$3(Al_2O_3)_{inc.} + 2(SiO_2)_{inc.} \longrightarrow (3Al_2O_3.2SiO_2)_{inc.} \quad (16$$

$$xCaO + yAl_2O_3 \longrightarrow (CaO)_x.(Al_2O_3)_y \quad (17$$

Specifications of inclusions in table7 show that deoxidation with aluminum and calcium/silicon reduce the amount of oxygen to 10 ppm and increase the cleanness by production of complex inclusions. Melting point and size of alumina-calcia-silica complex inclusions are more than the alumina inclusions that cause these particles to be separated by flotation mechanism[12]. In Figure 7, inclusion and its point analysis are shown.

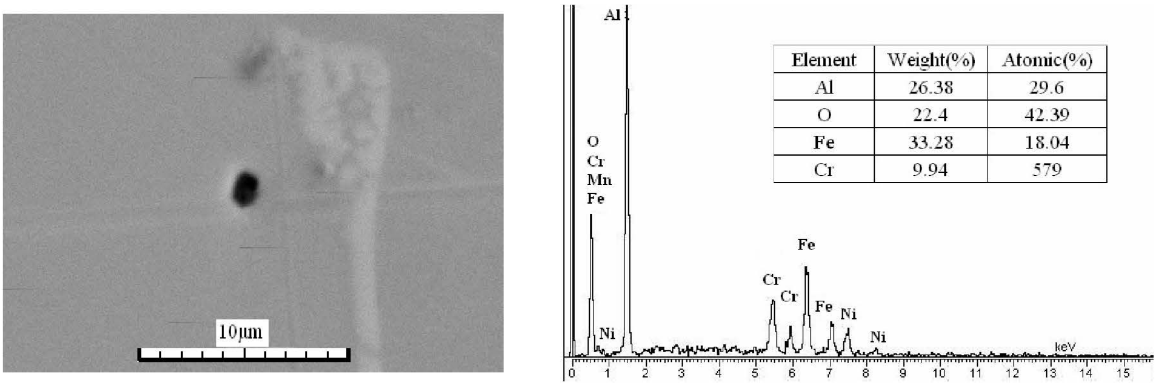

Fig. 6. Alumina inclusion and its point analysis (EDS).

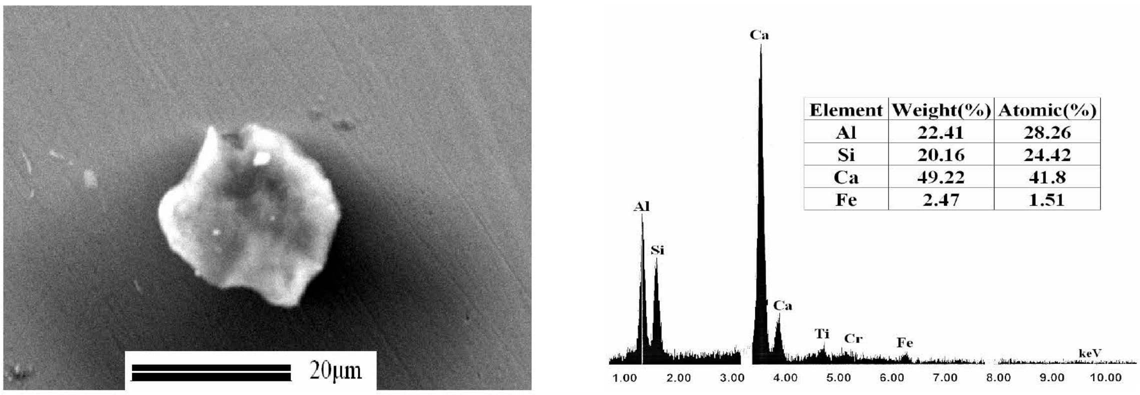

Fig. 7. Alumina-calcia-silica inclusion and its point analysis (EDS).

Conclusions

1- Deoxidation product in the VIM process is in gaseous state (CO) which is tapped by vacuum pump system. For this reason, vacuum treatment and deoxidation by carbon are the best ways for refining 316LVM steel.

2- Vacuum induction melting has no significant effects on reduction of sulfur and phosphorus.

3- Aluminum must be absent in primary ingots (before vacuum treatment) to avoid killing the C-O reaction at early stage of deoxidation.

4- Chromium reduces the activity coefficient of silicon and as a result, deoxidizing power of this element becomes weaker.

5- After vacuum refining, deoxidation of 316LVM stainless steel ingots by aluminum and calcium/silicon is the most effective method for reduction of oxygen.

Acknowledgement

The author is grateful to Mr. Saadat (Iran University of Science & Technology) for the casting of alloys with vacuum induction melting furnace.

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