

Oxidation Processes in Blowing Steel With Inert Gas into the Ladle

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Abstract. This work reports the possible development of oxidative processes in a metal when treating the melt in the ladle under intensive stirring with an inert gas. The industrial data have been received, confirming the possibility of reducing the concentration of silicon and aluminum in the metal, as well as changing the slag chemical composition with the bath blowing with the inert gas through the top submerged lance.

Introduction

When an inert gas is blown into steel, the oxidation process of silicon, manganese and chromium, with adding into a ladle to enhance its chemical composition, is possible to occur. Regardless of the source of oxygen, the element in a melt that is oxidized first has the highest deoxidizing capacity (affinity for oxygen) at a given concentration and temperature. In Table 1, the values of equilibrium oxygen concentrations are compared, with various contents of manganese, silicon and chromium at a temperature of 1580° C in the melt (Formula [1]). It also shows the oxygen content is balanced with aluminum. According to Table 1, with the concentration of aluminum being approximately 0.001%, the oxygen content is so small in the melt that manganese and chromium in structural steels can not react with oxygen coming from different sources. Aluminum binds to oxygen. The specified above content of aluminum is enough to prevent oxidation of silicon, if the silicon concentration does not exceed 0.3 - 0.4%. At higher concentrations of silicon, this aluminum content can not protect it against oxidation. In practice, the vast majority of melts contains more than 0.01% aluminum in the molten metal after tapping. At such aluminum concentrations, silicon is not oxidized despite any concentrations in the metal. The oxygen injected to the melt only oxidizes aluminum.

In cases of the melts blown with argon and their chemical composition not adjusted in the ladle at all, the oxidation process of silicon, manganese and chromium does not occur; contents of these elements in the ladle analysis and grade analysis samples were similar (with the observed deviations within the chemical tolerance limits). On the other hand, when argon is blown, the oxidation of aluminum occurs and its concentration in the steel decreases depending on the blowing time (τ) and its content in the ladle sample (Al_l)

$$\Delta Al = 0,2[Al]_l + 0,0012\tau - 0,04; \quad R_{MH} = 0,6. \quad (1)$$

According to this equation, when the content of aluminum in the ladle sample is 0.03%, its melting loss during the 6-minute blowing makes 0.009%.



Table 1. Equilibrium concentrations of oxygen dissolved in iron at various concentrations of manganese, chromium, silicon and aluminum at 1580°C

Element	Equilibrium concentration of oxygen with elements, $\times 10^3$, % by weight with the concentration of elements in iron, % by weight											
	0.001	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.6
Mn								97	66	50	40	27
Cr								57	47	42	37	25
Si			30	17	13	10	8	7	5	5	5	5
Al		0.8	0.7	0.4								

We assume the two main sources of oxygen to the metal: from ladle slag and atmosphere. In the case of the single-slag process, the metal and slag are de-oxidized during the tapping process when ferrosilicon, silicon manganese and aluminum are basically added. Table 2 summarizes the chemical compositions of slag after tapping and blowing with argon; it is observed, first, the concentration of ferrous and manganese oxides in the slag after tapping is relatively small - 5% maximum, with an average content of 2.6% and 2.1% accordingly in the investigated material mass, and, secondly, during the tapping process, the de-oxidation of slag is not able to complete. During the following argon blowing, a decrease in concentrations of both components is observed. It is proportional to the sum of these oxides in the slag before blowing: the higher their initial total concentration, the greater the reduction (Figure 1). They are apparently reduced with aluminum.

Table 2. Summarized data on the chemical composition of slag in the ladle after tapping and blowing

	Content, wt %							
	CaO	SiO ₂	MgO	FeO	MnO	Al ₂ O ₃	S	B=CaO/SiO ₂
After tapping	38.5-	16.7-	6.1-	1.3-	0.9-4.7	5.2-	0.11-	1.5-3.0
	53.2	27.6	19.9	5.3	2.12	12.5	0.61	
	45.4	22.3	13.9	2.61		9.7	0.35	
After blowing	37.2-	17.7-	6.5-	0.7-	0.53-	5.7-	0.15-	1.5-3.0
	53.4	28.0	22.1	2.8	3.95	14.6	0.71	
	44.9	23.1	14.4	1.66	1.31	11.0	0.38	

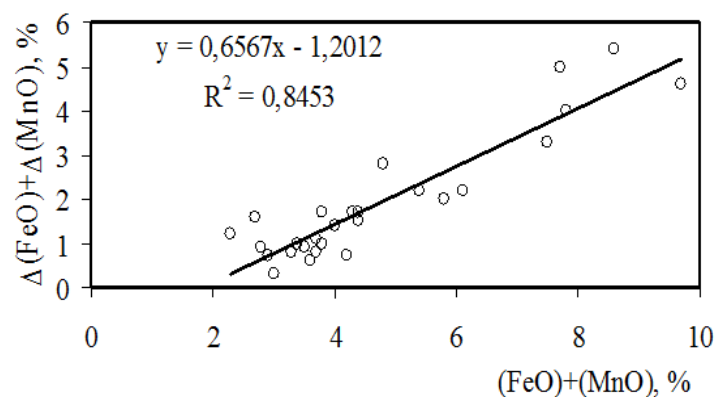
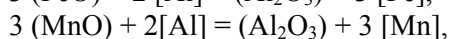
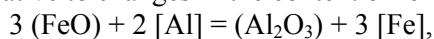


Figure 1. Reduction of ferrous and manganese oxides in slag when blowing with argon

The amount of the oxidized aluminum while the blowing process ($\Delta [Al]$) can be determined relative to changes in the content of ferrous and manganese oxides in the slag:



$$\Delta[\text{Al}] = \frac{2 \cdot 27 \cdot S(\Delta\text{RO})M}{3 \cdot 72 \cdot 10^4}, \% \quad (2)$$

where 27 is the atomic mass of aluminum; 72 is the molecular mass of ferrous oxide. When aluminum is oxidized with manganese oxide, the molecular mass of manganese oxide should be inserted into the formula (71). To simplify the calculations, there is no need to make such replacement due to negligibility of the error occurred.

S is the mass of slag, t; $\Delta(\text{RO}) = \Delta(\text{FeO}) + \Delta(\text{MnO})$ is the total decreasing in concentration of ferrous and manganese oxides, %; M is the mass of a melt, t. In further calculations we take $M = 110$ t.

In calculations based on this formula, it becomes difficult to define an amount of slag relative to a particular melt; the amount may range from 20 - 30 to 50 - 60 kg/t.

An attempt has been made to compare the expected "melting loss" of aluminum due to ferrous and manganese oxides with the actual loss observed for specific values ΔRO in the melts. For this purpose, the values $\Delta[\text{Al}]$ are derived from ΔRO at a slag mass of 2t, 3t and 5t, which are indicated by the lines in Figure 2. The points represent the actual values of ΔAl depending on the actual ΔRO . As it can be seen, the actual melting losses of aluminum in most melts are similar to those of with the slag mass ranging 3 - 5 t. Considering the slag layer thickness in the ladle, such amounts of slag are quite possible. When the slag density $\rho = 3\text{t/m}^3$ and ladle diameter $D = 3$ m, the slag layer thickness is 0.23 m at a slag mass of 5t, and 0.14 m at 3 t. The value of aluminum melting loss while oxidizing with slag can vary from 0.005 to 0.05%.

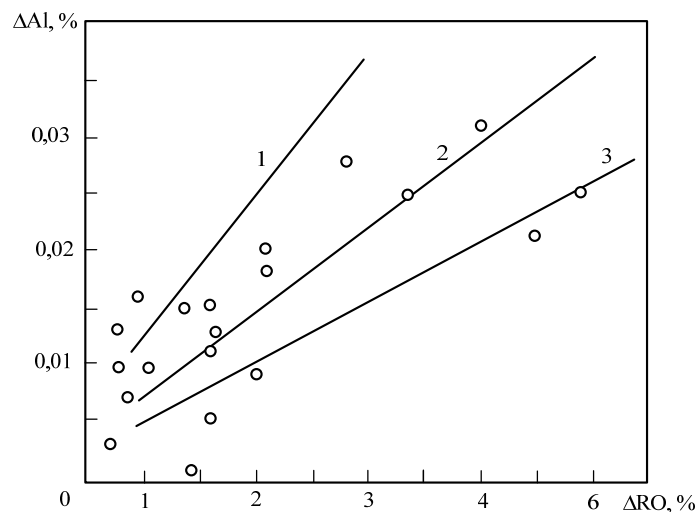


Figure 2. Aluminum loss depending on the total concentration of ferrous and manganese oxides in the slag

Another source of oxygen is the atmosphere. The amount of oxygen entering a metal from the air can be determined using the Temkin equation [2], with the activation energy $E = 117000$ J/mol. For calculating we have assumed that oxygen passes into the metal through the slag-free surface near the place where argon bubbles reach the surface forming a 1 m diameter. It turns out that the 6-minute blowing into the melt can result in absorption of 1.633 kg oxygen that is sufficient for the oxidation of 0.0018% aluminum in a 100-ton ladle. 0.0027% of aluminum can be oxidized under the similar conditions with the 10-minute blowing. Hence, the main source of oxygen that enters the metal while blowing with argon is slag. A portion of oxygen entering the melt from the air is considerably small.

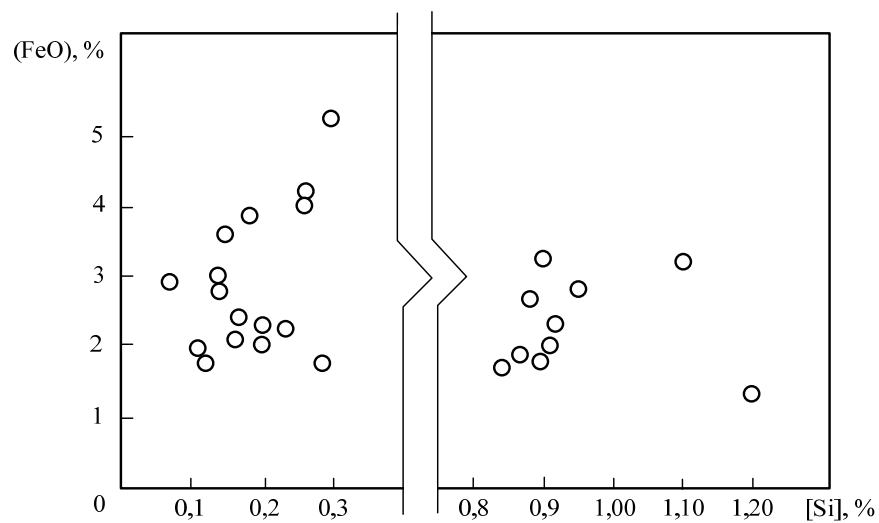


Figure 3. Influence of a content of silicon in the metal on the slag oxidation

Figure 3 gives the comparison between the content of ferrous oxide in the slag and silicon in the metal after tapping. As one might anticipate, the degree of slag oxidation should be higher when the content of silicon is low in the ladle analysis. Figure 3 gives no evidence to this: in cases of the experimental melts, the (FeO) content in slag practically does not depend on the concentration of silicon in metal. No evidence is given referring to aluminum (Figure 4).

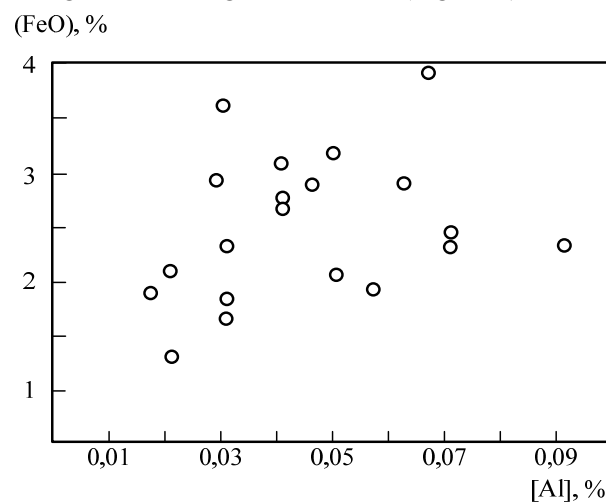


Figure 4. Influence of the aluminum content on the degree of slag oxidation

A higher concentration of aluminum in the ladle analysis sample does not prove sufficient de-oxidation of slag. This proves that at tapping, firstly, a considerable portion of aluminum is absorbed by metal, and second, the metal is not completely stirred with slag [3-15].

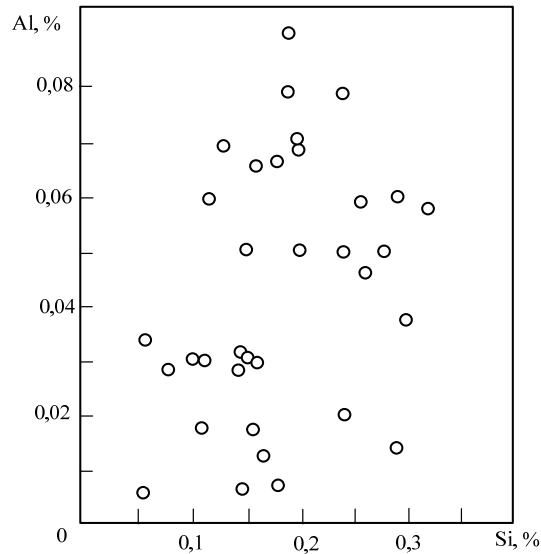


Figure 5. Relationship between the concentrations of aluminum and silicon in the ladle sample

As a result, the metal - slag system does not reach equilibrium as evidenced by the lack of relationship between the contents of silicon and aluminum in the ladle samples (Figure 5).

Conclusion

We have investigated the behavior of silicon, manganese and chromium added to the ladle to obtain the required chemical composition of steel, followed by blowing with an inert gas. It has been proven that absorbing elements mainly depends on the degree of de-oxidation in slag and metal, and first of all, the contents of FeO and MnO in slag and aluminum in metal.

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