

Effect of optical basicity on nitride capacity of titania containing slags.

Yu. I. Utochkin ^{*}, D. V. Stadnichenko ^{*}, V. T. Burtsev ^{**} and V. A. Grigoryan ^{*}.

^{*} Moscow steel and Alloys Institute, Russia

^{**} Institute of Metallurgy Russian Academy of Science

ABSTRACT

The nitride capacity (C_N) of $\text{CaO} - \text{Al}_2\text{O}_3 - \text{TiO}_x$ melts containing various amounts of components was determined by equilibrating the slags with gas mixtures and iron drop suspended in electromagnetic field. The values of C_N were calculated from nitrogen distribution ratios $\{(\text{pctN})/[\text{pctN}]\}$, coupled with oxygen potentials in system regulated by aluminium concentrations in the metal and activities of Al_2O_3 in slags. On the basis of these results and literature informations the relationship between C_N and optical slag basicity (λ) at 1873 K was obtained as $\log C_N = 9.09 - 27.67\lambda$. For all slags under study C_N decreased with increasing of λ from 0.64 to 0.84. The perspective of use titania containing slags with 20-30 pct of TiO_x for steel refining to remove nitrogen and sulfur as well as complex mechanism of denitrogenation in this case have been discussed.

INTRODUCTION.

Nitrogen for many steels is undesirable and detrimental impurity (as are oxygen, hydrogen and sulphur) and its content must be reduced to a minimum.

First this task is of the utmost importance for steels produced in electric arc furnaces that normally have higher nitrogen levels (80-120 ppm and even up to 250 ppm for alloyed steels) compared with steels produced in basic oxygen furnaces (30-40 ppm). In spite of many studies and efforts nitrogen has always been a very difficult element to remove from liquid metal. For example, hydrogen can be removed by vacuum degassing to about 1 ppm. But this degassing

is not sufficient effective in removing nitrogen because of its lower diffusion coefficient and activity in alloyed steel.¹ That is why under the best condition only about 30% of nitrogen can be removed by vacuum processes.²

For this reason it is very impotent to study the possibility of nitrogen refining by slag mixtures with high nitride capacities by ladle treatment of steel. Today a series of works have been reported on this problem²⁻¹⁹. As a result, titania containing slags appeared to be one of the most effective in slag denitrogenation.

In the present work the values for nitrogen capacity (C_N) in $\text{CaO-Al}_2\text{O}_3\text{-TiO}_x$ system containing various amounts of components were measured by equilibrating the slags with gas mixtures and levitated iron drop. On the basis of these results and previous investigations the relationships between C_N and optical slag basicity at 1873 K were obtained for TiO_x - based slags and another slag mixtures. The perspective of use titania containing slags for steel denitrogenation and desulphurization has been discussed.

EXPERIMENTAL PROCEDURE.

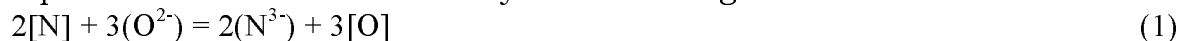
The technique of levitation melting for investigation of nitrogen equilibrium distribution between gas mixture, molten slag and iron drop suspended in electromagnetic field have been chosen. The principal advantage of this technique is the absence of the liquid metal and molten slag contacts with crucible. Details of the experimental apparatus and procedure have been described already in previous article²⁰.

Therefore, subject related to the present study are given briefly below. Five master slags with $\text{CaO/Al}_2\text{O}_3$ ratios equal 0.6 or 1.25 and titania contents varied from 10 to 46 % were prepared from high purity (>99.9 wt. %) calcium oxide, alumina and titanium oxide. The slag mixtures were premelted at 1873 K for about twenty minutes before being quenched, crushed and ground. The composition of these slag samples is shown in Table 1. Gas mixtures were prepared from high purity Ar and N_2 using a gas cleaning system. The nitrogen partial pressure (P_{N_2}) at the experiments was maintained equal 2 atm. The values of P_{O_2} in gas phase were controlled by a solid electrolyte cell. The samples of pure iron (mass 3 g) containing 0.001% [Ti], 0.119 % [Al], 0.003 % [O], 0.0029 % [S] and 0.0039 % [N] were used for investigations. The temperature in the reaction zone (iron drop and molten slag) was maintained at about 1873 ± 10 K in all experiments and measured by optical disappearing filament pyrometer. According to the previous results²⁰ and on the basis of time - dependence data obtained in this work it was found that 10 minutes is sufficient to attain the equilibrium of nitrogen distribution ratio under the experimental conditions because of metal and intensive stirring. For nitrogen analysis of slag the technique of oxidising fusion in a flow on inert gas with a chromatography apparatus described in details in previous articles was used^{6,12}. Oxygen and nitrogen contents in metal samples were analysed by extraction fusion using LECO analyzer, and sulphur content was determined by fusion-infrared absorptiometry.

RESULTS AND DISCUSSION

The results obtained from the gas - slag - metal equilibrium experiments are presented in Table 2.

The equilibrium nitrogen distribution between gas phase, molten slag and liquid metal can be described by the following reactions.



The equilibrium constant for equation (2) is:

$$K_2 = \frac{\{(\text{N}^{3-})\text{P}_{\text{O}_2}^{3/4} / \text{P}_{\text{N}_2}^{1/2}\} \{\gamma_{(\text{N}^{3-})} / (a_{\text{O}^{2-}})^{3/2}\}}{(4)}$$

and the nitride capacity (C_N) can be defined by:

$$C_N = \frac{\{(\text{N}^{3-})\text{P}_{\text{O}_2}^{3/4} / \text{P}_{\text{N}_2}^{1/2}\} \{K_2 (a_{\text{O}^{2-}})^{3/2} / \gamma_{(\text{N}^{3-})}\}}{(5)}$$

where (N^{3-}) is wt % nitrogen in the slag which is in equilibrium with the partial pressures of oxygen (P_{O_2}) and nitrogen (P_{N_2}) in the gas phase, $a_{(\text{O}^{2-})}$ is activity of free oxygen anions and $\gamma_{(\text{N}^{3-})}$ is activity coefficient of nitrogen in the slag.

According to reactions (1) and (3), noting that nitrogen distribution ratio $L_N = (\text{N}^{3-})/[\text{N}]$, the following expression can be derived:

$$\log C_N = \log L_N + 3/4 \log(\text{P}_{\text{O}_2}) - \log f_N + \log K_1 \quad (6)$$

where f_N is activity coefficient of nitrogen in the metal.

For reaction (3) $\Delta G^0 = 10500 + 20.37$ (Ref.1) and we can obtain the basic equation for C_N calculation using the experimental data for L_N :

$$\log C_N = \log L_N + 3/4 \log(\text{P}_{\text{O}_2}) - \log f_N - 850/T + 0.905 \quad (7)$$

The oxygen partial pressure in the system was controlled by aluminum in the metal and alumina in the slag according to the following reaction:



and from the equilibrium constant of equation (8):

$$\log(\text{P}_{\text{O}_2}) = 2/3 \{ \log K - 2(\log[\text{Al}] + \log f_{\text{Al}}) + \log a_{(\text{Al}_2\text{O}_3)} \} \quad (9)$$

The estimation of alumina activity in slag ($a_{\text{Al}_2\text{O}_3}$) have been given particular attention. For the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{TiOx}$ only a few data have been presented in literature¹⁴. For this reason the values of $a_{\text{Al}_2\text{O}_3}$ in these slags were calculated also using the theory of slag - melts as a phase with a collective electronic system¹.

The results for $a_{\text{Al}_2\text{O}_3}$ obtained by authors¹⁴ and in the present work coupled with corresponding values of $\log \text{P}_{\text{O}_2}$ and $\log C_N$ are shown in Table 2.

The nitride capacity for the slag system under study increases with titania content increasing (but not for 46% TiOx) and $\text{CaO}/\text{Al}_2\text{O}_3$ ratio decreasing.

Dependence of C_N on values of $a_{\text{Al}_2\text{O}_3}$ is not so considerable. In order to make comparisons these data with results for C_N obtained in the previous experiments using TiOx - based slags the nitride capacity was analyzed as a function on optical basicity (λ) which was chosen as a fundamental parameter of slag composition.

Figures 1 and 2 show the dependences of C_N on λ at 1873 K for titania containing slags and slags without TiOx content. The nitride capacities of all slags systems regardless of its constituents can be correlated with linear relationship. But it is necessary to notice that slags containing CaF_2 and more than 30% SiO_2 have not been included in this analysis because of complex mechanisms of nitrogen solubility in these system^{6,8,19}. The linear

regressions equations and the correlation coefficients R for nitride capacity have been obtained by statistical analysis as:

$$\log C_N = 9.09 - 27.67\lambda \quad R = -0.9828 \quad (10)$$

for titania containing slags and:

$$\log C_N = -3.03 - 12.16\lambda \quad R = -0.9639 \quad (11)$$

for slags without TiOx.

As it can be seen from Figures 1 and 2 for all slags under study C_N decreases with increasing of λ from 0.64 to 0.84.

The dependence of nitride capacity on slag composition can be described also by the following expression taking into account the effect of each component on the value of C_N .

$$\log C_N = \log C_N^0 + \sum b_i N_i' \quad (12)$$

where C_N^0 is nitride capacity of so called "standard" slag (50% CaO -50% Al_2O_3 aqual $10^{-12.9}$ at 1873 K (Ref. 11), N_i' is molar fraction of additional component in the "standard" slag:

$N'_{CaO} = X_{CaO} - \alpha X_{Al_2O_3}$; $N'_{Al_2O_3} = X_{Al_2O_3} - X_{CaO}/\alpha$; $\alpha = X_{CaO}^0 / X_{Al_2O_3}^0$ and for another components $N_i' = X_i$ (X_i is the molar fraction of any component in slag).

In Fig.3 relative nitride capacities $\log C_N' = \log C_N - \log C_N^0$ calculated for many slags²⁻¹⁹ are plotted against N_i' showing a linear relationships with values of b for Al_2O_3 , CaO, MgO, SiO_2 , TiOx and ZrO_2 equal 3.57, -1.96, -0.96, 1.71, 3.99 and 9.16 respectively. These data show that C_N values increase with increasing the contents of nitride formers and this effect of ZrO_2 is greater than TiOx and Al_2O_3 . It can be explained first of all by decreasing of $\gamma_{(N^3)}$ in slag mixtures according to equation(5). In Table 3 the experimental values of C_N obtained in present work are compared with the results calculated using equations (10) and (12). The most deviation (Δ) is 10.6% that shows the suitable reliability of these data.

On the basis of present study and previous articles^{4,15,17} it is possible to conclude that the use of titania containing slags (CaO- Al_2O_3 -TiOx) with high nitride capacities for steel refining from nitrogen under ladle treatment can be rather effective. The degree of denitrogenation (R_N) for treatment of liquid metal (mass m_{me}) by slag mixture (mass m_{sl}) in a ladle is described by the following equation¹⁷:

$$R_N = (1 - e^{-(m_{sl}/m_{me})L_N}) \cdot 100 \quad \% \quad (13)$$

In Fig. 4 the dependence of R_N on the mass of slag containing 27% CaO - 45% Al_2O_3 - 28% TiOx is shown. For example, when using 20 kg of this slag per tonne of steel that contains 0.06% [Al] ($\log P_{O_2} = -14.56$) the values of R_N is equal about 40%. The drawbacks of this treatment can be the reduction of TiOx and the transfer some titanium from the slag to the metal according to following reaction:



The concentration of titanium in steel reduced by 0.06 % of [Al] has been estimated from equation (14) as 0.1 %. However the residual content of [Ti] in iron samples after experiments was about 0.02%. This fact can be

explained that under treatment steel by TiOx - based slags the complex mechanism for nitrogen steel refining is realized: by extraction into slag with high C_N and by removal as TiN inclusions that precipitate preferentially in heterogeneous manner on the slag droplets as ready made receptors¹⁷.

It is necessary to notice that titania containing slags under investigation can be used for simultaneous refining steel from sulphur because of sufficient high sulphide capacities of these mixtures equal about $2 \cdot 10^{-4}$ (Ref. 21). For example, the degree of desulphurization (R_s) when using 20 kg of the TiOx - based slag per tonne of steel containing 0.06% [Al] can be more than 60% (Fig.4). In experimental samples the residual contents of sulphur in iron were about 0.002 %.

From the equation (10) for nitride capacity and relationship between sulphide capacity and optical basicity at 1873 K ²² ($\log C_s = 12.6\lambda - 12.3$), it is possible to obtain the dependence C_N on C_s for titania containing slags as:

$$\log C_N = -17.93 - 2.19 \log C_s \quad (15)$$

CONCLUSIONS.

The nitride capacity in CaO - Al₂O₃ - TiOx slags containing from 10 to 46% TiOx was measured by gas - slag - metal equilibrium using levitation melting technique. The values of C_N increased markedly with titania content increasing up to 30% and CaO/ Al₂O₃ ratio decreasing from 1.25 to 0.6. On the basis of these results and literature informations the relationships between C_N and optical slag basicity at 1873 K were obtained as $\log C_N = 9.09 - 27.67\lambda$ for TiOx - based slags and $\log C_N = -3.03 - 12.16\lambda$ for slags without titania. For all slags under study C_N decreased with increasing of λ from 0.68 to 0.82. The slags containing 20 -30 % TiOx can be used for rather effective steel refining under ladle treatment both from nitrogen and sulphur because of sufficient high nitride and sulphide capacities of these mixtures. The degrees of denitrogenation and desulphurization when using 20 kg of the slag per tonne of steel containing 0.06 % [Al] can be reached 40 and 60% respectively.

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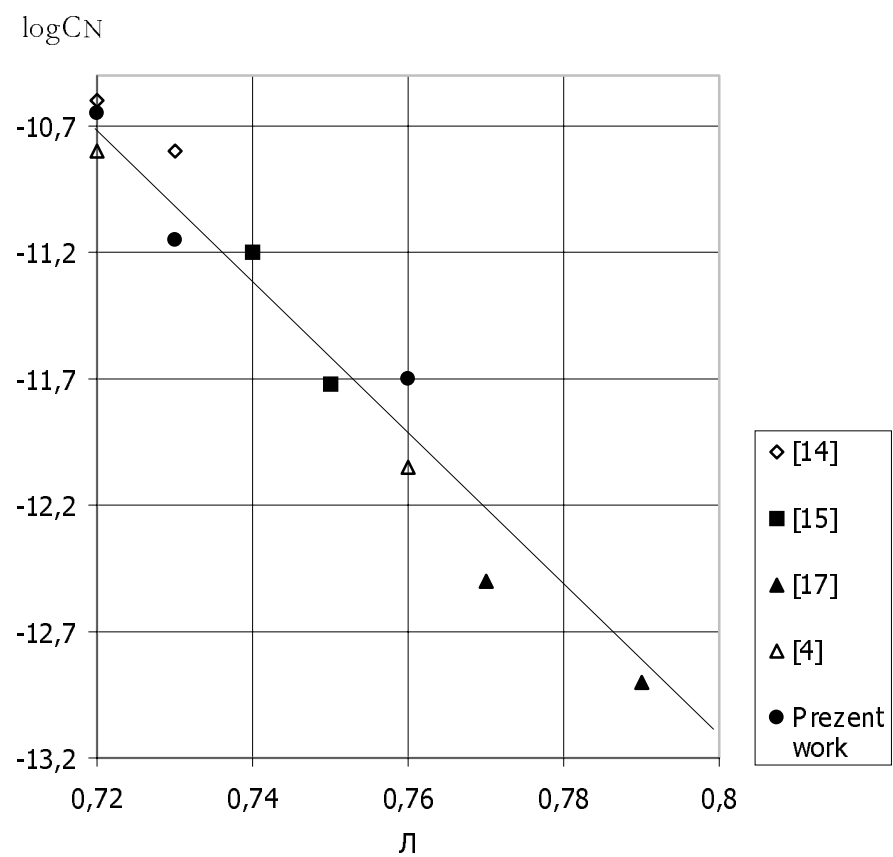


Fig 1. Nitride capacity C_N in titania containing slags as a function of optical basicity Λ at 1873 K.

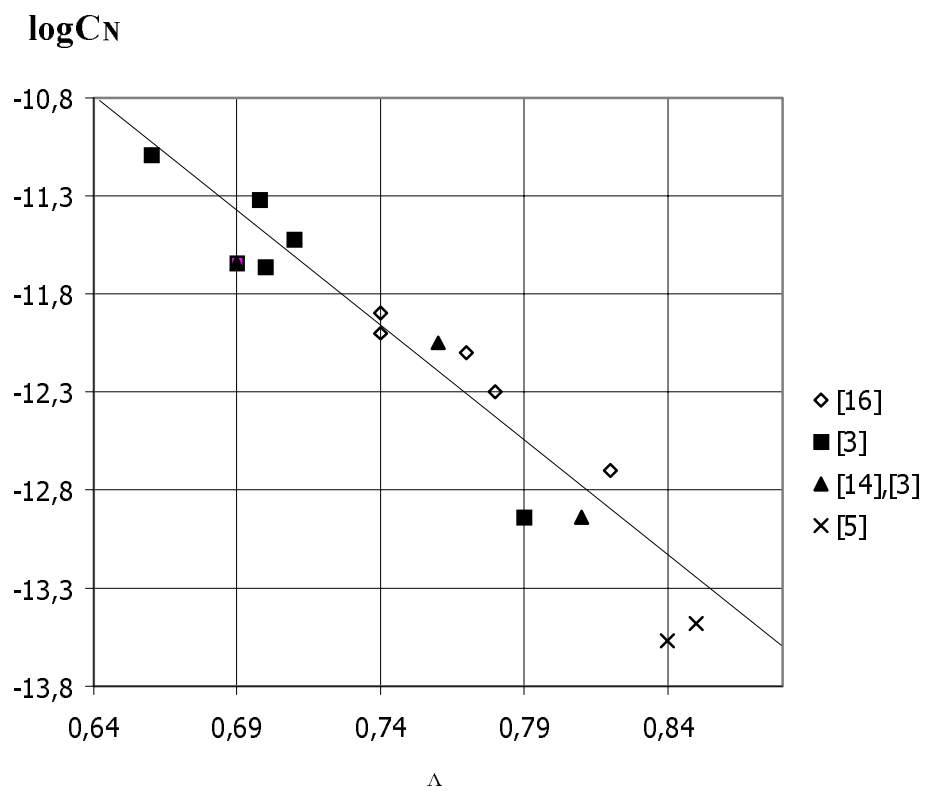


Fig. 2. Nitride capacity CN in slags without TiOx as a function of basicity Δ at 1873 K.

$$\log C_N = \log C_N - \log C_N^0$$

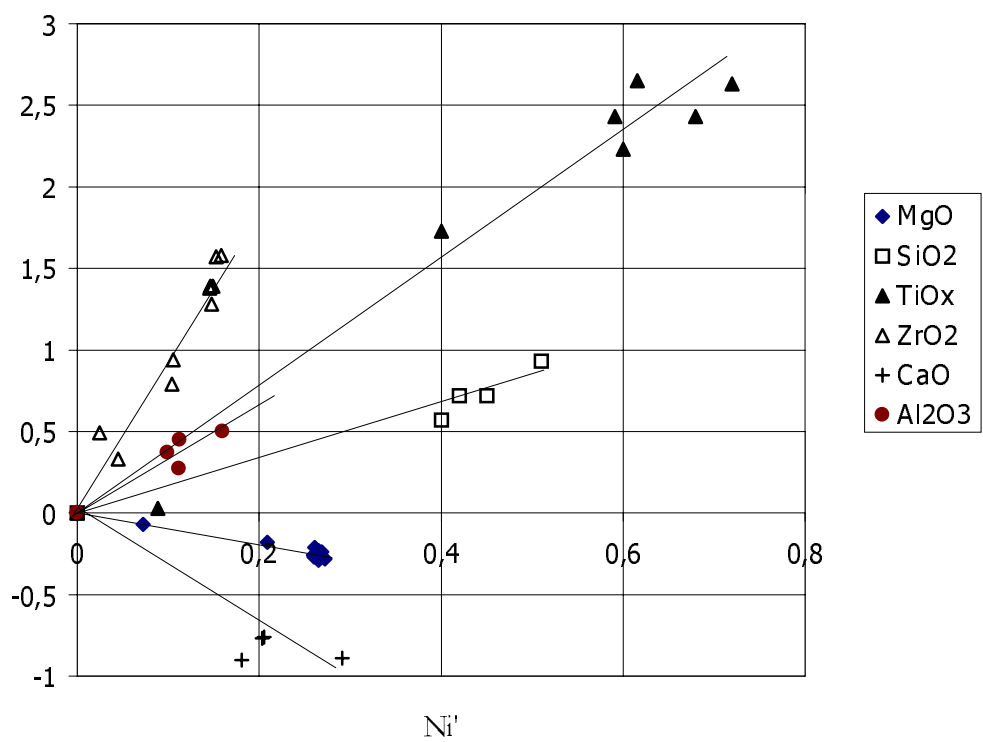


Fig. 3. Relative nitride capacity ($\log C_N' = \log C_N - \log C_N^0$) as a function of molar fraction of slag components N_i' .

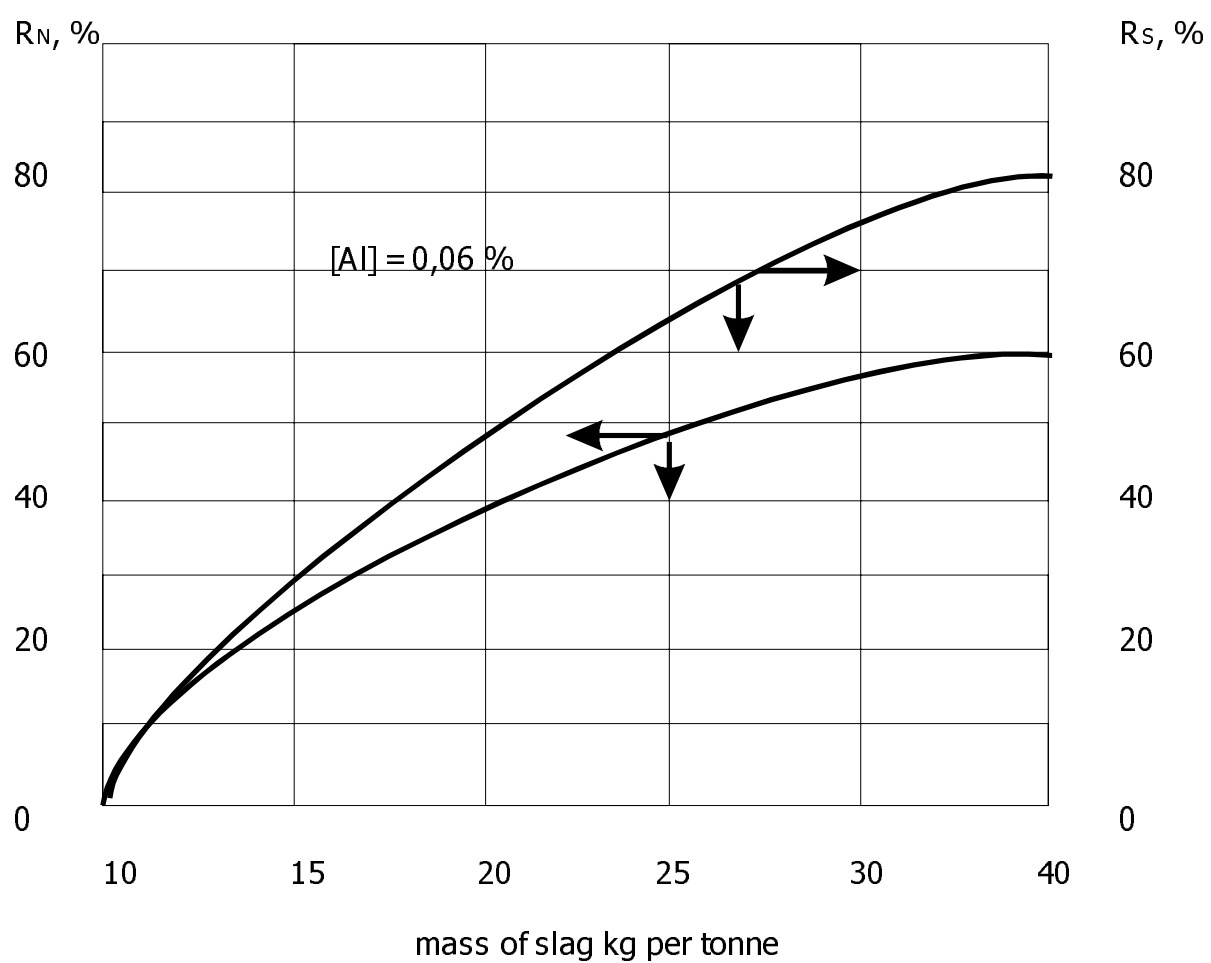


Fig. 4. Dependences of R_N and R_S for steel refining on the mass of slag mixture $CaO - Al_2O_3 - TiO_x$.

Table 1. Composition of slags under investigation.

№	CaO/ Al ₂ O ₃	CaO		Al ₂ O ₃		TiO ₂	
		%,wt	Xi	%,wt	Xi	%,wt	Xi
1	1,25	50	0,633	40	0,278	10	0,089
2	1,25	45	0,576	30	0,253	19	0,17
3	1,25	30	0,398	24	0,175	46	0,427
4	0,6	30	0,63	50	0,384	20	0,196
5	0,6	27	0,379	45	0,346	28	0,275

Table 2. Equilibrium data for the gas - slag - metal experiments in CaO - Al₂O₃ - TiO_x melts.

№	(N) wt%	[N] wt%	logL N	[Al] wt%	a _{Al₂O₃} (1),calc	a _{Al₂O₃} (2)) Ref.14	logPo ₂ (1),atm	logPo ₂ (2),atm	logC _N (1)	logC _N (2)	Δ, %
1	0,06 1	0,066	- 0,08	0,019 8	0,16	0,64	-14,28	-13,88	- 12,1 2	- 11,8 2	2,5 5
2	0,15 2	0,073	0,44	0,020 0	0,14	0,64	-14,33	-13,89	- 11,6 3	- 11,3 0	2,9 2
3	0,09 4	0,015	0,50	0,022 0	0,10	0,05	-14,43	-14,63	- 11,6 5	- 11,8 0	1,2 7
4	0,14 5	0,056	0,41	0,022 0	0,20	0,64	-14,22	-13,89	- 11,5 9	- 11,3 4	2,2 2
5	0,43 5	0,045	1,10	0,020 0	0,19	0,64	-14,24	-13,89	- 10,9 1	- 10,6 5	2,4 7

Table 3. The experimental values of nitride capacity in comparison with data calculated from equations (10) and (12)

Slag composition, wt%			logCN	logCN	$\Delta, \%$
CaO	Al ₂ O ₃	TiO ₂			
$\log C_N = 9.087 - 27.67\lambda$				experiment	
50	40	10	-11,982	-11,822	1,3
45	36	19	-11,571	-11,300	2,4
30	24	46	-11,149	-11,797	5,5
30	50	20	-11,068	-11,337	2,4
27	45	28	-10,127	-10,651	4,9
$\log C_N = \log C_N^0 + \sum b_i N_i$				experiment	
50	40	10	-12.86	-11,822	8,8
45	36	19	-12.50	-11,300	10,6
30	24	46	-11.39	-11,797	3,5
30	50	20	-11.60	-11,337	2,3
27	45	28	-11.35	-10,651	6,6