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INVESTIGATION OF NITROGEN SOLUBILITY IN SLAG MELTS UNDER DIFFERENT OXYGEN POTENTIALS

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Synopsis: Nitrogen solubility in various oxide-, silicate- and fluoride systems was measured by application of original experimental technique with regulation and precise control of oxygen partial pressure Po_2. A special chromatography technique was developed for accurate determination of nitrogen content in slag. Experimental findings indicate that nitrogen content in studied oxide- and silicate- melts is correctly described by the proper analytic equations. In fluoride slags this dependence has more complicated character. With increasing SiO_2 content in silicate melts from 20 pct to 40 pct nitrogen valence changes from -3 to -2 and nitrogen solubility has minimum according to two different mechanisms of nitrogen dissolution. Possibility of nitrogen dissolution not only as nitride form (at $\log Po_2 < -11$ atm) but as nitrate form (at $\log Po_2 > -11$ atm) has been shown for CaO-Al_2O_3 system.

Key words: oxygen potential, nitrogen solubility, nitrogen valence, solid electrolyte, nitride capacity, free nitride, incorporated nitride, ladle treatment.

1. Introduction

The reliable data on the solubility of nitrogen in slag melts are necessary to use them for removal of nitrogen from iron and steel as well as for the protection of steel from nitrogen absorbtion during the refining and continuous casting. Nitrogen solubility in oxide melts as any impurity depends not only on the composition and temperature of the slag but is strongly determined by oxidation potential of the system according to the following equation [1]:

$$(N) = C_N \cdot P_{N_2}^{1/2} \cdot P_{O_2}^{\nu_N/4} \qquad (1)$$

Where C_N is nitride capacity, ν_N is nitrogen valence in slag and Po_2 is oxygen partial pressure. At present there have been rather numerous experimental results on investigations of nitrogen dissolution in various slag mixtures [2]-[6]. However these data are often contradictive, as well as the points of view on this problem of various authors. This fact can be probably explained by the lack of reliable universal methods for the experimental study of nitrogen solubility depending on various parameters. In this work nitrogen solubility in molten oxide- (CaO-Al_2O_3, CaO-Al_2O_3-TiO_2), silicate- (CaO-Al_2O_3-SiO_2) and fluoride (MgO-CaF_2, CaO-CaF_2, TiO_2-CaF_2, BaO-BaF_2) systems has been measured by application of original experimental technique with regulation and precise control of the oxygen potentials over the range of $\log Po_2$ from -17 to -9 atm.

2. Experimental procedures

A thermodynamic equlibration technique used for saturation of slag by nitrogen is presented in Figure 1. Preliminarily smelted from chemical pure components 0.3-0.4 g slag sample was placed into experimental cell consisting of: $ZrO_2(Y_2O_3)$ crucible of 6 mm ID hermetically connected with protective Al_2O_3 tube; molybdenum wire inserted into the crucible; molybdenum capillary of 2mm ID to feed of high purity nitrogen into the cell; manostat to provide P_{N_2} = 1 atm. The inner surface of crucible was coated with thin molybdenum layer (< 20 μm) to prevent the interaction between the material of crucible as solid electrolyte and molten slag. Before the experiment the cell was blown by nitrogen with flow rate of 0.25-0.35 ml/s and then was slowly lowered into the alumina crucible with molten metal of 1 kg mass placed in the Tammann furnace at 1873 K. The following melts were used to provide the different oxygen potentials of metal-slag system: molten iron deoxidized by Al and Zr - for values of $\log P_{O_2}$=-13..-17 atm; iron-carbon alloys - for $\log P_{O_2}$=-11..-13 atm and molten nickel deoxidized by Cr - for $\log P_{O_2}$=-9..-11 atm. The time required to reach equilibrium ranged from 40 to 60 min. Equilibrium was attained either by adding TiN or AlN as a source of nitrogen to the slag sample or simply by using the samples without any initial nitrogen at the beginning.

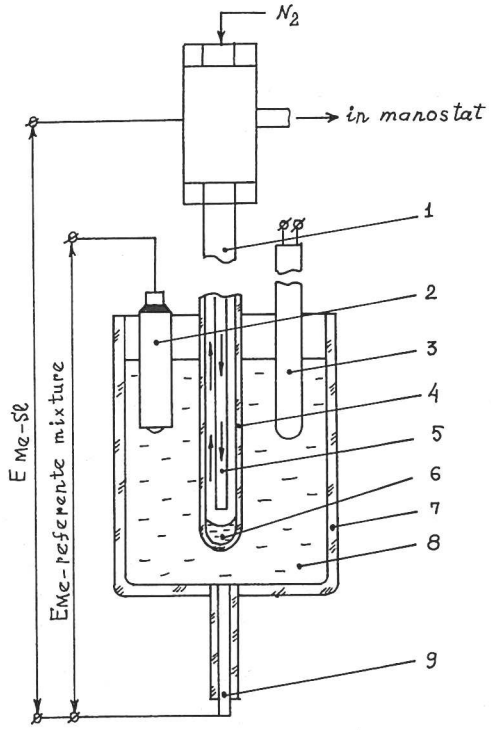

Fig.1 Schematic diagram of apparatus: 1-protective Al_2O_3 tube, 2-oxygen sensor, 3-thermocouple, 4-$ZrO_2(Y_2O_3)$ crucible, 5-Mo capillary, 6-slag sample, 7-alumina crucible, 8-molten metal, 9- Mo wire.

The electrochemical voltage of the cell (E_{Me-Sl} in Figure 1.) Mo | slag melt || solid electrolyte $ZrO_2(Y_2O_3)$ || liquid metal | Mo was continuously measured. Owing to the oxygen permeability of solid electrolyte in 10-15 min E_{Me-Sl} reduced to about zero i.e. oxygen potentials of slag melt and liquid metal were equal. The oxygen potential of metal was continuously measured by the use of the special worked out oxygen sensors for long-time measuring. Thus in the described technique metal bath played the role of the regulator and stabilizer of slag oxidation potential. After the attainment of equilibrium between molten slag and nitrogen the cell was pulled out and sample was quenched in nitrogen atmosphere and analyzed for the nitrogen content.

Nitrogen analysis of slag was given particular attention. The technique of oxidizing fusion in the flow of inert gas with chromatography apparatus was chosen [7]. This technique was based on the smelting of slag sample with the oxidizing flux (29 pct PbO, 29 pct PbO_2, 29 pct $PbCr_2O_3$ and 13 pct B_2O_3) in alumina boat placed into special reactor at 1373-1423 K. Nitrogen extracted from the melt was absorbed by the flow of helium running through the reactor. Nitrogen content was determined by chromatograph with pyroelectric detector.This method provided complete nitrogen extraction from the slag. The sensibility limit of nitrogen analyses was about 10^{-4} pct and reproducibility changed from 3 to 17 pct when nitrogen contents decreased from 0.1 pct to 0.001 pct for 0.1-0.2 g sample.

3. Results and discussion

In Figure 2 the nitrogen content in CaO-Al_2O_3 melts at 1873K is shown as a function of P_{O_2} with P_{N_2} = 1 atm. From this figure it can be simply inferred that nitrogen solubility for logP_{O_2}= -13..-16 atm is described rather correctly by Eq. (1). The slopes of the experimental curves in the plot of $\log\{(N)/\sqrt{P_{N_2}}\}$ versus logP_{O_2} have given the accurate values of nitrogen valence in slag. This is the advantage of the method under discussion. The linear regression equations and the correlation coefficients R for nitrogen solubility in studied slags have been obtained by statistical analysis of the experimental results at 1873 K.

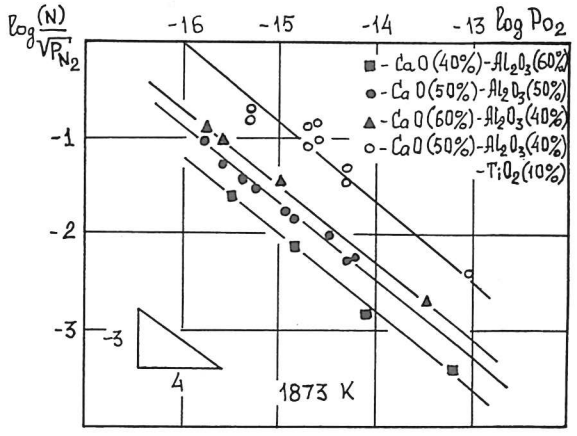

Fig.2 Nitrogen solubility in CaO-Al_2O_3 melts.

For CaO(50%)-Al_2O_3(50%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-13.76 \pm 0.83)+\{(-3.22\pm0.22)/4\}\log P_{O_2}; \quad (2)$$
$$R = -0.9954.$$

For CaO(60%)-Al_2O_3(40%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-13.58 \pm 1.26)+\{(-3.23 \pm 0.34)/4\}\log P_{O_2}; \quad (3)$$
$$R = -0.9987.$$

For CaO(40%)-Al_2O_3(60%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-14.26 \pm 1.90)+\{(-3.25 \pm 0.53)/4\}\log P_{O_2}; \quad (4)$$
$$R = -0.9969.$$

From Eq.(2)-(4) it follows that nitrogen capacities exhibit a tendency to the slight increasing with increasing of CaO/Al_2O_3 pct ratio in the melts. To some extent this fact contradicts the data of other authors [4], [5], [8], [9]. However if the confidence intervals for C_N are taken into account it can be concluded that present results practically correlate to previous data obtained in carbon presence and for γ_N strictly equal -3. As can be seen in Figure 2 the behavior of nitrogen solubility in the CaO-Al_2O_3-TiO_2 system is the same as in the CaO-Al_2O_3 melts. But the presence of TiO_2 in slag enhances the nitrogen content considerably under the identical conditions.

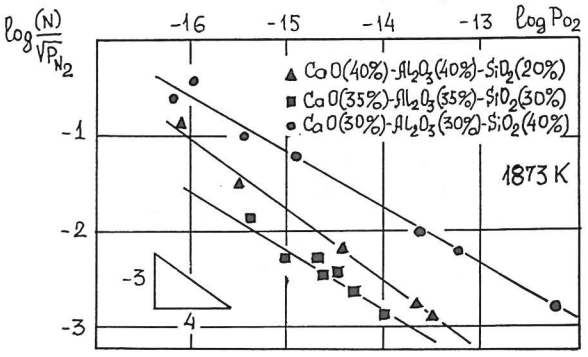

Fig.3 Nitrogen solubility in CaO-Al_2O_3-SiO_2 melts

The CaO-Al_2O_3-SiO_2 systems were studied to examine the dependence of nitrogen content on oxidation potentials and composition of the melts. In Figure 3 the total nitrogen contents for different concentrations of SiO_2 at 1873 K with CaO/Al_2O_3 = 1 on pct ratio basis and P_{N_2}=1 atm are plotted against P_{O_2}.

The proper linear regression equations and the correlation coefficients have been obtained as follows:

For CaO(40%)-Al2O3(40%)-SiO2(20%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-13.03 \pm 1.25)+\{(-2.99 \pm 0.34)/4\}\log P_{O_2}; \quad R = -0.9965. \tag{5}$$

For CaO(35%)-Al2O3(35%)-SiO2(30%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-11.56 \pm 2.21)+\{(-2.50 \pm 0.60)/4\}\log P_{O_2}; \quad R = -0.9660. \tag{6}$$

For CaO(30%)-Al2O3(30%)-SiO2(40%) melt:

$$\log(N)/\sqrt{P_{N_2}} = (-9.97 \pm 1.02)+\{(-2.34 \pm 0.28)/4\}\log P_{O_2}; \quad R = -0.9910. \tag{7}$$

As it is shown in Figure 4 the dependence of nitrogen solubility on silica content in slag has complicated character with minimum at about 30 pct SiO2. This fact may be explained proceeding from the assumption of two simultaneous mechanisms of nitrogen dissolution in silicate melts as free nitride or incorporated nitride [5]. According to the first one the reaction of nitrogen with a basic component of slag can be described, in general, by the following equation:

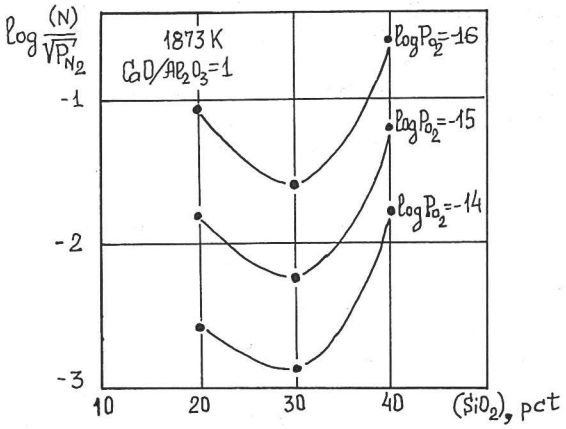

Fig.4. Nitrogen solubility in silicate melts as function of SiO2

$$1/2\ N_2 + 3/2\ O^{2-} = N^{3-} + 3/4\ O_2 \tag{8}$$

From Eq.(8) it is clear that free nitride ion content depends on the activity of O^{2-} which in turn is determined by the activity of CaO. With increasing SiO2 content in CaO-Al2O3-SiO2 slags the activity of CaO decreases and as a result nitrogen solubility decreases too. But at the concentrations of SiO2 more than 30 pct nitrogen may react with a silicate network replacing oxygen in the polysilicate ions. In this case the dissolution of nitrogen as incorporated nitride can be written by a series of possible equations considering the influence of the size and structure of polysilicate ions, the number of the bonds between nitrogen and polysilicate ions and other factors on this process [5]. If nitrogen is assumed to replace bridging or nonbridging oxygens having two bonds in silicate rings it will have valence equal -2. Really, experimental results {Eq.(5)-(7)} show that in silicate melts nitrogen valence changes from -3 to about -2 with increasing SiO2 content from 20 pct to 40 pct.

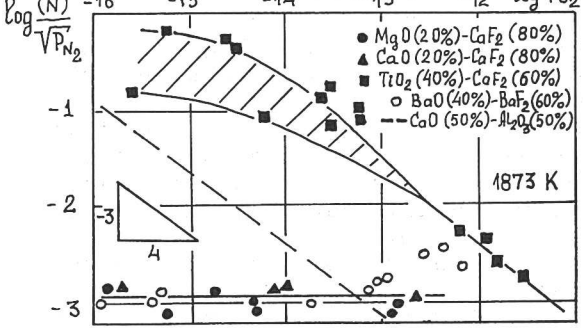

Fig.5. Nitrogen solubility in oxyfluoride melts.

In oxyfluoride (CaO-CaF2, MgO-CaF2 and BaO-BaF2) systems the dependence of nitrogen solubility on oxygen potential has not been revealed at all. As it is shown in Figure 5 the nitrogen concentrations in

these melts are very low not more than 10^{-3} pct at 1873 K, P_{N_2} = 1 atm and $\log P_{O_2}$=-13..-16 atm in contrast to literature data [10], [11]. However the latter was obtained by using graphite crucibles to provide the carbon saturation of slag samples. Of all studied slags the highest nitrogen solubility under the same nitrogen and oxygen pressures has been obtained in TiO_2(40 pct)-CaF_2(60 pct) melt (Figure 5). Thus in both oxide- and oxyfluoride systems the presence of TiO_2 enhances the nitrogen content considerably. At $\log P_{O_2} < -12.5$ atm, P_{N_2} = 1 atm and 1873 K in TiO_2-CaF_2 melt the oxynitride phase can be formed. The presence of thin oxynitride layer on the surface of the slag sample likely causes the large scattering of experimental data as can be seen in Figure 5.

Possibility of nitrogen dissolution not only as nitride form but as nitrate form at $\log P_{O_2} > -11$ atm has been shown for CaO(50 pct)- Al_2O_3(50 pct) system. In this case, shown in Figure 6, the plot of log(N) versus log P_{O_2} at constant P_{N_2} is presented by two straight-line branches with different slopes (-3/4 and +5/4 respectively) as it has been already known for sulphur and phosphorus [1]. Certainly the behavior of nitrogen solubility under oxidation conditions demands the further more detailed investigations.

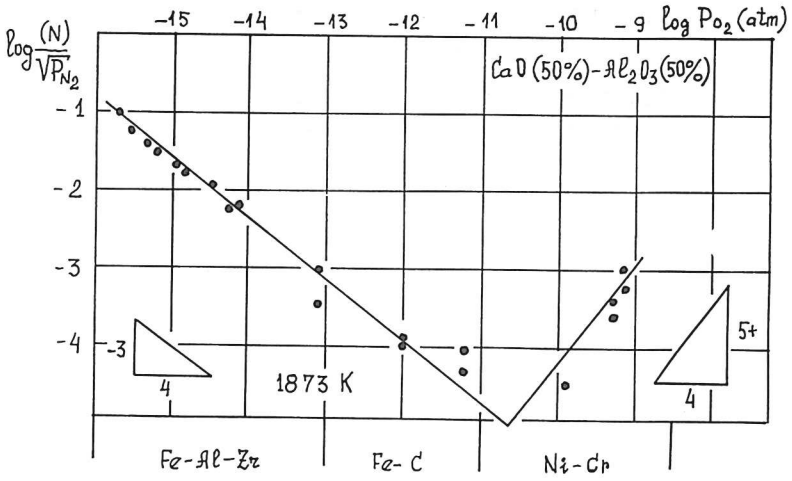

Fig.6. Nitrogen solubility in CaO-Al_2O_3 melts as nitride and nitrate forms

On the basis of present study the perspective of liquid metal refining from nitrogen under the ladle treatment by slag mixtures can be discussed. The good results may be obtained only by the use of slags containing TiO_2 with high values of nitride capacity and small initial nitrogen concentrations (<0.02 pct) under low oxygen potentials ($\log P_{O_2} < -16$ atm or $a_{[O]}<3.10^{-5}$) when the distribution coefficient $L_N=(N)/a_{[N]}$ is equal 30-50. Indeed the experimental data have shown that in this case the degree of denitration for liquid iron and alloyed steel reached 30-50 pct [12], [13].

4. Conclusions

1. The nitrogen solubility in oxide- and silicate melts is rather correctly described by Eq.(1) over the range of $\log P_{O_2}$=-12..-16 atm.

2. In the studied oxyfluoride (CaO-CaF_2, BaO-BaF_2, MgO-CaF_2) melts the nitrogen contents do not comply with Eq.(1) likely because of F^{-1} ions effect.

3. In silicate melts with increasing of SiO_2 content from 20 pct to 40 pct nitrogen valence changes from -3 to -2 and nitrogen solubility has minimum at about 30 pct SiO_2 according to two mechanisms of nitrogen dissolution.

4. The presence of TiO_2 in slags enhances nitrogen solubility markedly. The highest nitride capacity has been found in TiO_2(40 pct)-CaF_2(60 pct) system equal $10^{-11.6}$ at 1873 K.

5. Nitrogen in slag melts can dissolve not only as nitride form at $\log P_{O_2}<-11$ atm, but as nitrate form at $\log P_{O_2}>-11$ atm . It has been demonstrated for CaO(50 pct)-Al_2O_3(50 pct) system.

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