

Study on the Oxidation of Ti-Bearing Slag

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ABSTRACT: The study on the oxidation of (TiO_{1.5}) was carried out by oxygen sensor of the solid electrolyte. The rate and the kinetics equations for the oxidation were set up as :

$$\frac{dP_{O_2}}{dt} = \frac{DA}{\delta v} (P_{O_2}^* - P_{O_2}) = \frac{k_d A}{V} (P_{O_2}^* - P_{O_2}) = \frac{k_d}{h} (P_{O_2}^* - P_{O_2})$$

and

$$\ln \frac{P_{O_2}^* - P_{O_2}}{P_{O_2}^* - P_{O_2, t=0}} = -\frac{k_d}{h} t$$

The Arrhenius activation energies of oxygen diffusion in slag were obtained in the following: $E_A = 159.7 \text{ kJ} \cdot \text{mol}^{-1}$ (ferric oxide free sample), $E_B = 117.5 \text{ kJ} \cdot \text{mol}^{-1}$ (4mass% ferric oxide sample), $E_C = 111.5 \text{ kJ} \cdot \text{mol}^{-1}$ (8mass% ferric oxide sample). The oxygen diffusion coefficient D in molten slag is about 3.9 to $7.9 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

I. INTRODUCTION

In China, more than 3×10^6 tons of the exhausted slag baring titania (TiO₂.25%) are produced in Panzhihua iron making plant each year, so the comprehensive utilization of the slag is a urgent task. However, the dispersion and the fine grain of the mineral phases bearing Ti make it very difficult to recovery titania from the slag by metallurgical or mineral processes traditionally.

A novel technique to recovery titania from the slag is proposed, in which three continues processes are involved^[1-3]. The first process of that is the selective concentrating the dispersed

titania into a designed phase – Perovskite (CaTiO_3), which grows selectively up to larger grain and, then, is separated from tailing by mineral dressing. The experimental results showed that the amount of Perovskite phase is obviously affected by basicity and oxidability of the slag, the latter is associated with the oxidation of ($\text{TiO}_{1.5}$). Therefore, study on the oxidation kinetics is a key to the process.

Since a number of previous investigations on kinetics of Ti-bearing slag were almost concerned with the reduction process of titania oxide^[4-7], no published data could provide useful information about behavior of the ($\text{TiO}_{1.5}$) oxidation associated with oxygen migration within the molten slag.

In this paper, the subject is to investigate the behavior of ($\text{TiO}_{1.5}$) oxidation in order to set up the kinetic equation. It was carried out by monitoring the change of e. m. f. with time to determine an oxidization rate based on quasi-equilibrium principle^[8,9]. The experiments showed that the value of e. m. f. decreased with time regularly, which reflects upon the relationship between the ($\text{TiO}_{1.5}$) oxidation and time.

Comparing with the TGA and chemical analysis methods for kinetic study, E. M. F. is more accurate, instant, and convenient, and it has been widely used in steel-making monitoring process controlling and so on^[10-15]. For example, Ricket and Oberg etc. studied the oxygen diffusion in the metals by this method^[12-15], but no published reports involved the kinetics on ($\text{TiO}_{1.5}$) oxidation in Ti-enriched slag in this way until now.

II. EXPERIMENTAL DETAILS

A. Installation

1. The experiment was carried out in a platinum crucible with a vertical MoSi_2 furnace (Fig. 1). The Pt-13%Rh/Pt thermocouple, which was calibrated using a standard one, and the Shimaden SR-53 programmable temperature controller were used for temperature controlling (within ± 1). The installation detail for the experiment is shown in Fig. 1.

2. The arrangement of the oxygen concentration cell was schematically shown in Fig.2. The composition of solid electrolyte was $\text{ZrO}_2 + (9 \text{ pct CaO})$, and the reference electrode was a mixture of molybdenum and MoO_2 powder in the molar ratio 9 : 1. Pt wires served as the electrode lead for the electrodes. The e. m. f. of the cell $\text{Pt}, (\text{Slag}) \mid \text{ZrO}_2\text{-CaO} \mid \text{Mo, MoO}_2 \mid \text{Pt}$ was measured in the temperature range 1713K-1743K with Keithely 610C Solid State Electrometer ($10^{14}\Omega$) and a high input impedance ($10^{11}\Omega$) 192 digital Voltmeter.

B. Sample Preparation

The compositions of synthetic sample, which was made by purity 99 pct. oxides, are shown in Table I. All the slag samples were dried in an oven at the temperature of 453K for 3 h, and then were molted as well as reduced in a graphite crucible with an induction furnace (8kHz) at 1773K for an hour.

C. Experimental Procedure

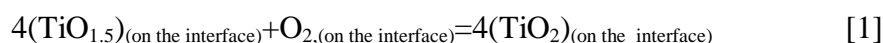
Sample was placed into the crucible by an alumina tube when designed temperature was reached. After the sample melted, the oxygen sensor was plugged into the predetermined position and fixed by a location ring (Fig.1) to monitor the e. m. f.. The values of e. m. f. were taken when their variation was within $\pm 3 \text{ mv}$ shown in Fig.3. The designed temperatures for the experiment were 1713K, 1723K, 1733K and 1743K.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Mechanism of Slag Oxidation

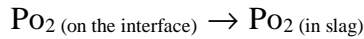
The oxidation mechanism for $(\text{TiO}_{1.5})$ can be described presumably as following four steps as in Fig. 4.

1. Oxygen molecules are diffused from air to the interface of slag/gas and then absorbed;
2. On the interface, chemical reaction [1] is occurred:



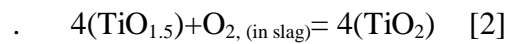
Therefore, the oxygen gradient is formed along the vertical direction progressively within slag;

3. (TiO₂) on the interface is diffused towards the interior of slag through the boundary layer and (TiO_{1.5}) in slag diffused up to the interface. Apparently, the oxide diffusions directly make the oxygen partial pressure in slag monitored by the cell increase with time, which could be expressed as:



Minoru SASABE et al had proved that the process is a .indirect transferring of oxygen^[17]. So the oxide diffusions could be treated as an oxygen diffusion, which means that the oxygen diffusion is carried out by above diffusions.

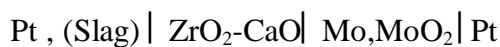
4. Meanwhile, the oxidizing reaction [2] takes place in slag as the increasing of the oxygen partial pressure.



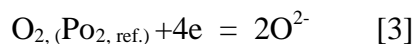
Since the rate of step 1, as gas transmission and absorption, is much faster than that of the oxygen diffusion in step 3^[18,19] and the chemical reactions [1] and [2] could reached equilibrium instantly at high temperature^{[8,9][18,19]}, thus, the oxygen diffusion in molten slag could be considered as the rate controlling step of the (TiO_{1.5})'s oxidation.

B. Experimental Results

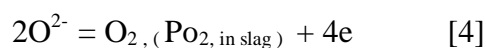
The concentration cell of oxygen is as follows:



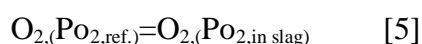
The half-cell reaction on the right side is



And the reaction on the left-hand side is



The overall reactions may be written as



Where $P_{O_2,ref}$ is the oxygen partial pressure of reference electrode and $P_{O_2,in\ slag}$ is the oxygen partial pressure of measured electrode which is just corresponding to the oxygen partial pressure in equilibrium with reaction [2] in slag^[16].

Gibbs free energy change associated with virtual cell reaction[5] calculated using following relationship:

$$\Delta G = RT \ln\left(\frac{P_{O_2,in\ slag}}{P_{O_2,ref}}\right) = -nEF \quad [6]$$

Where $n=4$, the number of electrochemical equivalents in the cell reaction; F is the Farady Cons., and E is e. m. f of the measured cell.

Omitted “in slag” from the $P_{O_2,in\ slag}$,

$$P_{O_2} = P_{O_2,ref} \cdot \exp\left(\frac{-4EF}{RT}\right) \quad [7]$$

The relationship between P_{O_2} and time (t), which could be calculated based on equation [7] with experimental data of $E-t$, is shown in from Fig.5 to Fig.8.

C. Kinetic equation

As the continuous migration of oxygen during the oxidation, the oxygen partial pressure of the reaction [2], $P_{O_2} (in\ slag)$, is increased, which depends on the rate of oxygen diffusion in slag.

Apparently, the oxidizing rate of $(TiO_{1.5})$ could be expressed by $\frac{dP_{O_2}}{dt}$ according to the reaction

[2]. If the deviation of P_{O_2} between the interface of gas/slag and in slag matrix is taken as the driving force of oxygen migration, the rate equation of the oxidation can be written as:

$$\frac{dP_{O_2}}{dt} = \frac{DA}{\delta v} (P_{O_2}^* - P_{O_2}) = \frac{k_d A}{V} (P_{O_2}^* - P_{O_2}) = \frac{k_d}{h} (P_{O_2}^* - P_{O_2}) \quad [8]$$

where $P_{O_2}^*$ (kPa) is the partial pressure of oxygen on the interface in equilibrium with reaction

[1], D diffusion coefficient of oxygen in slag ($m^2 \cdot s^{-1}$), δ the thickness of concentration boundary

layer (m), V the volume of molten slag (m³), A the area of interface (m²), h the depth of slag bath (h=V/A=0.02 m³/m²), and k_d the coefficient of mass transmission of oxygen ($k_d = D/\delta$) m·s⁻¹.

Integrating the equation [8], gives

$$\ln \frac{P_{O_2}^* - P_{O_2}}{P_{O_2}^* - P_{O_2,t=0}} = -\frac{k_d}{h} t \quad [9]$$

or,

$$P_{O_2} = P_{O_2}^* - (P_{O_2}^* - P_{O_2,t=0}) \cdot e^{-\frac{k_d}{h} t} \quad [10]$$

where $P_{O_2,t=0}$ is the value of P_{O_2} at the initial time (t=0). $P_{O_2}^*$ can be yield by [4] through extrapolating P_{O_2} at the time approaching to infinity (t..).

D. Calculation of k_d

The relationship of $\ln \frac{P_{O_2}^* - P_{O_2}}{P_{O_2}^* - P_{O_2,t=0}}$. t was calculated based on [4] and shown in Fig. 9 to

Fig.12.. k_d values obtained by the line's slops were shown in Table II in which they were varied from about 3.9×10^{-6} m·s⁻¹ to 7.9×10^{-6} m·s⁻¹. If 1×10^{-5} m is taken as the value of .(according to reference ^[18,19], mid-value) , the diffusion coefficient D of oxygen in the slag can be evaluated as $3.9 \cdot 7.9 \times 10^{-9}$ m²·s⁻¹, which is similar to King's data $0.6 \cdot 1.9 \times 10^{-9}$ m²·s⁻¹^[20].

Combing k_d values and the experimental data with the equation [10] plots of P_{O_2} against time (t) were obtained as in Fig. 5 to Fig. 8, which, obviously, are very close to the experimental results. It means that the values of P_{O_2} calculated by equation [10] is in good agreement with the experimental ones. Therefore, the presumed mechanisms for (TiO_{1.5}) oxidizing and the kinetics equation gotten based on this are reasonable.

E. Calculation Of Arrhenius Energy

The plots of $\ln k_d$ against $1/T$ is shown in Fig.13, the apparent activation energies can be calculated according to Arrhenius equation as follows:

$$E_A = 159.7 \text{ kJ}\cdot\text{mol}^{-1} \text{ (ferric oxide free sample)}$$

$$E_B = 117.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ (4mass\% ferric oxide sample)}$$

$$E_C = 111.5 \text{ kJ}\cdot\text{mol}^{-1} \text{ (8mass\% ferric oxide sample)}$$

Where E_A , E_B and E_C represents apparent activation energies of oxygen diffusion in molten slag respectively. The data published by K. NAGATA et al^[21] shows the activation energy of oxygen self-diffusion in blast-furnace-type slag, which is Al_2O_3 - SiO_2 - CaO system, is 126.5-185.8 kJ/mol. (34-40 kcal/mol. $\pm 11\%$). at temperature from 1335° to 1513°. Obviously, the present results are very close to K. NAGATA's value. According to the values of the activation energy, iron oxide added in slag could apparently drop the diffusion resistance of oxygen, but no big effects appears when the content of iron oxide is more than 4 mass%. The effect of iron oxide on the oxygen diffusion in the slag will be published in another paper in detail.

IV. CONCLUSIONS

A. At the investigated temperature range and in atmosphere, the rate controlling step of $(\text{TiO}_{1.5})$ oxidization in Ti-enriched slag is oxygen diffusion from the interface to the matrix. The rate of oxygen transmission can be improved by 4 mass % of iron oxide addition in the slag, as a result, the oxidation of $(\text{TiO}_{1.5})$ is accelerated.

B. The rate equation and the kinetics equation of the oxidization are as follows:

$$\frac{dP_{O_2}}{dt} = \frac{DA}{\delta v} (P_{O_2}^* - P_{O_2}) = \frac{k_d A}{V} (P_{O_2}^* - P_{O_2}) = \frac{k_d}{h} (P_{O_2}^* - P_{O_2})$$

and

$$\ln \frac{p_{O_2}^* - p_{O_2}}{p_{O_2}^* - p_{O_2, t=0}} = -\frac{k_d}{h} t$$

C. The apparent activation energies of oxygen diffusion in molten slag are respectively:

$$E_A = 159.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$E_B = 117.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$E_C = 111.5 \text{ kJ} \cdot \text{mol}^{-1}$$

D. The oxygen diffusion coefficient in the molten slag is about:

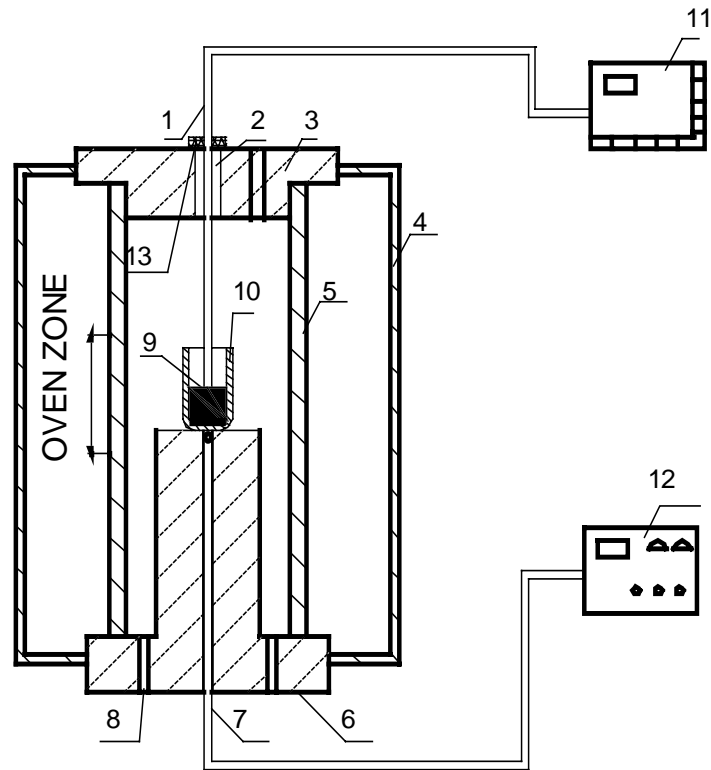
$$D = 3.9.7.9 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1} \text{ (T=1713K-1743K)}$$

ACKNOWLEDGMENTS

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1.Oxygen sensor 2. Measure hole 3.cover 4.crust of furnace 5.alumina tube 6.crucible supporter 7.Pt-13%Rh/Pt thermocouple 8.air inlet 9.slag 10.crucible 11.digital voltmeter 12.Shimaden SR-53 programmable temperature controller 13.location ring

Fig. 1: Schematic diagram of experimental apparatus

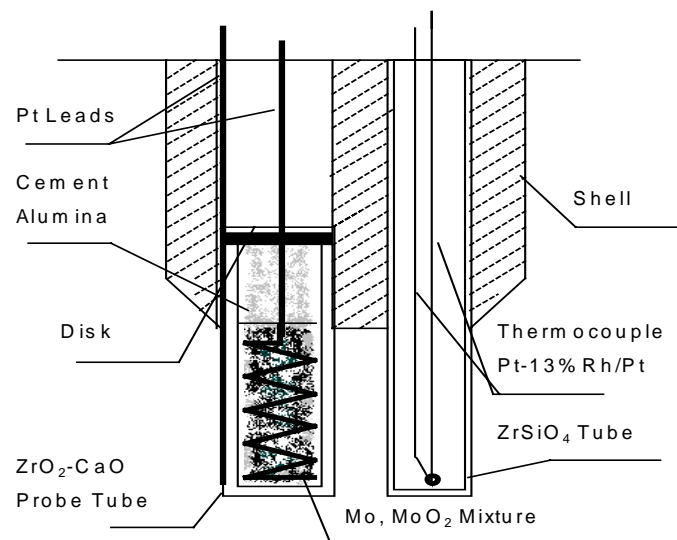


Fig. 2. A schematic diagram of the arrangement of the cell

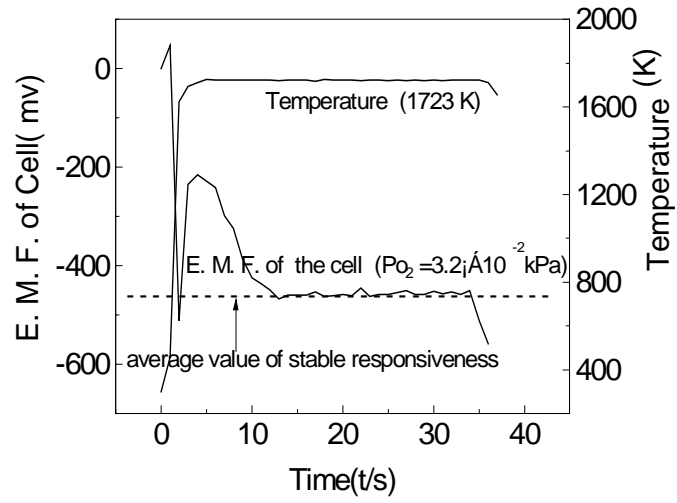


Fig. 3. A profile of electromotive force responsiveness

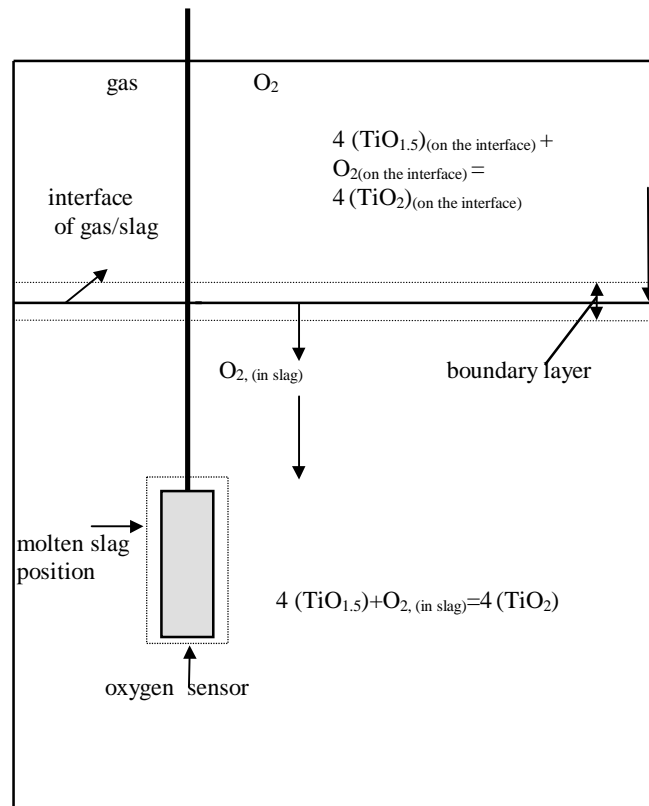


Fig. 4. Schematic diagram of the oxidation mechanism of $(\text{TiO}_{1.5})$

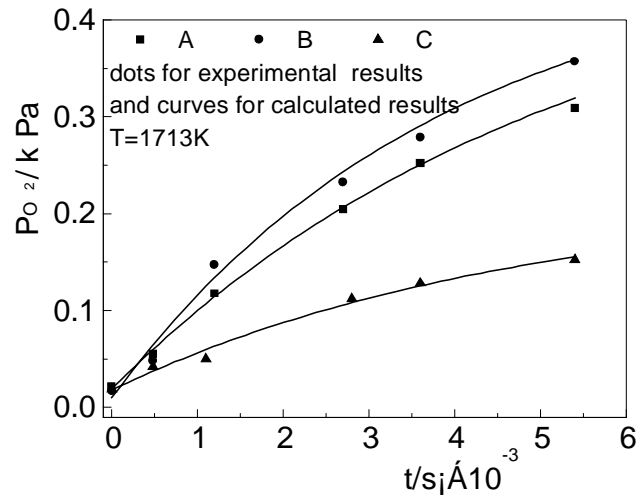


Fig. 5. P_{O_2} / kPa plot against $t/s \times 10^{-3}$

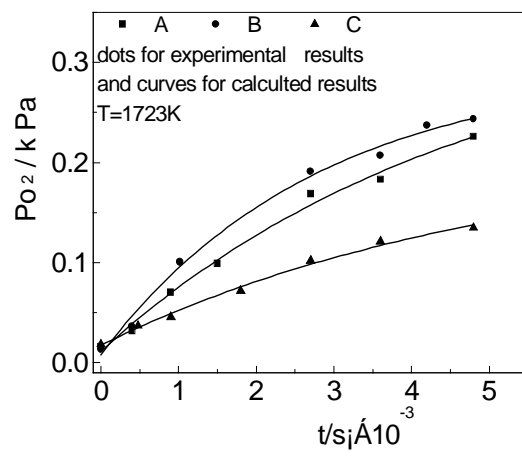


Fig. 6. P_{O_2} / kPa plot against $t/s \times 10^{-3}$

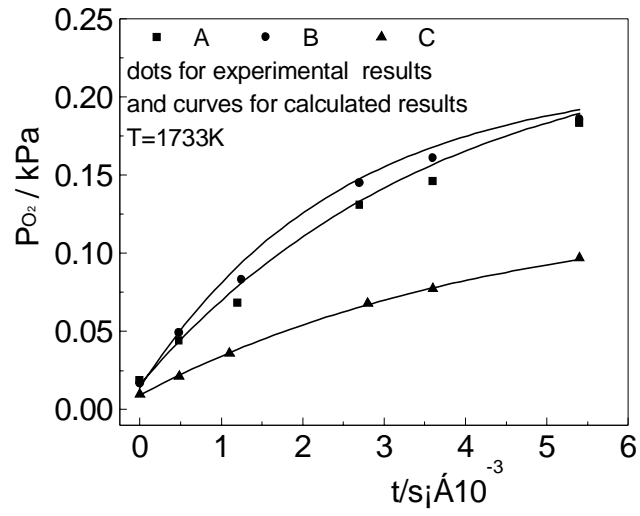


Fig.7. P_{O_2} / kPa plot against $t/s \times 10^{-3}$

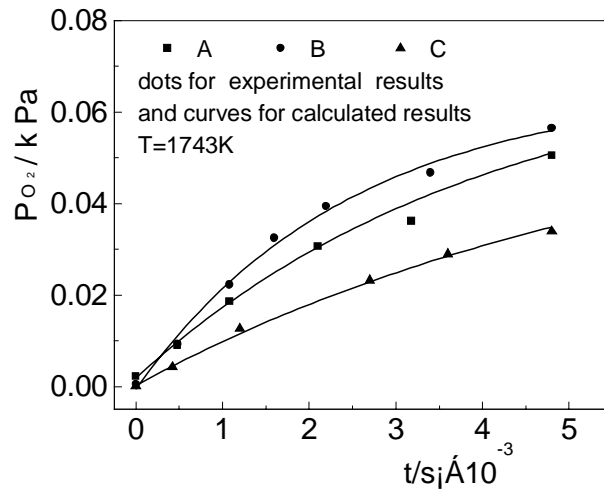


Fig. 8. P_{O_2} / kPa plot against $t/s \times 10^{-3}$

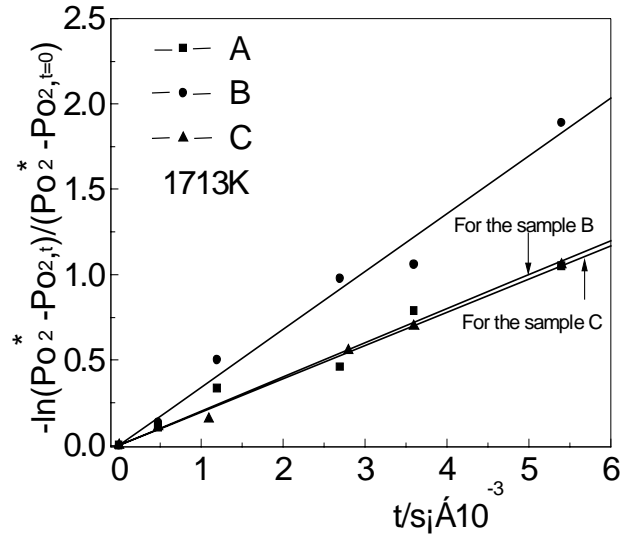


Fig.9. relationship between $-\ln(Po_2^* - Po_{2,t}) / (Po_2^* - Po_{2,t=0})$ and $t/s \times 10^{-3}$

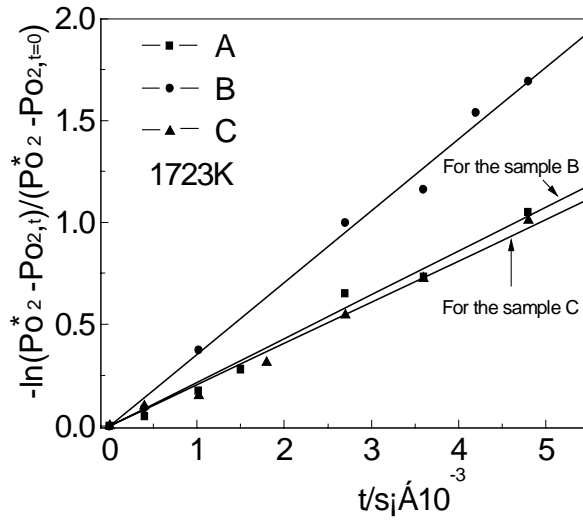


Fig. 10. Relationship between $-\ln(Po_2^* - Po_{2,t}) / (Po_2^* - Po_{2,t=0})$ and $t/s \times 10^{-3}$

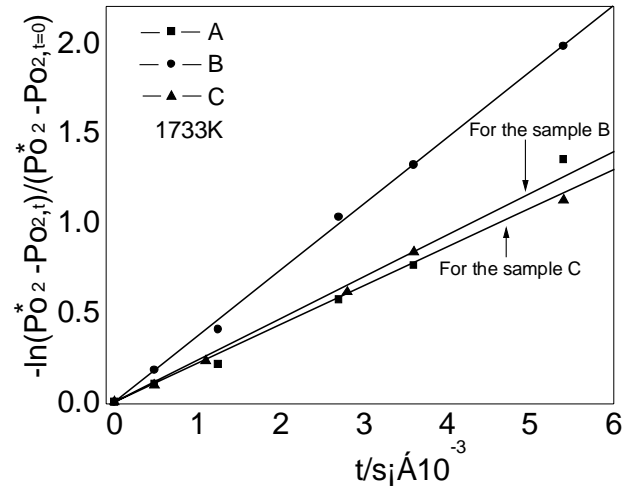


Fig. 11. Relationship between $-\ln(Po_2^* - Po_{2,t}) / (Po_2^* - Po_{2,t=0})$ and $t/s \times 10^{-3}$

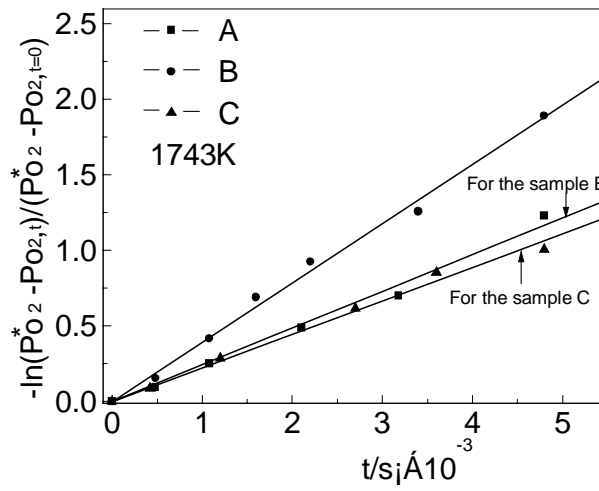


Fig. 12. Relationship between $-\ln(Po_2^* - Po_{2,t}) / (Po_2^* - Po_{2,t=0})$ and $t/s \times 10^{-3}$

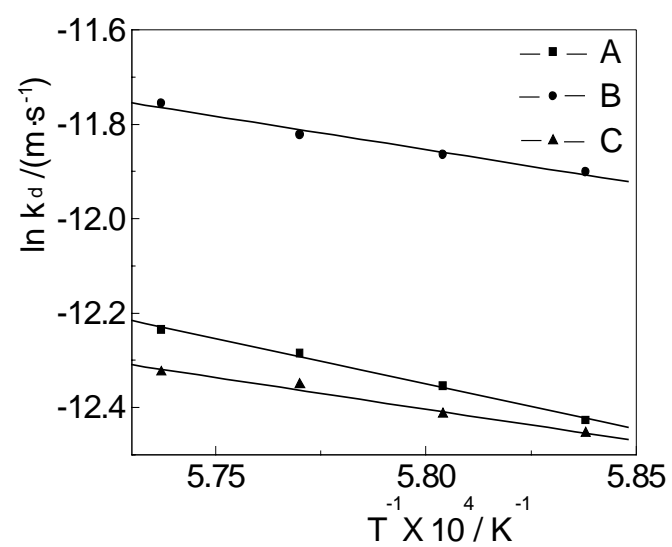


Fig. 13. Arrhenius plot of $\ln k_d / \text{m.s}^{-1}$ against $T^{-1} \times 10^4 / \text{K}^{-1}$

Table I. Compositions of Slag Sample

Samples	Fe ₂ O ₃	CaO	SiO ₂	TiO ₂	MgO	Al ₂ O ₃	CaO / SiO ₂
A	0.00	28.83	22.17	25.00	8.00	16.00	1.30
B	4.00	27.68	21.28	24.00	7.68	15.38	1.30
C	8.00	26.52	20.39	23.00	7.36	14.72	1.30

Table II . The Values of $k_d \times 10^6 \text{ m}^{-1} \cdot \text{s}$

Samples	1713K	1723K	1733K	1743K
A	4.01	4.31	4.62	4.88
B	6.78	7.04	7.34	7.84
C	3.91	4.06	4.32	4.44

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