

The Effect of Addition of Al_2O_3 on the Viscosity of CaO –“ FeO ”– SiO_2 – CaF_2 Slags

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The viscosities of CaO –“ FeO ”– SiO_2 – CaF_2 slags with various amounts of alumina addition were measured using a rotating-cylinder method in the temperature range 1714–1757 K. The first part of the experiments was conducted by measuring the viscosities under equilibrium conditions after small additions of Al_2O_3 . Similar experiments were also conducted with one commercial mould flux in order to compare the results. In both cases, the viscosities were found to increase with the addition of Al_2O_3 at all the experimental temperatures, the increase in viscosity being somewhat linear with Al_2O_3 addition. In the case of the commercial mould flux, even an addition of 2.6 mass% Al_2O_3 led to a significant increase in the viscosity.

Some isothermal experiments were also conducted with the above set of slags in the dynamic mode, wherein, the changes in the slag viscosities were monitored as a function of time as an Al_2O_3 disc dissolved continuously into the slag. The experiments were so designed that the dissolution of alumina occurred mainly along the vertical direction. The rate of dissolution of alumina is discussed in the light of the rate of change of viscosity as well as the composition profile in the slag after the experiments. An examination of the Al_2O_3 disc revealed the counter diffusion of the slag components into the solid alumina and that the dissolution took place by the solid product dissolving in the melt.

KEY WORDS: viscosity; dissolution of Al_2O_3 ; fluoride volatilisation; mould flux.

1. Introduction

The present work is part of a series of experiments with a view to provide a deeper understanding of the viscosity and lubrication effects of mould powders during continuous casting. It is common knowledge that mould powder provides not only chemical protection and thermal insulation to the top metal surface but also lubrication at the mould/metal interface and uniform heat transfer between mould and strand. In this respect, viscosity of the slag formed by the mould flux is an important parameter.

It is well-known that the slag film formed by the mould flux is also a receptor of oxide inclusions in the molten slag pool. This phenomenon, along with the evaporation of F^- containing species from the mould flux is likely to affect the chemical and physical properties of the slag film formed, influencing the lubrication effect in the casting process. The latter is a critical factor with respect to the quality assurance during high speed casting process. The present work was conducted in order to examine the effect of the dissolution of Al_2O_3 (which is a common deoxidation product in steel melts) in the slag and the consequences of the same on the viscosity.

A number of experimental studies have earlier been carried out to obtain viscosity data for mould fluxes.^{1–8)} However, the need for a model that could accurately predict the continuous changes in viscosities due to increase in the

alumina content of the fluoride-containing slags as well as the evaporation of fluorides from the slag has strongly been felt. In view of this, a research program was initiated in the present laboratory to describe the viscosities of mould fluxes as a function of both composition and temperature. The project consists of two parts, (i) determination of slag and flux viscosities under well defined experimental conditions and (ii) development of a viscosity model for fluorine-containing slags and fluxes based on the experimental data. Several experimental studies^{9–11)} have been carried out in the present laboratory to measure the viscosities of fluoride-containing slags in lower order systems. From these, a model structure is being developed to predict the viscosities of fluoride-containing slags from the viscosities of lower order systems. Further, this enabled the quantification of the effect of fluoride evaporation on viscosities. The viscosities of slags in the CaO – SiO_2 – CaF_2 system⁹⁾ “ FeO ”– SiO_2 – CaF_2 system¹⁰⁾ and CaO –“ FeO ”– SiO_2 – CaF_2 system¹¹⁾ were determined using a rotating-cylinder method. As a continuation of the previous work, the present investigation aims at an examination of the effect of alumina addition on the viscosities of CaO –“ FeO ”– SiO_2 – CaF_2 slags. For this purpose, measurements are conducted under both equilibrium as well as dynamic conditions.

2. Experimental

The rotating-cylinder method was employed in this work. The preparation of the slags, the experimental setup as well as the procedure adopted for viscosity measurements under equilibrium conditions have been described in detail in earlier publications.^{9–11} Only a brief description is provided here in order to outline the salient features of the technique adopted; but the experimental details are elaborated for dynamic measurements.

The synthetic slags studied were prepared by mixing the individual components, CaO, “FeO”, SiO₂, CaF₂ and Al₂O₃. The composition of “FeO” (51 mole percent of oxygen, corresponding to the composition of the liquid oxide in equilibrium with Fe at 1 673 K¹²) was prepared by mixing iron and Fe₂O₃ powders. The purity levels and the suppliers of the raw materials are listed in **Table 1**. The powders of SiO₂, CaO and Al₂O₃ were calcined for 12 h at 1 273 K before use. Fe₂O₃ powder was dried at about 400 K before use. The CaF₂ powder was dried under a vacuum of 10⁻¹ Pa in a stepwise heated furnace, with a cold trap of dry ice/alcohol mixture placed between the furnace and the pump.⁹ In the dynamic viscosity measurements, Al₂O₃ discs with a thickness of 6 mm were used. The supplier and the purity of the Al₂O₃ discs are also presented in Table 1.

To prevent the slag samples from both oxidation and reduction, an argon atmosphere having an oxygen partial pressure of 10⁻⁵ Pa was used both during the preparation of the slag as well as during the viscosity measurements. The purity level and supplier of the argon gas are also listed in Table 1. The gas cleaning system has been described in detail in an earlier publication.⁹

Pure iron crucibles (Armco iron, Middletown, OH), with inside dimensions 103 mm in height and 40 mm in diameter and spindles (Armco iron, Middletown, OH), composed of a bob and a shaft were employed in the experiments. Detailed specifications of the crucibles and spindles can also be found in the earlier publication.⁹

Four types of experiments were carried out, *viz*

- (i) viscosity measurements of CaO–CaF₂–Al₂O₃ ternary slags;
- (ii) viscosity measurements with the additions of definite quantities of alumina into the premelted master slag containing CaO, “FeO”, SiO₂ and CaF₂;
- (iii) viscosity measurements in an industrial mould flux slag and
- (iv) dynamic viscosity measurements following the dissolution of alumina into a master slag.

In order to prepare the slags for the type (i) measurements and the master slags for the measurements of types (ii) and (iv), mixtures of components, CaO, SiO₂, CaF₂, Fe, Fe₂O₃ and in some cases, Al₂O₃ were premelted in an iron crucible under purified argon atmosphere.⁹ The volatilisation of fluoride species would be expected to be significant mostly during the long period of premelting of the slags, considering that CaF₂ added would have unit thermodynamic activity before the melting and homogenisation process. In order to ascertain the composition of the premelted slag, these slags were sent for chemical analysis. The contents of SiO₂, CaO, Al₂O₃ and “FeO” in these samples were analyzed by using X-ray fluorescence spec-

Table 1. Materials employed in this study.

Materials	Purity	Supplied by
Silicon oxide, (SiO ₂)	Professionally analysed grade	E. Merck, Darmstadt, Germany
Calcium oxide, (CaO)	Anhydrous, analytical reagent grade	Fisher scientific, New Jersey, USA
Calcium fluoride, (CaF ₂)	Precipitated pure	E. Merck, Darmstadt, Germany
Carbonyl iron, (Fe)	Professionally analysed grade	E. Merck, Darmstadt, Germany
Iron oxide, (Fe ₂ O ₃)	Professionally analysed grade	E. Merck, Darmstadt, Germany
Aluminium oxide, Al ₂ O ₃	anhydrous, analytical reagent grade	Fisher Scientific, New Jersey, USA
Al ₂ O ₃ Round Disc OD (mm), 40; Thick (mm), 6	99.5–99.7%	Alfa Aesar (Johnson Matthey GmbH)
Al ₂ O ₃ , as small particles of sintered	99.5–99.7%	Halden Wanger, Germany
Argon, (Ar)	Argon plus	AGA gas, Stockholm, Sweden

trospectroscopy (XRF) and CaF₂ contents by using ion selective electrode after dissolving the sample in NaOH solution.

A schematic diagram of the experimental setup consisting of a high temperature furnace and a viscometer is shown in **Fig. 1**. The Brookfield digital viscometer used for the measurements had a full-scale torque of 7.187×10⁻⁴ Nm and was controlled by a PC through a DV-III controller. The iron crucible used for the premelting of the slag was transferred, along with the premelted slag, to the viscometer unit for viscosity measurement. The total experimental uncertainty is estimated to be less than 10%.

2.1. Viscosity Measurements under Equilibrium Condition

The premelted slag was heated up to the required temperature at a heating rate of 5 K/min. When the temperature of the sample had stabilized, the spindle, rotating at a speed of 40–60 rpm was lowered into the slag. An equilibration time of approximately 30 min was kept for the first measurement at each temperature. Five different rotation speeds of the spindle were employed at each temperature to ensure that the melt was behaving in a Newtonian manner. The spindle required approximately 2 min to reach a constant angular velocity. Average viscosity values were derived from the results of the five measurements.

To study the effect of alumina content on the viscosity, alumina pieces, obtained by breaking of a dense, recrystallized Al₂O₃ rod to small pieces of about 1–2 mm thick were added to the melt from the top of the reaction chamber. The viscosities of the slags with different Al₂O₃ contents could be measured by several Al₂O₃ additions. After each addition, the melt was stirred by the spindle for about 180 min to allow complete dissolution of the alumina into the slag. The reproducibility of the viscosity values obtained at different rotation rates provided a good indication of the complete dissolution. Thereafter, viscosity values were registered.

In the case of the measurements with the commercial mould fluxes, the fluxes were decarburised in air at 1 073 K overnight and then premelted in an iron crucible before introducing into the viscometer arrangement. The measurements were carried out as in the earlier case.

2.2. Dynamic Viscosity Measurements Following Alumina Dissolution

In this type of experiments, an Al₂O₃ disc, 6 mm in thick-

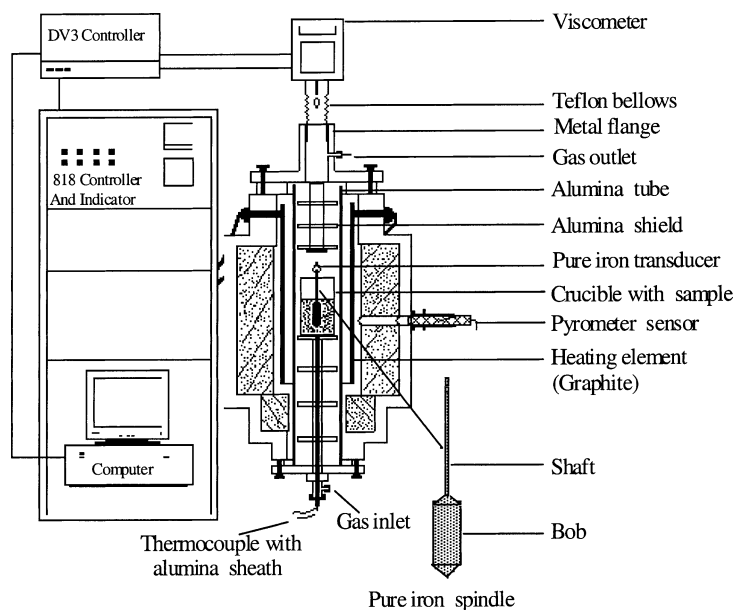


Fig. 1. Schematic setup for viscosity measurements.

ness, was fixed to the bottom of a crucible using three small iron pins. The premelted master slag was placed above the Al_2O_3 disc before the crucible was introduced into the reaction chamber. The arrangement of the Al_2O_3 disc in the crucible is shown in Fig. 2(a). The crucible along with the master slag and the Al_2O_3 disc was heated to the experimental temperature in purified argon atmosphere. The molten state of the slag could be verified by the lowering of the spindle, which was rotating at 40–60 rpm, into the slag without meeting resistance. Viscosity of the melt was then measured as a function of time. The viscosity at the start of the measurements was in agreement with the viscosity values of the premelted slags without alumina, confirming thereby that the amount of Al_2O_3 dissolved in the slag during the heating stage was negligible. Figure 2(b) shows the concentration profile of Al_2O_3 in the vertical direction.

3. Results

It was found in a previous study⁹⁾ that the volatilisation of fluorides from CaF_2 containing slags occurred predominantly during the long premelting periods, primarily as SiF_4 and FeF_2 . The change in slag composition during the viscosity measurement, on the other hand, was found to be insignificant.⁹⁾ Hence, the results of the chemical analyses of the premelted slags were adopted as the starting compositions of the slags. Further, in order to confirm the effect of the fluorine evolution on the viscosity values, the changes in viscosities of two CaO –“ FeO ”– SiO_2 – CaF_2 slags were monitored over an extended time period at 1741 and 1757 K, respectively. The results of these two measurements are plotted as function of time in Fig. 3. It is seen that, while the viscosity values show a slight tendency to increase, the changes are less than 5 percent of the measured viscosities, which is still within the range of experimental uncertainties.

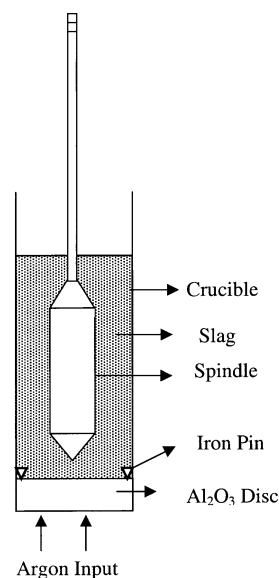


Fig. 2a. The arrangement of the Al_2O_3 disc in the crucible.

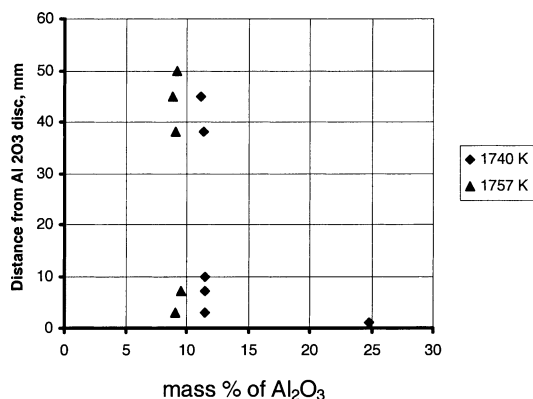


Fig. 2b. The vertical concentration profile of Al_2O_3 (in mass).

3.1. Viscosity Measurements under Equilibrium Conditions

Three CaO–Al₂O₃–CaF₂ slags were studied. The viscosi-

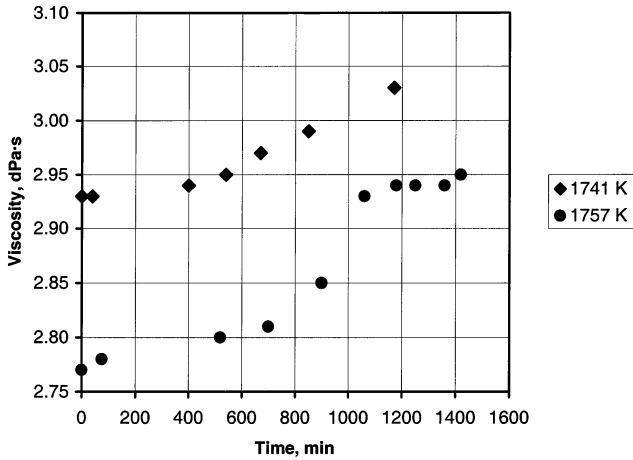


Fig. 3. The variation of viscosity of the CaO–“FeO”–SiO₂–CaF₂ slag with time at two different temperatures.

ties of these slags along with the slag compositions are listed in **Table 2**. The table shows a general trend that an increase in CaF₂ content results in a decrease of the viscosity. The table also shows that the viscosities of the slags have considerable dependence on temperature. A number of studies have been carried out to measure the viscosities of CaO–Al₂O₃–CaF₂ slags.^{14–27} **Figure 4**, which is reproduced from the first edition of Slag Atlas¹³) presents the viscosity values at 1773 K reported by different research groups. It should be mentioned that using the figure in the first edition of Slag Atlas¹³) is because the corresponding figure presented in the second edition of Slag Atlas²⁸) has some errors. The present viscosity data, obtained at the highest experimental temperature, are also included in the figure for comparison. It is seen that the present experimental results follow the general trend revealed by the literature data.

Three CaO–“FeO”–SiO₂–CaF₂ master slags were prepared. While the original intention was to synthesize slags of identical compositions in different batches, a slight variation in the compositions of these master slags was observed in the composition after the preparation as seen from

Table 2. The measured viscosity values of the CaO–CaF₂–Al₂O₃ slags at different temperatures with different amount of CaF₂.

Sample No.1		Sample No.2		Sample No.3	
46.2mass%CaO-28.9mass%CaF ₂ -24.9mass%Al ₂ O ₃		46.9mass%CaO-31.0mass%CaF ₂ -22.3mass%Al ₂ O ₃		43.8mass%CaO-34.6mass%CaF ₂ -21.6mass%Al ₂ O ₃	
Temp, K	Viscosity, dPa·s	Temp, K	Viscosity, dPa·s	Temp, K	Viscosity, dPa·s
1758	0.42	1758	0.39	1758	0.36
1733	0.44	1732	0.41	1731	0.38
1715	0.46	1715	0.42	1715	0.40
1697	0.48	1697	0.44	1684	0.42
1684	0.50	1684	0.45	1671	0.44
1671	0.52	1671	0.47	1652	0.46
1658	0.54	1653	0.49	1634	0.49
1641	0.58	1634	0.52	1619	0.51
1626	0.63	1619	0.54	1594	0.55
1617	0.66	1602	0.59		

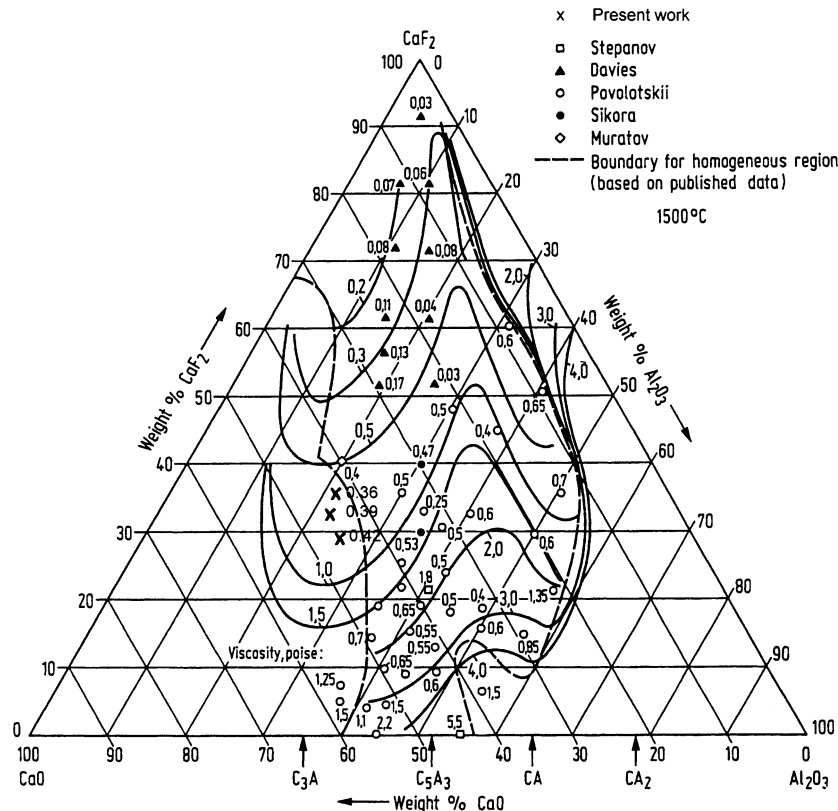


Fig. 4. Viscosities (dPa·s) in the CaO–CaF₂–Al₂O₃ system at about 1773 K.

Table 3a. Slag compositions and measured viscosities at 1714 K.

Status	Composition					Viscosity, dPa·s
	CaO (mass%)	FeO (mass%)	SiO ₂ (mass%)	CaF ₂ (mass%)	Al ₂ O ₃ (mass%)	
After premelting (post-measured)	40.2	5.7	49.1	5.0	0	3.92
After addition of 2% Al ₂ O ₃ (as prepared)	39.4	5.6	48.1	4.9	2.0	4.02
After addition of 5% Al ₂ O ₃ (as prepared)	38.3	5.4	46.8	4.8	4.8	4.25
After addition of 7% Al ₂ O ₃ (as prepared)	37.6	5.3	45.9	4.7	6.5	4.57
After addition of 10% Al ₂ O ₃ (as prepared)	36.5	5.2	44.6	4.5	9.1	5.8
After addition of 12% Al ₂ O ₃ (as prepared)	35.9	5.0	43.8	4.5	10.7	6.22
After addition of 15% Al ₂ O ₃ (as prepared)	35.0	4.95	42.6	4.4	13.0	7.03
After addition of 15% Al ₂ O ₃ (post-measured)	35.8	5.0	43.4	4.5	11.3	

Table 3b. Slag compositions and measured viscosities at 1740 K.

Status	Composition					Viscosity, dPa·s
	CaO (mass%)	FeO (mass%)	SiO ₂ (mass%)	CaF ₂ (mass%)	Al ₂ O ₃ (mass%)	
After premelting (post-measured)	39.5	6.1	49.7	4.7	0	3.03
After addition of 2% Al ₂ O ₃ (as prepared)	38.8	6.0	48.7	4.6	2.0	3.29
After addition of 5% Al ₂ O ₃ (as prepared)	37.6	5.8	47.3	4.5	4.8	3.66
After addition of 7% Al ₂ O ₃ (as prepared)	36.9	5.7	46.5	4.4	6.5	4.13
After addition of 10% Al ₂ O ₃ (as prepared)	35.9	5.5	45.2	4.3	9.1	4.50
After addition of 12% Al ₂ O ₃ (as prepared)	35.3	5.4	44.4	4.2	10.7	4.79
After addition of 15% Al ₂ O ₃ (as prepared)	34.4	5.3	43.2	4.1	13.0	5.45
After addition of 15% Al ₂ O ₃ (post-measured)	36.5	5.3	43.0	3.9	11.3	

Table 3c. Slag compositions and measured viscosities at 1757 K.

Status	Composition					Viscosity, dPa·s
	CaO (mass%)	FeO (mass%)	SiO ₂ (mass%)	CaF ₂ (mass%)	Al ₂ O ₃ (mass%)	
After premelting (post-measured)	39.7	6.4	49.4	4.5	0	2.74
After addition of 2% Al ₂ O ₃ (as prepared)	39.0	6.2	48.4	4.4	2.0	2.92
After addition of 5% Al ₂ O ₃ (as prepared)	37.8	6.1	47.0	4.3	4.8	3.29
After addition of 7% Al ₂ O ₃ (as prepared)	37.1	5.9	46.2	4.2	6.5	3.56
After addition of 10% Al ₂ O ₃ (as prepared)	36.1	5.8	44.9	4.1	9.1	4.04
After addition of 12% Al ₂ O ₃ (as prepared)	35.5	5.7	44.1	4.0	10.7	4.37
After addition of 15% Al ₂ O ₃ (as prepared)	34.5	5.5	43.0	3.9	13.0	4.86
After addition of 15% Al ₂ O ₃ (post-measured)	35.4	6.0	43.5	4.0	11.1	

the chemical analysis results. These compositions, obtained by chemical analysis for the master slags, were used as the initial slag compositions at temperatures, 1714, 1740 and 1757 K, respectively. At each temperature, the alumina pieces were added to the melt and the viscosities of the slags with different contents of Al₂O₃ could be measured. Six additions were made in each experiment. The slag compositions were computed on the basis of the amount of alumina added. These, along with the measured viscosities at 1714, 1740 and 1757 K are listed in **Tables 3a, 3b and 3c** respectively. The tables show that the viscosity increases with the increasing alumina concentration irrespective of the temperature. To the knowledge of the present authors, no experimental information of the viscosities in the Al₂O₃-CaO-“FeO”-SiO₂-CaF₂ system has so far been reported.

In order to examine the effect of alumina addition on the

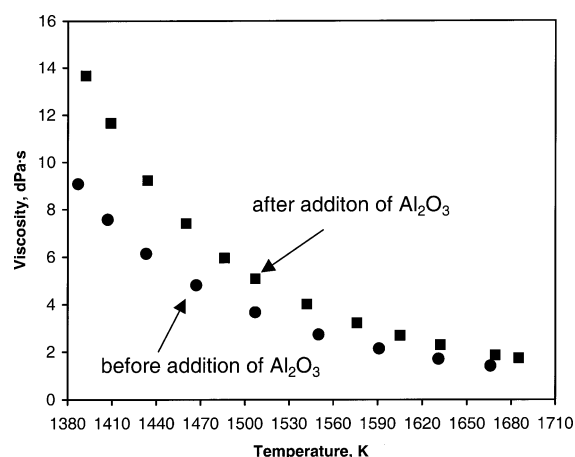

Fig. 5. The variation of viscosity of the industrial mould powder (SPH-SL 450/5D) with temperature, before and after addition of 3 mass% Al₂O₃.

Table 4. The composition of quaternary CaO-“FeO”-SiO₂-CaF₂ slag after premelting and after the last measurement of dissolution of Al₂O₃ disc.

Status	Composition weight %				
	CaO	FeO	SiO ₂	CaF ₂	Al ₂ O ₃
After premelting (1714K)	39.6	5.5	49.9	5.05	0
After viscosity measurement (1714)	35.9	4.9	44.0	4.4	10.8
After premelting (1740K)	39.6	5.5	49.8	5.0	0
After viscosity measurement (1740K)	36.1	5.0	44.2	4.3	10.4
After premelting (1757K)	39.8	5.4	49.7	5.0	0
After viscosity measurement (1757K)	36.2	5.3	44.6	4.4	10.0

viscosity of industrial mould flux, measurements of the viscosities of an industrial mould flux (SPH-SL 450/5D) with and without alumina addition was carried out. The Al₂O₃ addition corresponds to 3 mass%. The chemical analyses showed that the compositions of the mould flux before and after alumina addition were 9.6mass%Al₂O₃-30.3mass%CaO-4.4mass%FeO-11.5mass%Na₂O-36.1mass%SiO₂-8.2mass%F and 12.3mass%Al₂O₃-30.0mass%CaO-4.5mass%FeO-11.0mass%Na₂O-35.3mass%SiO₂-7.3mass%F, respectively. The experimental viscosity values obtained are plotted as functions of temperature in **Fig. 5**.

3.2. Dynamic Viscosity Measurements

Three CaO-“FeO”-SiO₂-CaF₂ master slags were prepared in order to study the variation of viscosity with the dissolution of alumina. The design of the slag compositions was that these should be identical to those in the case of the equilibrium measurements. But, as it turned out, slight compositional changes were observed on chemical analysis, which was unintentional. The compositions of the slags before and after viscosity measurements at different temperatures are presented in **Table 4**. It is to be mentioned that the chemical analysis showed a systematic error with respect to alumina concentration. Chemical analysis of some slags with well-defined compositions gave about 2 mass% lower value. As to be shown in the discussion part, the loss of aluminium as fluoride is less likely in view of the low partial pressures of AlF₃ and AlOF. The reason for this systematic error could not be traced; but is attributed to the sampling and analysis procedures. In view of this, the alumina concentrations were assumed to be the same as the amounts

Table 5. The results of the viscosity measurements of CaO–“FeO”–SiO₂–CaF₂ slag with Al₂O₃ dissolution with time at three different temperature.

Time, min	Viscosity, dPa·s	Time, min	Viscosity, dPa·s	Time, min	Viscosity, dPa·s
1714 K		1740 K		1757 K	
80	4.07	0	3.00	0	2.78
165	4.09	35	3.21	15	2.88
210	4.12	75	3.41	33	3.05
255	4.15	97	3.42	48	3.11
300	4.22	145	3.47	76	3.14
395	4.26	187	3.55	116	3.19
440	4.29	225	3.67	157	3.24
495	4.33	265	3.70	205	3.29
555	4.39	320	3.75	275	3.37
795	4.65	370	3.79	315	3.40
1200	5.18	412	3.83	354	3.43
1295	5.23	612	3.94	381	3.46
1310	5.25	1072	4.41	441	3.54
1360	5.39	1312	4.75	456	3.55
1385	5.43	1342	4.77	471	3.57
1475	5.58	1379	4.81	525	3.66
1545	5.69	1419	4.85	561	3.71
1635	5.94	1559	5.01	781	3.88
1730	6.09	1659	5.18	1168	4.43
1760	6.22	1709	5.27	1416	4.76
1810	6.31	1747	5.35	1481	4.79
1870	6.56	1797	5.40	1551	4.92
1925	6.67	2067	5.69	1641	4.98
1963	6.71	2477	5.99	1715	5.07
2223	6.89	2737	6.19	1745	5.09
2643	7.10	2762	6.26		
2693	7.15	2907	6.37		
2768	7.29	3007	6.06		
2793	7.29	3067	6.15		
2803	7.32	3087	6.15		
2873	7.40	3137	6.15		
2878	7.42				
2960	7.51				
3043	7.56				
3108	7.61				
3183	7.69				

added. The variations of the viscosities with time at 1714, 1740 and 1757 K are presented in Table 5. The increase of viscosity with time is evident in the case of all three temperatures, indicating thereby that addition of alumina increases the slag viscosity irrespective of the temperature.

4. Discussion

4.1. Evolution of Fluorine Species

The main reactions responsible for the evolution of fluorine species in the case of CaO–“FeO”–SiO₂–CaF₂ system have been discussed in the previous publications.^{9–11)} Thermodynamic analysis has shown that the formation of gaseous species SiF₄ and FeF₂ is the major source for compositional changes. An analysis based on both thermodynamic and kinetic considerations has indicated that fluorine evolution would occur predominantly during the premelting process, when the activity of CaF₂ is high and the duration is long.^{9–11)} When Al₂O₃ is introduced, the following reactions are likely to occur:



The activities of CaF₂, Al₂O₃ and CaO were assumed to be ideal in the absence of reliable thermodynamic data. The Gibbs energy changes of the compounds were obtained from Kubaschewski.²⁹⁾ The partial pressures of AlF₃ at 1773 K with 2 and 15 mass% Al₂O₃ were estimated to be 2×10^{-2} and 4×10^{-2} Pa, respectively. The partial pressures of AlOF with 2 and 15 mass% Al₂O₃ additions at 1773 K were also found to be of the same order of magnitude, the value at 2 mass% being 1×10^{-2} Pa and the one at 15

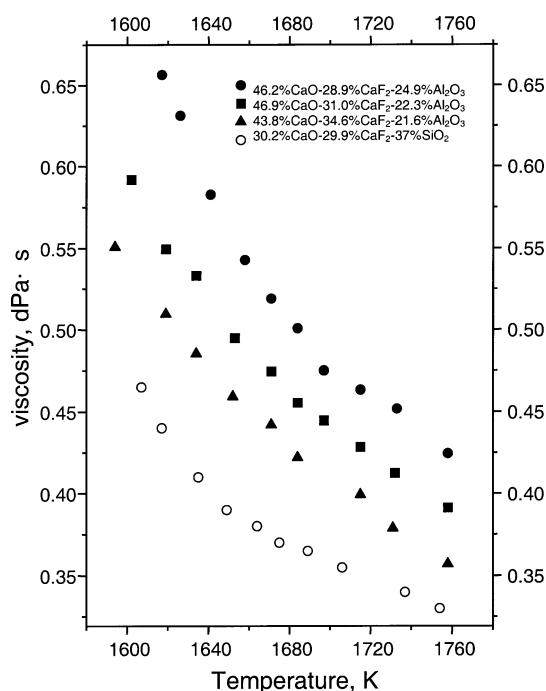


Fig. 6. The variation of viscosity of the CaO–CaF₂–Al₂O₃ slag at different temperatures with different amounts of CaF₂.

mass% 3×10^{-2} . These low values of the partial pressures of AlF₃ and AlOF at the experimental temperature would suggest an insignificant loss of these vapour species during the experiment.

4.2. Viscosity Measurements at Equilibrium Condition

In industrial practices for making clean steel, the pickup of Al₂O₃ in the slag pool of the mould due to the reoxidation is about 2 mass%. The two viscosity curves in Fig. 5 show that the viscosity increases substantially with 3 mass% addition of alumina. Since an increase of viscosity would increase the thickness of the flux film as well as the friction force acting on the solidified shell,³⁰⁾ a viscosity model of high precision would be essential for an accurate simulation of the continuous casting process.

In Fig. 6, the viscosities of the three Al₂O₃–CaO–CaF₂ slags are compared with the viscosities of a CaO–SiO₂–CaF₂ slag⁹⁾ at different temperatures. The CaO–SiO₂–CaF₂ slag contains 30.2 mass% CaO, 37.0 mass% SiO₂ and 29.9 mass% CaF₂. This CaF₂ content is close to those of the three Al₂O₃–CaO–CaF₂ slags.

In the molten slags containing Al₂O₃, aluminate complexes Al₃O₇⁵⁻, AlO₂⁻ and AlO₃³⁻ can be formed. With increasing amount of CaF₂, the aluminate anions get depolymerized. Ionic radii of Ca²⁺ and F⁻ ions are smaller than those of the aluminate complexes. The disintegration of aluminate complexes into the smaller units AlOF₂⁻ and AlO₂⁻ results in the decrease of viscosity.

It is seen in Fig. 6 that the viscosities of the CaO–SiO₂–CaF₂ slag are lower than the viscosities of the three Al₂O₃ containing slags at corresponding temperatures, although the CaO content in the SiO₂ containing slag is much lower. This comparison would provide some experimental indication to why addition of Al₂O₃ into mould fluxes usually increases the viscosities of the melts.

The compositions of the three CaO–“FeO”–SiO₂–CaF₂

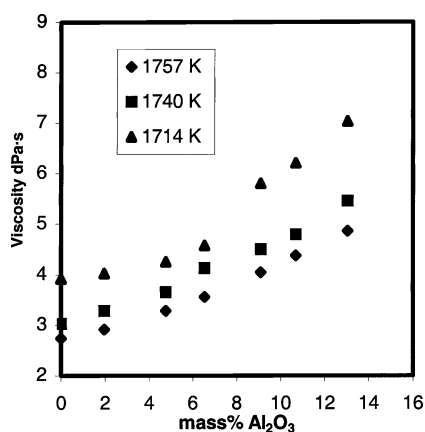


Fig. 7. The variation of viscosity of CaO-“FeO”-SiO₂-CaF₂ slags with different amounts of Al₂O₃ at different temperatures.

master slags are expected to undergo very similar variations in compositions after the addition of Al₂O₃. In Fig. 7, the viscosities at 1714, 1740 and 1757 K are plotted as functions of alumina content. A substantial increase in viscosity is observed in all the three cases in the experimental temperature range. The viscosity varies nearly linearly with the alumina content at the two higher temperatures. The near linear increase of the viscosity with the alumina concentration in the slag would have important impact on the modelling of mould fluxes. Figure 7 also shows that the slag having higher alumina content has stronger temperature dependency. A simple mathematical regression leads to the following expression on the viscosities of the slags having the mass ratio, (mass%)CaO/(mass%)FeO/(mass%)SiO₂/(mass%)CaF₂=39.7/6.36/49.4/4.52:

$$\eta(\text{dPa}\cdot\text{s})=61.6-0.0337T+32.4(\text{mass}\%)\text{Al}_2\text{O}_3,\dots\dots(3)$$

Generally, Al₂O₃ in (SiO₄)⁴⁻ network is classified as intermediate because it would either join the continuous network or only occupy the holes between the (SiO₄)⁴⁻ tetrahedra according to its surrounding conditions. The Al³⁺ substitutes for a Si⁴⁺, i.e. an AlO₄⁻⁵ (ionic radius=2.5 Å) tetrahedron can be formed which joins in the network formed by the SiO₄⁻⁴ (ionic radius=2.5 Å) tetrahedra, provided that an additional cation is available and can be located in a hole nearby to preserve electrical neutrality. The longer chain thus formed leads to lesser mobility of the species in the system with consequent increase in the viscosity.

4.3. Dynamic Viscosity Measurements

In order to gain an insight into the mechanism of Al₂O₃ dissolution into the slag, the reacted alumina discs were examined under a Scanning Electron Microscope (SEM) attached with an Electron Dispersion Spectroscopy (EDS) analyser. Figure 8 presents the photomicrograph of the vertical section of the disc after the viscosity measurement. Two layers are observed in the section. A layer of a single phase, labelled 1, either a solid solution or a compound, having an approximated composition of 0.2Al₂O₃-0.3SiO₂-0.45CaO-0.05“FeO” was formed in contact with the liquid slag. Beneath this single phase layer, another layer with three coexisting Phases 1, 2 and 3 was observed. The

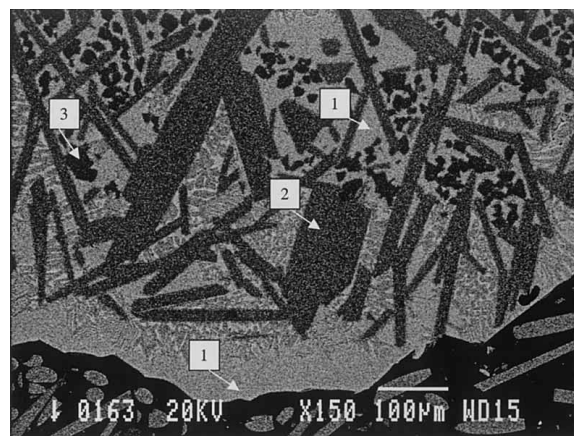


Fig. 8. The photomicrograph of the vertical section of the Al₂O₃ disc after viscosity measurements.

light phase marked as Phase 1 in this layer has the same composition as in the single phase layer near the slag. The composition of Phase 2 in the second layer suggests that this phase is likely to be CaO·6Al₂O₃. Phase 3 in this layer was alumina which was present only in small amounts. No fluorine content was detected in the disc. However, it should be pointed out that the analysed results of fluorine could only be used qualitatively due to the limitation of EDS in analysing light elements. The microstructure shown in Fig. 8 indicates that slag has penetrated into the original Al₂O₃ disc. The formation of the single phase layer on the top of the disc would provide resistance for the dissolution of alumina into the slag. It is expected that the interface reaction after the formation of the single protecting layer would be the dissolution of the protecting layer accompanied by the diffusion of Al₂O₃ into the slag.

A uniform slag composition along the length of the bob of the spindle would be a necessary condition to relate the measured viscosity value to the slag composition. In order to check whether alumina concentration gradients occurred along the length of the crucible due to the dissolution of Al₂O₃, the slag compositions below the lower tip of the spindle and above the higher tip of the spindle were analysed. The positions, where the chemical analyses were made are shown in Fig. 2(b). The concentration profile of Al₂O₃ is also schematically presented in this figure, wherein even the analysed results are presented. It is seen that the compositions above and just below the bob are very close, while concentration gradients are found near the surface of the remaining part of the alumina disc

The viscosities at 1714, 1740 and 1757 K are plotted as functions of time in Fig. 9. As can be seen in Tables 3a-3c, the alumina concentrations in the final slags of the dissolution experiments were all lower than the highest alumina concentrations in the equilibrium experiments. On the other hand, the viscosity values at the final stage of the dynamic measurements are about 10% higher than highest viscosity values obtained in the equilibrium study. While 10% difference in the viscosity values is still within the uncertainty range of the experimental method, the same trend shown at all three temperatures seems to suggest that the analysed alumina concentrations could be associated with considerable uncertainties.

Since the master slags used for both dynamic viscosity

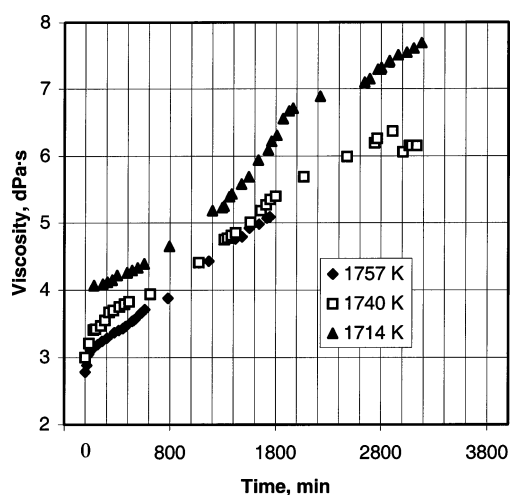


Fig. 9. The variation of viscosity with time, resulting from the dissolution of Al_2O_3 at three different temperature.

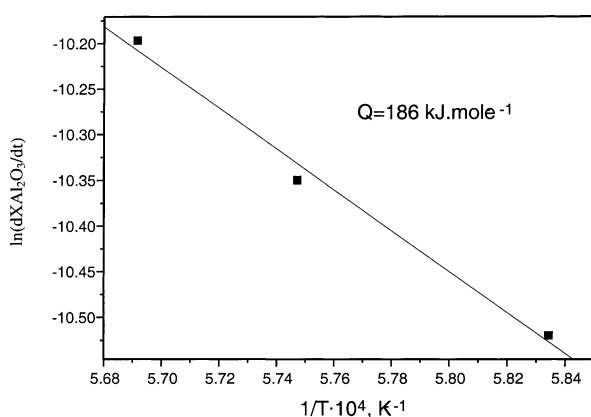


Fig. 10. Arrhenius plot for the dissolution rate.

measurements and the measurements under equilibrium conditions were very similar, the alumina concentration in the bulk of the crucible (along the bob) at a given moment can be evaluated using the viscosity values on the basis of Eq. (3). As mentioned in the previous section, the dissolution process was controlled by dissolution of the protecting layer accompanied by the diffusion of Al_2O_3 into the slag after the initial stages. The rates of the dissolution process at 1714, 1740 and 1757 K were evaluated using the data obtained between 200 and 700 min. An Arrhenius plot is presented in Fig. 10 on the basis of the reaction rates. The plot reveals an apparent activation energy of $186 \text{ kJ} \cdot \text{mol}^{-1}$ for the dissolution.

5. Summary

The effect of addition of Al_2O_3 on the viscosity of CaO–“FeO”– SiO_2 – CaF_2 slag was studied experimentally using a rotating-cylinder technique. Experiments were first carried out under equilibrium conditions at 1714, 1740 and 1757 K. In these experiments, the change in the viscosity of the slag due to the additions of different amounts of alumina was followed at a constant temperature. The effect of alumina addition on the viscosities of a commercial mould flux was also examined. It was found that even an addition of 3 mass% Al_2O_3 led to a significant increase in the viscosity of the mould flux. Dynamic viscosity measurements fol-

lowing continuous alumina dissolution were also conducted. In this series of experiments, the changes in the slag viscosities were followed as a function of time as an Al_2O_3 disc dissolved continuously into the slag. EDS analyses in the reacted slag in the vertical direction of the crucible revealed a uniform slag composition along the length of the bob of the spindle. Concentration gradients were only observed in the vicinity of the alumina disc. The bulk concentrations of alumina were evaluated on the basis of the viscosity values and the relationship between viscosity and alumina concentration were obtained in the experiments under equilibrium conditions. An apparent activation energy of $186 \text{ kJ} \cdot \text{mol}^{-1}$ for the alumina dissolution was evaluated based on the rates of dissolution.

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