1. Introduction

The viscosity of metallothermic slags plays a major role not only in clear separation of metal and slag but also in deciding the degree of completeness of reduction reaction. The viscosity of these melts depends on the composition of the slag which contains the bulk of oxides of the reductant (mainly alumina) along with unreduced oxides and other gangue materials present in the raw material. It is the interaction of these various compounds present in the ionic state that governs the viscosity through ionic structure. As the ionic structure of the slag affects the viscosity, in a similar way the viscosity data can help predicting the possible structure of the slag.

A lot of investigation has been made in the past on the structure–viscosity relationship of oxide melts and to some extent the role of fluorides in the oxide melts.

When CaF$_2$ is added to a binary silicate melt F$^-\text{ions replace the O}^{2-}\text{ions in silicate structure.}^{11}$ Decrease of viscosity with increasing addition of CaF$_2$ in CaO–Al$_2$O$_3$–SiO$_2$ melts has been reported by Bills, Kozakevitch and Back. They reported that the decrease of viscosity may be due to depolymerisation and decreasing intensity of interactions among various anions and cations in the melt.

2. Experimental

Altogether 24 slags were prepared in four different groups, each group comprising of six number of slags with CaF$_2$ contents varying from 0–10 mass% in steps of 2 mass%. The Al$_2$O$_3$/CaO mass ratios in these four groups are kept at 2.0, 2.5, 3.0 and 3.4. The composition of these 24 slags in four different groups is presented in Tables 1–4. As observed in the above four tables the composition of

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Viscosity of Molten Al$_2$O$_3$–Cr$_2$O$_3$–CaO–CaF$_2$ Slags at Various Al$_2$O$_3$/CaO Ratios

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other constituents like MgO, Na₂O, Cr₂O₃, SiO₂ and FeO are so adjusted that the variation is well within the range of compositions of aluminothermic ferrochrome slags.

The constituents are dried/calcined if necessary, weighed in pre-determined proportion, mixed in planetary ball mill for 24 h, melted, remelted for thorough homogenisation, the homogenisation being checked by XRD.

Random samples were collected for chemical analysis after remelting. The composition of five such fluoride added slags is given in Table 5. A comparison of the slag composition, given, in Tables 1–4 and that in Table 5 shows that there is a minor variation of CaF₂ content, the loss being probably due to formation of volatile aluminium fluorides, though melting and remelting was done in closely covered molybdenum crucibles.

The furnace used for melting and viscosity measurement is a graphite resistance furnace fabricated in the laboratory as reported in a previous paper.²²) The Brookfield synchronLEC electric viscometer with molybdenum spindle and bob as described earlier is used for viscosity measurement.

Measurement was carried out at an interval of 20–25 K both during increasing and decreasing temperatures. During

Table 1. Compositional details of slags of Gr. 1. (CaF₂ variation at Al₂O₃/CaO=2.00)

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Slag No.</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Cr₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>CaF₂</th>
<th>Al₂O₃/CaO (mass ratio)</th>
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<td>1 2</td>
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<td>3</td>
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</tr>
<tr>
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<td>4.75</td>
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<td>2.10</td>
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<tr>
<td>6</td>
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<td>25.00</td>
<td>2.33</td>
<td>4.82</td>
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Table 2. Compositional details of slags of Gr. 2. (CaF₂ variation at Al₂O₃/CaO=2.50)

<table>
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<th>Slag No.</th>
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<th>MgO</th>
<th>Na₂O</th>
<th>Cr₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>CaF₂</th>
<th>Al₂O₃/CaO (mass ratio)</th>
</tr>
</thead>
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Table 3. Compositional details of slags of Gr. 3. (CaF₂ variation at Al₂O₃/CaO=3.00)

<table>
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<th>Sl No.</th>
<th>Slag No.</th>
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<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Cr₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>CaF₂</th>
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<tr>
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</table>

Table 4. Compositional details of slags of Gr. 4. (CaF₂ variation at Al₂O₃/CaO=3.40)

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Slag No.</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Cr₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>CaF₂</th>
<th>Al₂O₃/CaO (mass ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 19</td>
<td>62.00</td>
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<tr>
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<tr>
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<td>6 24</td>
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<td>16.57</td>
<td>2.27</td>
<td>3.70</td>
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<td>3.08</td>
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</table>
the viscosity measurement at a particular temperature, the bath temperature is kept fairly stable with an accuracy of ±3 K by regulating the power supply through Dimmerstat. Care is taken to see that the temperature is constant while taking measurement at three different speeds of meter rotation, twice at each speed, once while the temperature is being raised and once while the temperature is being lowered.

3. Results and Discussion

The experimental results are plotted against the variables such as composition and temperature to note their effect on viscosity.

Calcium fluoride, better known as fluorspar commercially, is found to increase the alloy yield and metal recovery in aluminothermic melts for production of ferrotitanium. The improved result is possibly due to lowering of liquidus temperature with CaF₂ addition as discussed in a previous paper and also due to improved fluidity. Hence CaF₂ has been added to synthetic ferrochrome slags to study its effect. The maximum temperature at which the viscosity values have been recorded is 1993 K due to experimental constraints.

Figures 1–4 show the change of viscosity with temperature at different CaF₂ contents for Al₂O₃/CaO mass ratios of 2.0, 2.5, 3.0 and 3.4 respectively. The general trend is same in all the four cases i.e., viscosity decreases with increase in temperature as well as with increase in CaF₂ contents in the slags of all the four groups. Another general trend that is observed is that with increase in CaF₂ contents the slags behave as ‘long’ slags i.e. with increase in CaF₂ contents there is more gradual change of viscosity with temperature. This trend is more pronounced at low Al₂O₃/CaO ratios. However, for most of the slags the concept of ‘short’ slags as defined in the liquidus temperature measurement does not hold good in case of viscosity measurement, because the viscosity measurement has been made at temperatures much above the ‘flow-temperatures’.

A minimum viscosity of 0.182 Pa·s at 1993 K is obtained for slag of Al₂O₃/CaO mass ratio 2.0 with 10 mass% calcium fluoride content. The viscosity values obtained are comparable to those obtained at same temperature in slags with low Al₂O₃/CaO mass ratios without CaF₂ or in slags of Al₂O₃/CaO mass ratio of 2.5 with high MgO contents. This shows that the mechanism of viscous flow is the same as in case of slags with CaO or MgO i.e., addition of F⁻ ions results in breakdown of large and low mobility aggregate of complex aluminate anions to smaller sizes, resulting in greater fluidity. At low fluoride contents, temperature plays a greater role in reducing the number of bonds with concomitant decrease in viscosity where as at high fluoride contents F⁻ ions play greater role in breaking the structure.

![Graph](attachment:graph.png)

Fig. 1. Relationship between viscosity and temperature at Al₂O₃/CaO mass ratio=2.00.

![Graph](attachment:graph2.png)

Fig. 2. Relationship between viscosity and temperature at Al₂O₃/CaO mass ratio=2.50.

However, the fluoride addition did not result in higher decrease of viscosities. Probably with all precautions to prevent fluoride reacting with alumina, some AlF₃ was pro-
duced during prolonged measurement. The reactions of some CaF₂ with Al₂O₃ would have produced some CaO with more O²⁻ ions. The O²⁻ ions carry twice the charge of the F⁻ ions and increase in the O²⁻ concentration would probably result in tighter bonding and a more rigid structure.

The viscosity isotherms of these four groups of slags are shown in Figs. 5–8 respectively. In all these graphs, it is seen that at all temperatures there is a fast decrease of viscosity initially and at higher mole percent of CaF₂, the decrease is less. This is possibly due to the fact that within the compositions studied which have other network breaking constituents like CaO, MgO and Na₂O, the CaF₂ is not very much effective at concentrations higher than 6–8 mass%. It is further observed that the rate of decrease of viscosity with increasing CaF₂ additions is more at low Al₂O₃/CaO ratios than at high ratios. This observation is, however contradictory to the observations made by Nakamura and Yanagase who have suggested that in the ternary system CaF₂–Al₂O₃–CaO, CaF₂ has a little effect on the structure of aluminate anion for CaO rich compositions but influences the structure of aluminates at other compositions. This is probably due to the fact that their observation is made for ranges of CaF₂ higher than 30 mass% and other oxides such as MgO, Cr₂O₃, which have some interactions were not present in their melts. It is possible that at lower Al₂O₃/CaO ratios, i.e., at higher CaO contents, CaO tends to release part of O²⁻ ions and forms simple structures like AlO₃ and AlO₂ which decrease the viscosity. These results have been presented in a different form in Figs. 9–13.
for CaF$_2$ mass percent of 2 to 10 respectively. The figures show that whatever may be the CaF$_2$ concentration (within the range studied) Al$_2$O$_3$/CaO ratio has a greater effect on viscosity which is decreased as the ratio is decreased. This decrease at any temperature is more at lower CaF$_2$ contents than at higher values. Hence, it may be concluded from both these observations that within the range of compositions studied both CaO and CaF$_2$ are effective in breaking down the network structure and thus decreasing the viscosity.

The logarithmic viscosity and inverse temperature relationship has been plotted in Figs. 14–17 respectively for slag groups with Al$_2$O$_3$/CaO ratios 2.0, 2.5, 3.0 and 3.4. Though in case of slags of Al$_2$O$_3$/CaO ratio 3.4 it is linear within the temperature range measured (1 923–1 993 K) the relationship does not follow a single straight line relationship throughout the temperature range for slags of other three ratios i.e. with 2.0, 2.5 and 3.0 except at 0% CaF$_2$ content. The relationship has been shown to split up into two different straight lines with lines of greater slope at low temperature. The temperatures of discontinuity are 1 893 to 1 923 K, 1 893 to 1 923 K and 1 938 to 1 973 K for the slags with Al$_2$O$_3$/CaO ratio of 2.0, 2.5 and 3.0 respectively.

The activation energy of viscous flow, $E_m$, has been shown as a function of mole percent of CaF$_2$ in Figs. 18–21 respectively for slags with four different Al$_2$O$_3$/CaO ratios. The activation energy for viscous flow for all the slags of the three groups as mentioned above except at 0% CaF$_2$ is lower at high temperatures than at low temperature. Our re-
results very much agree with the observations made by Basov et al \cite{26} in the slag melts of the system CaO–Al₂O₃–CaF₂–Na₂O. From the results it may be concluded that for a slag of given composition containing calcium fluoride there is breakdown of discrete aluminate anion at discontinuity temperatures. It may further be observed that as the Al₂O₃/CaO ratio increases from 2.0 to 3.0 the difference between the high temperature activation energy and low temperature activation energy narrows down and at Al₂O₃/CaO ratio of 3.4 the activation energy of viscous flow remains constant throughout the temperature range measured. The latter may be partly because the range of temperature at which the viscosity has been measured is short (70 K only) and partly due to the fact that at high Al₂O₃/CaO ratio i.e., at low CaO content, the thermal energy (temperature effect) is not sufficient to breakdown the aluminate anion. The difference between the \( E_m \) values at high and low temperatures, at the other three ratios, however, does not have a regular trend with increase in fluoride content as the extent of break up of network structure is influenced by the type and number of other cations such as Ca\(^{++}\), Mg\(^{++}\), Na\(^+\) and...
Cr\textsuperscript{+++} in a complicated way.

In general it may be said that in aluminothermic melts containing high alumina, Al–O complexes like Al\textsubscript{5}O\textsubscript{7}\textsuperscript{5-} and AlO\textsubscript{3}\textsuperscript{3-} etc. predominate due to considerable amount of covalent bonding and addition of CaF\textsubscript{2} results in the breakdown and consequent reduction in size of the complex anions.

Low viscosity values at higher CaF\textsubscript{2} contents as well as at the lower Al\textsubscript{2}O\textsubscript{3}/CaO ratios (i.e., higher CaO contents) may be due to solvating effect of CaF\textsubscript{2} suggested by Bills\textsuperscript{2} and Back\textsuperscript{10} in case of silicate melts. According to their postulation, CaF\textsubscript{2} reacts with calcium ions to form two CaF\textsubscript{1+} ions:

\[
\text{Ca}^{1+} + \text{CaF}_2 \leftrightarrow \text{2CaF}^{1+}
\]

These CaF\textsuperscript{1+} ions attach themselves to singly bonded oxygens of the flow units, thus decreasing the attractive interaction between the singly boned oxygen (O\textsuperscript{-}) and calcium ions. This results in a lowering of the viscosity. Another
parameter, which has been recently mentioned as the degree of polymerization (or depolymerization) is the optical basicity, which represents the power of an oxide to donate a negative charge. The corrected optical basicity $D_{corr}$ (after the charge balance), has been used by Mills to denote the degree of polymerization in silicate melts. The corrected optical basicity for all the slags in the present investigation without and with CaF$_2$ were calculated, with the help of the procedure described by Mills and were found to vary within a narrow range, i.e., from 0.58 to 0.67. A plot of log viscosity as well as activation energy of viscous flow against the corrected optical basicity, as shown in Figs. 22 and 23, however, shows a sharp change. This is probably due to the fact that no compensation of cations has been made for charge balancing of some complicated alumina oxyfluorides that are formed.

Hence the overall conclusion that may be made is that the decrease in viscosity with the increase of fluxing constituents is not only due to depolymerization but also due to the decreasing intensity of interactions between various anions and cations present in the melt.
Fig. 21. Relationship between activation energy of viscous flow and mol% CaF₂ at Al₂O₃/CaO mass ratio = 3.4.

Fig. 22. Relationship between corrected optical basicity and log viscosity at temperatures close to liquidus temperature.

Fig. 23. Relationship between corrected optical basicity and activation energy of viscous flow.
4. Conclusion

It is observed in all slags that viscosity decreases with increase in temperature as well as with increase in CaF₂ contents. It is further observed that at all temperatures, there is a fast decrease of viscosity initially at lower CaF₂ contents but the decrease is less at higher mole percent of CaF₂. The rate of decrease of viscosity is more at low Al₂O₃/CaO ratios than at higher ones, the values decreasing with decrease in Al₂O₃/CaO ratios. The straight line relationship between \( I/T \) and log \( \mu \) is not seen in slags with CaF₂ contents except for slags of Al₂O₃/CaO of 3.4. With increase in Al₂O₃/CaO ratio from 2.0 to 3.0, the difference between high temperature activation energy of viscous flow and low temperature activation energy narrows down and at Al₂O₃/CaO ratio of 3.4 the activation energy remains constant throughout the temperature range studied. It is concluded that the extent of break up of the network structure is influenced by other cations such as Ca\(^{++}\), Mg\(^{++}\), Na\(^{++}\), Cr\(^{+++}\).

REFERENCES

2) P. M. Bills: JISI, 20 (1963), 133.