The Existence of a Ternary Phase in the Al$_2$O$_3$–CaO–FeO System

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In a preliminary study$^{1)}$ to determine the viscosities of some slags in the Al$_2$O$_3$–CaO–FeO system, the experimental results indicate the possibility of the existence of a ternary compound in this ternary. The present communication intends to report further experimental evidences regarding the existence of such a ternary compound using differential thermal analysis (DTA), scanning electron microscope examination (SEM) and X-ray diffraction technique.

The phase diagram of the Al$_2$O$_3$–CaO–FeO (saturated with iron) ternary system recommended by Slag Atlas$^{2)}$ is due to Wrampelmeyer et al.$^{3)}$ This diagram is reproduced in Fig. 1 along with the phase diagrams of the three binary systems.$^{2)}$ The phase relationships proposed by Wrampelmeyer et al.$^{3)}$ do not seem to suggest the existence of any ternary compound in the temperature range close to 1 823 K. It was on the basis of this phase diagram, viscosity measurements in the present laboratory were planned.

Attempts were made to carry out viscosity measurements in the composition range covering most of the liquid region. The eleven slag compositions studied are marked in Fig. 1. The compositions in mass percent are presented in Table 1.

The viscosity measurements were carried out on a Brookfield digital viscometer (model R VDV-III) using rotating cylinder method. The oxygen partial pressures in the reaction chambers were followed by oxygen sensors during the whole course of the sample-preparation and viscosity measurement. An oxygen partial pressure of about 10$^{-10}$ atm was observed in both cases. The samples were prepared by mixing precalcined Al$_2$O$_3$ and CaO with FeO synthesized$^{3)}$ in appropriate proportions in a ball mill for 1 h. The samples were directly used in the case of DTA measurements. Reproducible results from DTA measurements could not be obtained in the case of the samples S6–S11, due probably to incomplete slag formation. For viscosity measurements, 200 g of the powder mixture was premelted at a maximum temperature of 1 753 K. The premelting was carried out in a crucible with a composition suggested to be pure iron oxide. Beside oxygen, only Al and Ca were detected in phase 4. The ratio of atomic fraction of Al to atomic fraction of Ca suggests phase 4 being the binary compound, CaO·Al$_2$O$_3$. Phase 5 is surrounded by phase 6. Al, Ca, Fe and oxygen were found in both of the two phases. The atomic fractions of Al, Ca and Fe in phase 5 were found to be 0.37, 0.19 and 0.44, while the atomic fractions of these elements in phase 6 were found to be 0.11, 0.32 and 0.57. Only traces of phase 7 were found in the sample. EDS analysis revealed that this phase was metallic iron. The amount of pure iron phase was so little, so that only one small phase region of phase 7 was found in the sample. The presence of the traces of iron would confirm the fact that the sample was in equilibrium with iron.

Detailed description of the experimental setup and procedure for the viscosity measurements has been given in an earlier publication.$^{2)}$ The use of iron crucible and spindle restricted the maximum temperature of the measurements to 1 763 K. While successful measurements were made for the slags 1–5, no measurement could be conducted for slags 6–11. The samples behaved as two-phase mixtures at 1 763 K even after a couple of hours of equilibration and the spindle could not be immersed entirely into the samples. Repetition of some of these experiments with longer premelting time did not show any improvement. Examination of the prepared samples revealed that the samples were not completely molten. On the other hand, the ternary phase diagram along with the three binary phase diagrams shown in Fig. 1 suggests that the melting temperatures of the samples should show a decreasing trend with increasing FeO content along the 12CaO·7Al$_2$O$_3$–FeO join. The disagreement between the experimental observation and the phase diagram information seems to suggest the existence of an unknown ternary compound above 33 mass% FeO.

If a ternary compound is formed below a certain temperature, evidence should be found in some of the samples after cooling. In view of the fact that slags 1–5 were completely molten at 1 753 K and would therefore provide uniform sample for SEM analysis, sample 4 was prepared for SEM after viscosity measurement. A scanning electron microscope, model Jeol JSM-840, connected with an EDS (Electron Dispersion Spectroscopy)-detector, Link AN-10000 was employed to study the microstructure of the sample and the chemical composition of the phases present. In view of the uncertainties associated with the EDS analysis on oxygen, only the ratios of the metallic elements were employed to analyse the results, while oxygen concentration was used qualitatively to identify the presence of oxygen. Figure 2 shows the microstructure of sample 4 after the viscosity measurement. Seven phases were detected in the sample. It is seen that the area of phases 1+2 exhibits an eutectic structure indicating that an eutectic phase transformation has occurred during cooling. Phase 3 is identified by EDS analysis to be pure iron oxide. Beside oxygen, only Al and Ca were detected in phase 4. The ratio of atomic fraction of Al to atomic fraction of Ca suggests phase 4 being the binary compound, CaO·Al$_2$O$_3$. Phase 5 is surrounded by phase 6. Al, Ca, Fe and oxygen were found in both of the two phases. The atomic fractions of Al, Ca and Fe in phase 5 were found to be 0.37, 0.19 and 0.44, while the atomic fractions of these elements in phase 6 were found to be 0.11, 0.32 and 0.57. Only traces of phase 7 were found in the sample. EDS analysis revealed that this phase was metallic iron. The amount of pure iron phase was so little, so that only one small phase region of phase 7 was found in the sample. The presence of the traces of iron would confirm the fact that the sample was in equilibrium with iron.

Figure 2 was critically examined in order to follow the solidification history of the sample S4. The shape and the distribution of phase 5 would indicate that this phase precipitated first from liquid during cooling. This phase was
not abundant and was not found to be distributed in the sample. This was also surrounded by phase 6 which also was a ternary phase. These evidences indicate the initial precipitation of phase 5 when the slag is cooled as the liquidus temperature is reached. Phase 5 was observed even in sample S5. When the sample was cooled down further, CaO·Al₂O₃ marked as phase 4 would have precipitated. The precipitation of this binary compound would lead to the remaining liquid rich in FeO. Hence, further decrease of the sample temperature would have resulted in the precipitation of pure FeO (phase 3) with some liquid left over. This argument is supported by the morphology of the sample. As seen in Fig. 2, CaO·Al₂O₃ phase is always surrounded by the FeO phase and the liquid phase, which undergoes an eutectic transformation resulting in phases 1 and 2 later at lower temperature. It is noted that there is no clear boundary between phase 6 and phase 3 as well between phase 6 and phase 4. This fact along with the coexistence of phases 6 and 5 would suggest that phase 6 is frozen liquid. The presence of the ternary compound would explain the increasing melting temperature as the stoichiometry of the compound is approached.

It is well known that experimental measurements of the liquidus temperatures of slags are difficult since slags invariably supercool. While DTA technique is a well established method to detect phase transformations, it has limited use in determining the liquidus temperatures in the case of slag systems. The exothermic peak during cooling mode associated with the solid separation at the liquidus temperature occurs at much lower temperatures due to supercooling effect. During the heating mode, the compositional inhomogeneities would make the results somewhat uncertain and irreproducible. However, the DTA study on some of the present samples would provide a rough idea regarding the lowest temperatures at which, the solid phase precipitates.

DTA studies on slags 4, 5 and 10 were carried out on a SETARAM DSC-2000K under purified argon atmosphere. Platinum crucibles with dimensions of 6 mm in height and 5 mm in diameter were used. The highest temperatures, at which the thermal peaks were detected, are listed in Table 2. While the peaks of highest temperature in the case of sample 4 and 5 were detected during heating cycle, the peak of the highest temperature of sample 10 was observed during cooling. As mentioned earlier, the peaks obtained due to heating are unreliable because of the sample being inhomogeneous due to various phases formed during the previous solidification of the slag. With regard to the observation during the cooling mode, in view of the supercooling effect, it is reasonable to expect that the liquidus temperature of this sample could be higher than 1 694 K. Although the results of DTA measurements are not conclusive, they are in line with the result of SEM analysis indicating the separation of a high-temperature solid phase. Moreover, the DTA peaks shown in Table 2 suggest that solid precipitation occurs at higher temperature at compositions of higher FeO and Al₂O₃ contents. This finding agrees with the observation that no viscosity measurement could be conducted for the slags with high FeO contents, viz. slags 6–11 below 1 753 K and these slags were two-phase mixtures after preparation.

Seetharaman et al.⁵ have recently proposed that the second derivative of the activation energy for viscous flow with respect to temperature would show a discontinuity in the vicinity of the liquidus temperature. This has been verified in the case of viscous flows for pure water as well as binary and complex silicate melts. These authors⁵ have suggested that this second derivative approach can be used to estimate the liquidus temperatures of multicomponent silicates.
which are often difficult to determine due to supercooling effects. In order to further examine the temperatures of solid precipitation in the sample, the second derivative approach was applied to slags 4 and 5.

The results of viscosity measurements of slags 4 and 5 are presented in Fig. 3. The results shown in Fig. 3 correspond to an average of a set of viscosity measurements at different rotation speeds indicating that the slags were behaving like Newtonian liquids. The lowest temperature for the viscosity measurement of slag 4 is almost 200 K higher than that of slag 5. The measurement in the case of slag 4 had to be terminated at 1,709 K. Below this temperature, the results for slag 4 were not reproducible, indicating non-Newtonian behaviour of the sample. This could be due to the precipitation of the solid phase, presumably the ternary compound (phase 5 observed in Fig. 2).

Figures 4(a) and 4(b) present the second derivatives of the activation energy divided by the gas constant \(Q/R\) respective to temperature, (a) slag 4, (b) slag 5.

### Table 2. The thermal peaks of the highest temperature in DTA measurements.

| Sample  | Onset Temperature of the Peak (K) |
|---------|-----------------------------------|
| Sample 4* | 1679 |
| Sample 5* | 1660 |
| Sample 10 | 1694 |

* Peak detected during heating cycle

The results of the viscosity measurements of slags 4 and 5 were reproducible, indicating non-Newtonian behaviour of the sample. This could be due to the precipitation of the solid phase, presumably the ternary compound (phase 5 observed in Fig. 2). Figures 4(a) and 4(b) present the second derivatives of the activation energy divided by the gas constant \(Q/R\) respective to temperature.

The results show a discontinuity at 1,749 K as the temperature is decreased in the case of slag 4. A similar discontinuity in the case of slag 5 occurs at 1,683 K.

The temperatures at which these discontinuities occur are marked in the figures. While the temperature of the discontinuity of slag 5 compares well with the DTA peak, the predicated liquidus temperature using the second derivative approach is somewhat higher than the DTA peak. The measurement in the case of slag 4 is almost 200 K higher than that of slag 5. The measurement in the case of slag 4 had to be terminated at 1,709 K. Below this temperature, the results for slag 4 were not reproducible, indicating non-Newtonian behaviour of the sample. This could be due to the precipitation of the solid phase, presumably the ternary compound (phase 5 observed in Fig. 2).

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