Effect of Al_2O_3 and TiO_2 Additions on the Lubrication Characteristics of Mould Fluxes

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ABSTRACT

The continuous casting of steel results in the absorption of Al_2O_3 and TiO_2 by the mould flux. Rotational viscometry was carried out on fluxes used for the casting of various grades of steel with varying amounts of Al_2O_3 and TiO_2 added up to 10% wt. It was found that Al_2O_3 increased the viscosity of all the fluxes to a significant degree, whilst the effect of TiO_2 was dependant upon the temperature and flux saturation limits; both additions decreased the solidification temperature.

1. INTRODUCTION

Mould fluxes are synthetic slags applied to the meniscus of the steel in the mould during casting. On melting, these fluxes control the removal of heat from the solidifying strand and provide the lubrication necessary to prevent sticking of the steel strand to the copper mould, which can result in a breakout of liquid steel. Mould fluxes serve five purposes in the casting of steel. These are [1-6]:

1) Prevention of reoxidation of the meniscus by atmospheric oxygen.
2) Prevention of rapid heat loss from the meniscus.
3) Absorption of non-metallic inclusions from the liquid steel.
4) Control of the transfer of heat between the strand and the mould.
5) Prevention of steel sticking to the copper mould by providing sufficient lubrication.

The composition of mould fluxes will vary in accordance with the casting conditions, but most have compositions within the pseudo-wollastonite region of the silica-lime-alumina ternary phase diagram. Other oxides such as Na_2O, B_2O_3, MgO, and Fe_2O_3 may be added to control heat transfer and lubrication characteristics.

1.1 Effect of metal oxide additions

The ability of an oxide to form a network can be expressed in terms of its local field strength, given by[7]:

$$F = \frac{Z_c}{a^2} \qquad (1)$$

F = the field strength,
Z_c = the valance of the cation and
a = the distance between the centre of the radii of the cation and oxygen ions.

A cation with a higher field strength (F~1.5) is more able to attract oxygen to achieve a denser packing and become a glass former. Field strengths of ~0.1-0.4 characterise network modifiers which tend to lose oxygen when dissolved in a slag.

Network modifiers break up the silicate network by adding oxygen to the network of silicate tetrahedra[8]. This causes the network of silica tetrahedra to separate as each tetrahedra can have its own oxygen ion. The cation will be accommodated at the breaks in the silicate structure. This results in the formation of discrete molecules which decrease steadily in size as more basic oxides are added to the melt. Fluorine, added either as CaF_2 or NaF, acts as a fluidiser, reacting with the divalent oxygen in the silica network. This results in a breakdown of the Si-O network as no bonding between tetrahedra takes place[1]. B_2O_3, a network former, increases the silica chain length, however because it also lowers the solidification temperatures of the flux, the net effect is a decrease in the viscosity of the mould flux[1].

In multicomponent slags, Al^{3+} (F=0.96) assumes a coordination number of 4 and forms tetrahedrons of $[AlO_4]^{5-}$ which are a similar size to the silica tetrahedron $[SiO_4]^{4-}$, so that in such systems aluminium is a glass former. In order to substitute Al^{3+} for Si^{4+} in the silica chain and maintain electrical neutrality, the presence of divalent cations such as Ca^{2+} is required. Thus the ability of alumina to increase the silica chain length is dependant upon the concentration of the basic oxides.

There is little literature on the effect of TiO_2 on the viscosity of SiO_2-CaO-Al_2O_3 slags. In silica glasses the coordination number of Ti^{4+} (F=1.04) is usually 6 which precludes the formation of a tetrahedron capable of forming a network with silica[7]. Thus TiO_2 will lose oxygen to the silica network and should decrease the viscosity of the slag[9,10]. In contrast to this, some researchers[11,12] suggest that the addition of TiO_2 increases the average molecular chain length. However, due to the relative weakness of the Ti-O-Si bond compared to the Al-O-Si bond, TiO_2 additions should have a relatively small effect on the viscosity.

1.2 Viscosity of Mould Fluxes

The temperature dependence of viscosity of Newtonian fluid can be expressed by Eqn (2)[13].

$$\log \eta = \frac{\Delta G_f}{2.303 \times RT} + \log \frac{hN}{V_m} \qquad (2)$$

η = viscosity
h = 6.63 x 10^{-34} J.s
N = 6.02 x 10^{23} molecules/mole
R = 8.314 J.mol^{-1}.K^{-1}
V_m = the molar volume (m^3/mol)
ΔG_f = the activation energy for viscous flow (J/mol) and
T = the temperature (K)

The basic building block of these fluxes is the $[SiO_4]^{4-}$ tetrahedron. For flow to occur, bonds must be broken between tetrahedra. This requires considerable shearing stress (the viscosity of pure silica is 1.5 x 10^5P at 1940°C[14]). An increase in the basic oxide content up to 20% results in a reduction in the number of highly directional Si-O bonds and the activation energy for flow can decrease by up to 60%[15] .

2. EXPERIMENTAL

In this project the effect of Al_2O_3 and TiO_2 absorption on the viscosity of three mould fluxes was assessed. The amounts of additions was varied from 2% to 10% by weight and the viscosity measured from 1300°C to the flux solidification temperature using rotational viscometry techniques. Three mould fluxes were used in this project; Their composition is given in Table I.

Table I. Composition (in %wt) of mould fluxes used.

Component	A	B	C
SiO_2	36.72	30.45	31.24
Al_2O_3	4.14	4.5	2.68
CaO	31.25	33.63	40.80
Fe_2O_3	1.64	1.65	0.95
Na_2O	10.05	3.12	6.45
MgO	3.71	6.63	5.18
F	9.61	5.27	6.81
MnO	0.05	2.22	0.07
TiO_2	0.103	0.098	0.092
S	0.29	0.31	0.13
B_2O_3	-	5.5	-
P_2O_5	0.03	0.04	0.53
Basicity	0.95	1.32	1.47

The fluxes studied cover a range of casting conditions:

Flux A: This is used for the high speed (~1.6m/min) casting of Low Carbon, Aluminium Killed (LCAK) steel.
Flux B: This is used for the high speed casting of Ultra Low Carbon (ULC) steel.
Flux C: This is used for the low speed (<1.2m/min) casting of Medium Carbon (MedC) steel.

2.1 Sample Preparation

Prior to mixing the samples, the fluxes were decarburised by heating at 650°C for 3 hours. After decarburising, the flux was ground, weighed and the required additions were added. The mixture was then sized through a 500μm sieve and mixed using a rotary tumbler.

2.2 Viscosity Testing

A viscosity - temperature profile was produced for each sample from 1300°C until solidification. The flux was considered solid once viscosity measurement became impossible.

The viscosity measurements were carried out using a rotational viscometer "Model BL" manufactured by Tokimec of Japan. The viscometer was located above a pot furnace as shown in Fig. 1. The furnace is controlled by a type J thermocouple located in the interior of the furnace.

304 Stainless steel crucibles, rotors and spindles were used in this project due to their availability, high temperature strength and relative inertness. The spindle is connected to the viscometer using a mild steel connecting rod 2.5 mm in diameter.

2.3 Experimental Procedure

A crucible containing 580g of molten flux was then placed in the furnace at 1300°C. The furnace was then closed and the temperature bought up to 1300°C. At this temperature, 30 minutes was allowed for thermal equilibrium to be established and then the first viscosity measurement was taken. The temperature was lowered at 40 to 50 degree intervals until it was within 50 degrees of the expected solidification temperature, at which time the temperature was lowered at 10 degree intervals. Viscosity measurements were taken after allowing 20 minutes for thermal equilibrium to be attained.

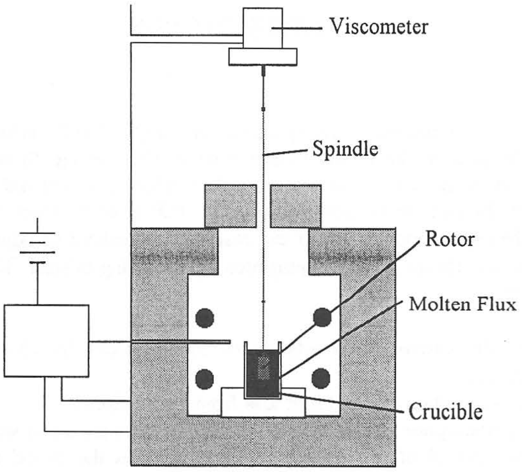

Fig. 1. Furnace and viscometer layout.

There were a number of possible errors associated with this work. Errors relating to the accuracy of the viscometer were estimated to be within 5% up to 5P. At viscosities in the range of 20P, the error was estimated to be 30%.

3. RESULTS

3.1 Viscosity of LCAK Casting Flux with Al_2O_3 additions

The viscosity of the LCAK casting flux with increasing Al_2O_3 additions was determined using rotational viscometry. The results are shown in Fig. 2. The given Al_2O_3 content includes that of the base flux.

The addition of Al_2O_3 increased the viscosity of the base flux at all temperatures and decreased the solidification temperature. The relationship between log η and 1/T is linear until a temperature is reached where viscosity measurement becomes impossible. The temperature at which this occurred decreased with increasing Al_2O_3 content.

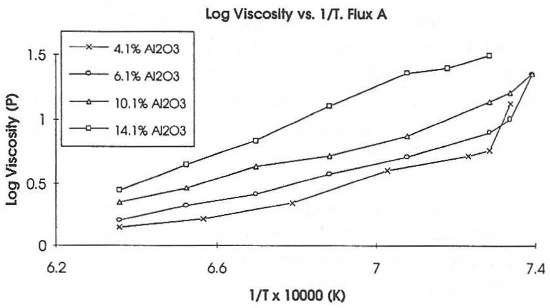

Fig. 2. Effect of Al_2O_3 on the viscosity of the LCAK casting flux

3.2 Viscosity of the ULC casting flux with TiO_2 additions

The viscosity of the ULC casting flux with increasing TiO_2 additions was determined using rotational viscometry. The results are shown in Fig. 3. TiO_2 has no significant effect on the viscosity of the flux at temperatures between 1150 and 1300°C. At lower temperatures, only TiO_2 additions of 10% increased the viscosity markedly. The addition of TiO_2 suppressed the solidification temperature and eliminated the gradual increase in viscosity seen in the base flux prior to solidification.

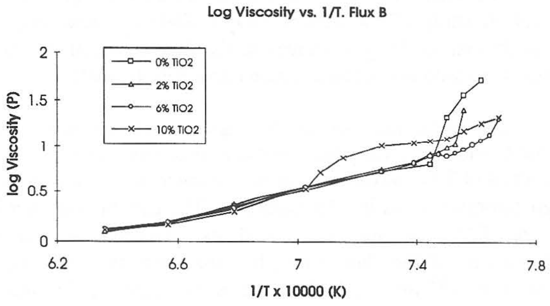

Fig. 3. Effect of TiO_2 on the viscosity of the ULC casting flux.

3.3 Viscosity of the MedC casting flux with TiO_2 and Al_2O_3 additions

The viscosity of the MedC casting flux with both TiO_2 and Al_2O_3 additions was determined using rotational viscometry and the results are shown in Fig. 4. This flux has a much higher solidification temperature than LCAK or ULC casting fluxes. The effect of TiO_2 on the viscosity of the flux is negligible between 1250 and 1300°C, but at lower temperatures the effect depends upon the amount of TiO_2 present. TiO_2 additions up to 6% decrease the viscosity of the flux slightly but TiO_2 additions of 10% dramatically increase the viscosity. TiO_2 suppressed the solidification temperature slightly; the addition of 10% TiO_2 decreasing the solidification temperature by 10°C.

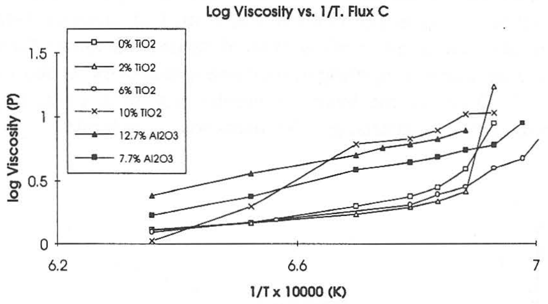

Fig. 4. Effect of TiO_2, Al_2O_3 on the viscosity of the MedC casting flux.

The addition of Al_2O_3 significantly increases the viscosity of flux over all temperatures to a much higher extent than found with the addition of TiO_2 to the same extent.

4. DISCUSSION

4.1 Effect of Al_2O_3

The variation of the activation energy for viscous flow, ΔG_f, of these fluxes with increasing Al_2O_3 is shown in Fig. 5. Al_2O_3 forms networks within the molten flux, increasing the molecular size and decreasing the molecular mobility.

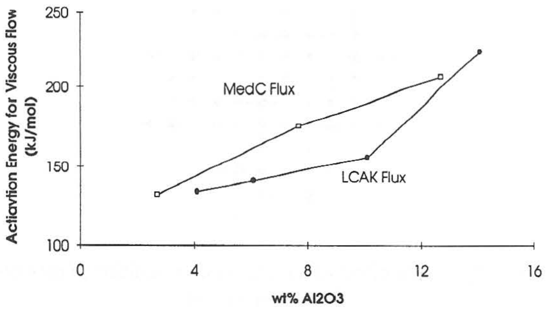

Fig. 5. Variation of ΔG_f with increasing Al_2O_3.

The solidification temperature of both fluxes was suppressed by 10^oC with the addition of 6% Al_2O_3. The effect of 10% Al_2O_3 on the solidification temperature could not be determined due to the viscometer reaching is measuring limit.

The variation of the molar volume of these fluxes with increasing Al_2O_3 content is shown in Fig. 6. The addition of Al_2O_3 to the fluxes increased their molar volume. This is because the molecular size has been increased. The base LCAK flux had a molar volume of $8.847cm^3mol^{-1}$. Increasing the Al_2O_3 content by 6% increases the molar volume to $27.14cm^3mol^{-1}$. Increasing the Al_2O_3 content to 14.1% increases the molar volume to $3630cm^3mol^{-1}$, a 300 - fold increase on the base value.

A simple model was formulated to investigate the effect that the addition of a network former had on the average molecule size (in terms of atoms per molecule) of a melt of arbitrary binary molecules. The addition of one atom of the network former formed a large molecule comprising of four binary molecules, as shown in Fig. 7. Once all the binary molecules had been used, larger macromolecule comprising of 37 atoms were then formed.

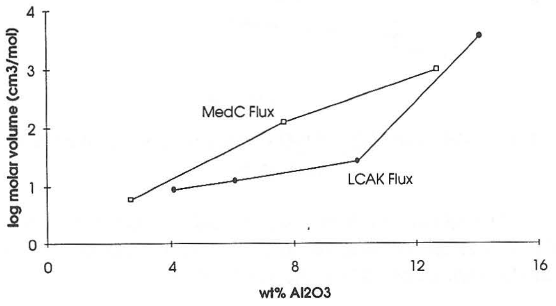

Fig. 6. Variation of V_m with Al_2O_3.

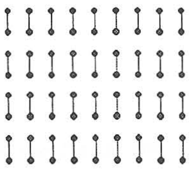

Fig. 7(a) . An imaginary melt of 36 binary molecules

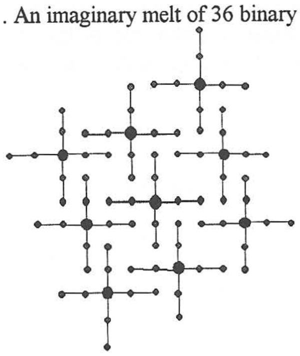

Fig. 7(b) . The effect of 11.1% mole wt addition of network former on the melt.

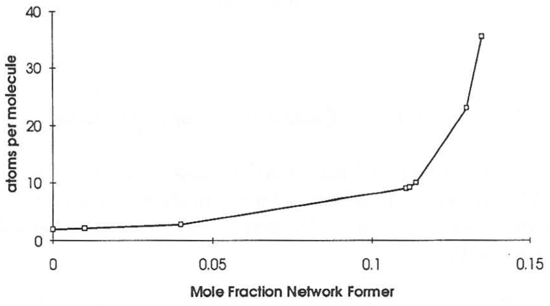

Fig. 8. Modelled effect of network former additions on a binary melt.

As the mole fraction of the networking additions increases towards saturation, the molecular size increases dramatically. These results reflect the experimental observations that the molar volume increases exponentially with additions of Al_2O_3 up to 6%. At this stage most of the smaller molecules in the flux have been combined to form larger molecules. With further additions, a saturation is reached where these large molecules must then combine to form macromolecules, sharply increasing the molecular volume, as indicated by the increase in V_m of 130 times at 14.1 %wt Al_2O_3 (Fig. 8).

This model is oversimplistic and does not take into account factors that may limit molecular growth, but it does provide a basis for understanding the effect that saturation of networking ions may have on the molecular size, and viscosity, of these fluxes.

4.2 Effect of TiO_2

The addition of TiO_2 to the ULC casting flux had very little effect in the temperature range from 1300^oC to 1150^oC. The addition of TiO_2 did however alter the solidification characteristics. The base flux solidified over a range, indicating that some crystalline regions may have nucleated. The emergence of these pores increases the viscosity of the flux. The addition of TiO_2 prevented this from occurring. This the behaviour expected from a network former.

The addition of TiO_2 lowers the solidification point of the fluxes. A study of the ternary SiO_2-CaO-TiO_2 phase diagram suggests that as TiO_2 is increased, the flux composition moves from the pseudo wollastonite region into a eutectic valley.

The large increase in the viscosity of the flux below 1150^oC with 10% TiO_2 may be due to flux saturation or may be the result of TiO_2 having a different, stronger networking effect at high saturations and low temperatures. The coordination number of the Ti^{4+} ion may be related its concentration and the temperature of the flux. At high saturations, the coordination number of Ti^{4+} may be 4 which will result in the rapid formation of networking tetrahedra.

The activation energy for viscous flow, ΔG_f, of the ULC casting flux increases with TiO_2, as shown in Fig. 9. At 10% TiO_2, ΔG_f has been increased by 46%.

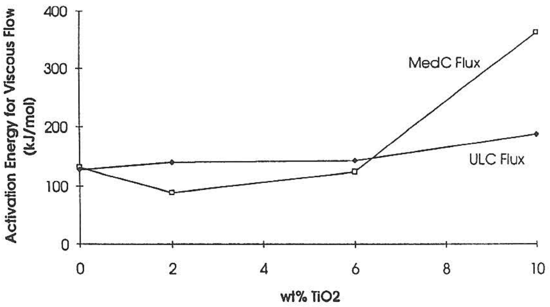

Fig. 9. Variation of ΔG_f with TiO_2.

TiO_2 additions up to 6% had very little effect on the viscosity of the MedC flux. The fluxes with 2% and 6% TiO_2 had a lower viscosity than the base flux over all temperatures. This is different to the effect that TiO_2 had on the ULC casting flux, where the addition of even a small amount of TiO_2 increased ΔG_f. TiO_2 is not acting as a network former at low concentrations in the MedC flux.

The MedC casting flux with 10% TiO_2 had a much higher viscosity than the base flux over all the temperatures ranges except at 1300°C. At 1300°C, the viscosity of the base flux was decreased from 1.30 to 1.06 Poise with 10% TiO_2. The changing effect of TiO_2 on the viscosity is reflected in the variation in molar volume of the flux with TiO_2, as shown in Fig. 10. At low concentrations, TiO_2 does not significantly increase the molar volume of the MedC flux however it does increase the molar volume of the ULC flux uniformly. At high concentrations of TiO_2, the molar volume of the MedC casting flux is suddenly increased, which could be due to saturation or changes in the coordination number of the Ti^{4+} ion. These effect are not seen in the ULC flux, possibly because saturation has not been reached. TiO_2 is always acting as a network former in the ULC flux.

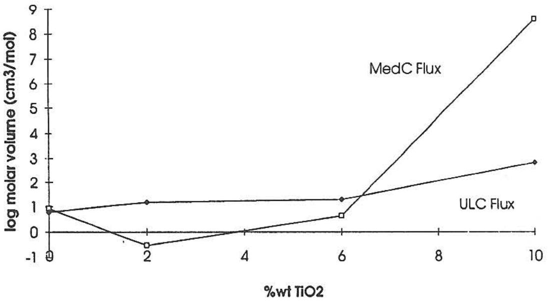

Fig. 10. Variation of V_m with TiO_2.

It is not clear why TiO_2 additions up to 6% decreased V_m and ΔG_f of the MedC flux. TiO_2 may be acting as a network modifier at low concentrations, donating O^{2-} to the silica network and decreasing the molecular size. At high saturations, the solubility limit of Ti^{4+} in the flux may be exceeded and it begins to network, increasing the silica chain length, ΔG_f and V_m.

This behaviour was not found in the ULC casting flux and could a result of the difference in compositions. The MedC casting flux does not contain any B_2O_3 and forms a more basic flux. Ti^{4+} may replace Al^{3+} in the network, due to its higher affinity for oxygen. The Al_2O_3 content of this flux is 2.68 %wt. It could be expected that TiO_2 additions up to about 4% should displace the Al^{3+} from the silica chain, thereby decreasing ΔG_f due to the weaker nature of the Ti-O-Si bond. Beyond this concentration, Ti-Al networks may begin to form as rutile and alumina, increasing the average molecule size.

5. SUMMARY

Al_2O_3 consistently increases the viscosity of LCAK and MedC casting fluxes. The effect on the LCAK casting flux is greater because saturation is reached at lower additions of Al_2O_3. As networking occurs, the average molecule size increases which results in a larger molar volume. The absorption of Al_2O_3 by the mould flux during casting will dramatically increase the viscosity of the flux. If the Al_2O_3 content in the flux increases by 10 %wt, the shear stress on the steel shell will be doubled. This could easily lead to breakouts unless the velocity profile across the mould-shell gap is reduced by decreasing the machine speed rapidly. A consequence of a flux having a higher viscosity is that its capacity to remove inclusions from the steel is reduced. This leads to reduced product quality and possible downgrading of cast slabs.

TiO_2 has a negligible effect on the viscosity of ULC and MedC casting fluxes at low concentrations. At higher saturations the viscosity of the flux will increase sharply as a result of massive networking and molecular growth. TiO_2 decreases the solidification temperature of the flux and inhibits crystallisation.

The absorption of 6% TiO_2 does not increase the viscosity of the flux markedly. In the MedC casting flux, it was shown that a small amount of TiO_2 in the flux decreased the viscosity of the flux. It should not be necessary to alter the casting speed when casting titanium bearing steels unless the TiO_2 content in the flux is approaching 10 %wt.

The decrease in the solidification temperature with increasing TiO_2 may lead to more rapid heat transfer and may increase the instances of longitudinal cracking in the cast slab.

6. ACKNOWLEDGMENT

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