DEVELOPMENT OF FLUORIDE-FREE FLUXES FOR BILLET CASTING(1)

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Abstract

More than 90% of the world's steel is produced using the continuous casting process, a method that has seen enormous advances over the last forty years. Mould fluxes play an important part in this process. These fluxes contain fluorides, which can volatilize at operational temperatures polluting both the plant air and cooling water. Airborne fluoride could potentially be a health and safety issue. Waterborne fluoride forms hydrofluoric acid (HF), which can cause plant corrosion, and may lead to contamination of watercourses necessitating water treatment schemes. This adds to production costs and may present potential environmental hazards. These concerns could be reduced or eliminated by removing fluoride from mould fluxes. The present study examines the effect of different fluxing agents upon key mould flux properties. When substituting fluorides for alternative fluxing agents the key design properties of the fluoride-containing flux must be replicated; namely, (i) flux viscosity at 1300°C, (ii) break temperature and (iii) percentage of crystallinity in the solid slag layer. This is to ensure 'optimal casting' where operational problems, such as sticker breakouts and defects such as longitudinal cracking, are minimized. In addition, the quality of the steel should not be affected by the substitution. Therefore, any substitute/additive or combination of additives would have to possess the capacity to replicate the effects that fluorine has on mould flux behaviour. This study focuses on B_2O_3 and Na_2O as alternative substitutes for CaF_2 in billet fluxes. The new flux has been successfully trialed on continuous casting plant.

Key-words: Continuous casting, Fluoride-free mould fluxes.

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INTRODUCTION

More than 90% of the world's steel is produced using the continuous casting process (Figure 1a), a method that has seen enormous advances over the last forty years. In this process molten steel is delivered through a submerged entry nozzle (SEN) into a water-cooled copper mould. The steel solidifies to form a shell.

Mould fluxes are fed onto the free surface of the liquid steel on top of the mould where a number of processes come into play; (i) the mould flux gradually moves down through the flux bed, (ii) carbon particles in the powder react with oxygen in the air to form a reducing atmosphere of $CO_{(g)}$ which protects the molten steel from oxidation, (iii) mineral components eventually form a sinter layer and then (iv) melt to form a liquid pool and spread over the liquid steel surface, which both protects the steel from oxidation and acts as a reservoir for slag infiltration into the mould/shell channel (Figure 1b). The pool should have a depth of >10mm to ensure (i) good slag infiltration into the mould/shell channel(1,2) and (ii) cover any standing wave caused by the metal flow.

The first slag to penetrate into the shell/mould channel solidifies against the water-cooled copper mould to form a slag film consisting of a solid (usually glassy) layer (ca. 2mm)(3) with a liquid layer (ca. 0.1 mm), which lubricates the newly formed shell. As casting proceeds, the hotter regions of the glassy layer tend to crystallize.

A successful casting flux must carry out the following functions:

1) protect the meniscus of the steel from oxidation;
2) provide thermal insulation to prevent the steel from solidifying;
3) provide liquid lubrication for the strand;
4) provide the optimum level of horizontal heat transfer for the steel grade being cast; and
5) absorb inclusions from the steel.

Figure 1. Schematic drawings of (a) the continuous casting process(4) and (b) the various slag layers formed in the mould(5)

Synthetic mould fluxes typically have (CaO/SiO_2) ratios in the range 0.7 to 1.3 with flux additions of up to 10% (usually CaF_2 and Na_2O) and about 5% Al_2O_3. Mould fluxes usually contain carbon to control the rate of liquid slag production, i.e. melting rate, (ca. 4% C for casting slabs and up to 20% C for casting billets). Further background information can be found in a recently published review on mould fluxes(6).

WHY REMOVE FLUORINE? ENVIRONMENTAL PRESSURES

The environmental pressures upon pyrometallurgy (including steelmaking) have increased substantially during recent years, due to concerns about (i) carbon emissions (Kyoto protocol) and energy input in general, (ii) landfill waste and (iii) toxic emissions, to name but three. Taxes are now being collected in Britain and Europe for (i) and (ii) and other fines can be levied by the courts for breaching regulations covering toxic emissions. Taxes, as a means of reducing environmental impact, are increasing in popularity. However they can have unwanted effects, as regulation tends to make polluters adopt a specific technology, or the same sort of clean-up regardless of individual costs(7). In addition, taxes and regulation (by raising the price of local output) will reduce consumer demand (the purpose of the tax) and the industries' demand for labour(7). The national economy will be further reduced if production is displaced to less-regulated jurisdictions, while the global environment is still being degraded. Green taxes may also yield little revenue in the long run, since if they are successful polluters will move to cleaner, less-taxed technological alternatives. Fluorine emissions are the main environmental concern surrounding the continuous casting of steel, since fluoride flux additives (i) emit gaseous HF, SiF_4, NaF etc. into the atmosphere (they contribute to acid rain), (ii) are leached from landfill sites into ground-water, (iii) corrode plant equipment and (iv) are possibly detrimental to staff health(8). The two primary research objectives of the Japanese steel companies are currently (i) to reduce overall slag volumes and (ii) to reduce CaF_2 content in slags(9), this study is directly relevant to these objectives. Removing fluoride additives from mould fluxes would eliminate the problems outlined above, but fluorides are used for a number of specific technical reasons, such as reduction of melting temperatures, viscosities etc. Thus any substitutes would have to replicate the technical benefits provided by fluorine. There are various candidates among the oxides that can substitute for fluorides, primarily B_2O_3 and Na_2O.

DESIGN FRAMEWORK

In this study 'optimum casting' is defined as the minimization of both operational problems (such as sticker breakout) and defects (such as longitudinal cracking). Other defects (e.g. transverse cracking, depressions) are also related to a lack of lubrication. Powder consumption (Q_s) is a measure of lubrication. Optimum powder consumption can be calculated from empirical rules. The relationship due to Ogibayashi et al.(10):

$$Q_s = 0.6/\eta V_c \qquad (1.)$$

where η is the viscosity and V_c is the casting speed, was found to have the strongest performance across a wide range of casting conditions(11,12). However, there are other more complex relationships that include the crystallization temperature and the oscillation characteristics(13). Therefore, lubrication can be related to η. Thus η becomes the first critical design parameter.

Longitudinal cracks are particularly prevalent in medium carbon (MC) steel grades and arise from a mismatch in the shrinkage coefficients of δ- and γ-Fe leading to residual stresses which are relieved by cracking. It is well known that longitudinal cracking can be minimized by reducing the horizontal heat transfer which is achieved with a thick crystalline solid slag layer(11). The crystallites scatter radiation. The density of the crystalline phase is greater than that of the glassy phase so crystallization is accompanied by shrinkage causing 'surface roughness' on the mould side, which in turn creates an air gap. Therefore the second critical design parameter is degree of crystallinity in the solid slag film.

Sticker breakouts occur when the steel ferro-static pressure exceeds the mechanical strength of the steel shell. This is overcome with a thicker steel shell, requiring an increase in the horizontal heat transfer, which is achieved by a thin glassy solid slag layer. The thickness of the solid slag film is related to the break (or solidification) temperature $(T_{br})^{*(11)}$. A high T_{br} will result in a thick solid slag film and a low T_{br} in a thin solid slag film. Therefore, the third critical design parameter is the break temperature.

The required viscosity can be related to the break temperature (Figure 2a) where the x axis can be thought of as lubrication and the y axis as horizontal heat transfer. In summary, the three critical mould flux design parameters are:

- the viscosity of the liquid mould flux (for the casting conditions) usually taken at 1300°C;
- the solidification or break temperature, which determines the thickness of the solid slag layer (and the liquid layer thickness); and
- the degree of crystallinity developed in the slag film.

EFFECT OF SUBSTITUTION ON THE CRITICAL FLUX POWDER PROPERTIES

Effect of B_2O_3 on Viscosity

The viscosity of the slag is very dependent upon its chemical structure. In silicates, 4 Oxygen atoms surround a Silicon ion in tetrahedral co-ordination. Borates can have 3-fold and/or 4-fold co-ordination at the boron centre. Borosilicates also display 3-fold and/or 4-fold co-ordination and thus the relation between viscosity and composition is dependent upon the nature of the coordination and is difficult to predict. B_2O_3 additions have been reported to both decrease and increase the viscosity (Figure 2b-e). Consequently, the effect of B_2O_3 on mould fluxes was determined in this study.

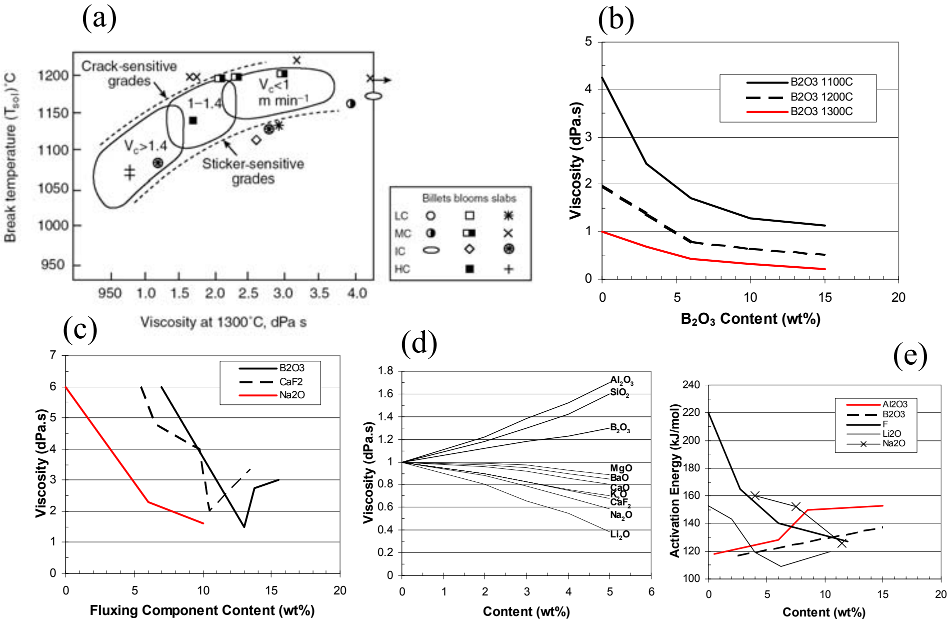

Figure 2. (a) Relation between viscosity, break temperature and casting speed(14) (b) Effect of B_2O_3 on viscosity of mould flux(after 15) (c) Effect of various components on viscosity of mould flux(after 15) (d) Effect of various additions on the viscosity of a flux used for high-speed casting(after 16) and (e) Effect on various additions on activation energy (E□) for viscous flow of mould flux(after 17).

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[*] In this study the break temperature is preferred to the solidification temperature, because conditions in the mould are considered to be similar to those found in the viscometer, where the break temperature is measured.

Effect of B_2O_3 on Solidification (or Break) Temperature

The solidification temperature (T_{sol}) (or crystallization temperature (T_{crys})) is usually measured by DTA/DSC or by the optical thermocouple method. The break temperature (T_{br}) is the temperature below which there is a dramatic increase in viscosity. Various investigations have found that T_{sol} is close to T_{br} in some cases but can vary by up to 80°C in other cases. This may be related to heterogeneous nucleation in the DTA crucible. The effect of different oxide components on crystallisation temperature is shown in Figure 3a. Figure 3b shows the effect of B_2O_3 on freezing and softening points. Kim et al$^{(17)}$ reported the following equation for the "crystallisation" or solidification temperature:

$$T_{crys} = 1241.6^{o}C - 2.15x_{MgO} - 1.41x_{Al_2O_3} - 4.49x_{Na_2O} - 8.55x_{CaF_2} - 6.4x_{Li_2O-}15x_{B_2O_3} \quad (2.)$$

where x is the mole fraction.

The approximate mean of the effect of B_2O_3 on T_{sol} or T_{crys} (ΔT_{sol}) shown in Figure 9.2 lead to:

$$T_{sol} = \Delta T_{crys} \approx -20K(\%B_2O_3)^{-1} \quad (3.)$$

Kijak et al.(18) have also reported:

$$T_m \approx -17K(\%B_2O_3)^{-1} \quad (4.)$$

Sridhar and Mills$^{(19)}$ carried out numerical analysis of break temperature as a function of chemical composition. They had insufficient data to determine a reliable value for the effect of B_2O_3 on T_{br}. The effect on solidification and melting points of common mould flux components are shown in Table 1.

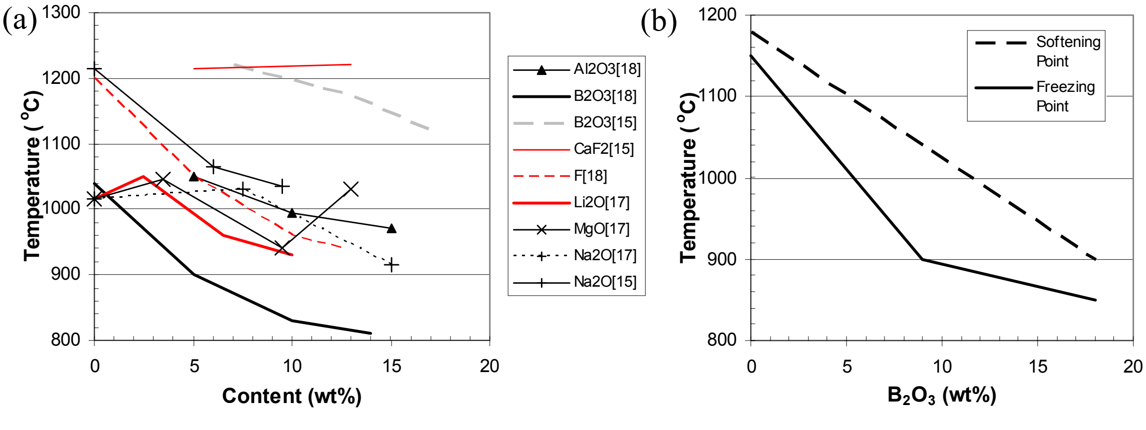


Figure 3. (a) Effect of various additions on "crystallization" temperature$^{(after\ 18,\ 17\ and\ 15)}$ (b) Effect of B2O3 addition on softening and freezing point $^{(after\ 20)}$

The Effect of B_2O_3 on Percentage of Crystalline Phase in the Slag Film

The literature contains no information about the crystallinity of solid slag films for fluoride-free mould fluxes. However, simulation experiments have been reported, which provide a ranking of the crystallization tendency and thus offer a good opportunity to examine what effect B_2O_3 has on the crystallinity of the solid slag film. Chang et al.(21) developed a test in which a known mass of molten slag is poured from a platinum dish into a water-cooled, copper block$^{(21)}$. The thickness of the crystallized layer is measured and the percentage crystallization determined according to:

$$\%\,\text{Crystallization} = \frac{\text{Thickness of Crystallized Layer}}{\text{Thickness of Solid Slag}} \times 100 \qquad (5.)$$

Chang et al.(21) reported that fluorine increased the percentage of crystallinity, whereas both B_2O_3 and MgO decreased the percentage of crystallinity. If F^- is replaced by B_2O_3 the crystalline fraction in the solid slag film will be decreased (Figure 4a). This will have to be offset by increasing either (i) CaO/SiO_2 ratio or (ii) Na_2O content (not cited by Chang(21)). The effect of B_2O_3 on crystallinity of mould fluxes was examined in this study.

PLANT TRIALS

It was decided to take an existing fluoride-containing powder as the basis of this study. This approach was chosen to allow for the conservative nature of the industry and difficulty in obtaining trials. It was decided to remove all of the fluorine. This would change the three critical design parameters of the powder, requiring addition of substitute oxides in order to match the original values. The resulting composition should be inside the 'optimum casting' window.

Frequently, 'high-viscosity' fluxes are used to cast billets(22). These fluxes do not have a marked break temperature, but show a gradual increase in viscosity with decreasing temperature, because these glassy slag form super-cooled liquids (Figure 4b). This means that the only design parameter which needed consideration was the viscosity (as there is no break temperature and no crystalline fraction of the solid slag layer). Therefore billet powders were selected as the starting point for this study.

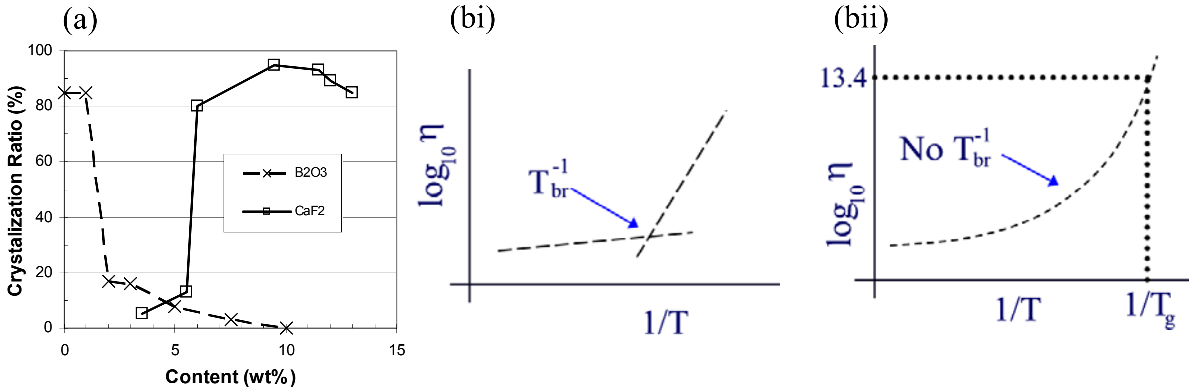


Figure 4. (a) Effect of F and B2O3 additions on the crystallization ratio of mould flux(21) (b) Schematic diagram of log10 viscosity as a function of reciprocal temperature (1/K) for (i) conventional fluxes and (ii) for glassy, high-viscosity billet fluxes(11)

EXPERIMENTAL

The experimental work consisted of three parts. Firstly, various B_2O_3 additions were made to an existing fluorine-free trial flux composition used by Sidenor I+D. Measurements were carried out on these compositions to determine the effect of B_2O_3 on viscosity, break temperature and crystallinity. Secondly, an existing fluorine-containing flux powder composition was supplied by Sidenor I+D (including its measured viscosity at 1300°C). The Iida temperature-composition-viscosity model was used to calculate the viscosity when fluorine is removed, and replace with an amount of B_2O_3 / Na_2O that would result in a flux powder giving the same viscosity as the original. The experimental samples were made up as glass frit by Borax Europe

Limited. Raw material components were mixed to give the target glass composition, then melted in an electric furnace and poured through water to quench to a glass. Thirdly, Carboox prepared samples using the chemical composition determined before and designed the optimum raw materials combination in order to obtain the adequate melting rate, so guaranteeing the performance of the F-free flux in the mould during the plant trials.

Viscosity Measurements

At Imperial College a Brookfield LVDV II viscometer with Fe suspension links was used. Fe crucibles (of dimensions 30mm outer diameter, 26 mm internal diameter and 52 mm in height) and Fe bobs (8mm diameter) were used in the measurements. The bob was positioned in the melt such that (i) a gap of 10 mm was maintained with the base of the crucible and (ii) the throat of the rotor is covered to a depth of 2 - 4 mm. This means that any torque arising from either the rotor throat or the base is negligible. A protective Ar atmosphere was used. Viscosimeter performance was regularly checked in calibration experiments using Brookfield standard oils (at 20 – 30°C) to reduce systemic errors.

At Nippon Thermochemical the “Rotating Cylinder Method" was also applied. Molten slag was supplied between crucible and spindle. The torque was supplied by rotating the spindle and measured. The calibration curve was prepared with standard oil of known viscosity.

CRYSTALLINITY MEASUREMENTS

The degree of crystallinity was measured using the Li test(23). This is similar to the Chang test(21) but differs in that the molten sample is not quenched on a Cu block but is poured into a stainless steel crucible and then held at 610°C for 20 minutes, to simulate the annealing of mould flux film between mould and steel shell. Li et al.(23) noted that the Chang test(21) does not correlate strongly with the crystallinity measured in actual slag film samples(24). The addition of the holding step however is reported to improve this correlation considerably.

VISCOSITY MODELING

The viscosity of the standard fluorine-containing flux powder was supplied by Sidenor I+D (This was 12.7 dPa.s at 1300°C). The viscosity when fluorine is removed from this composition was then calculated using the Iida model(25) (the viscosity increased). Finally a set level of B_2O_3 was added to the composition and the level of Na_2O required to match the original viscosity was calculated. This was the composition of the F-free flux used in the plant trial.

BORON PICK-UP EXPERIMENTAL MEASUREMENTS

Steel samples cast (i) from the F-free flux trial and (ii) as a control from the conventional flux under normal production were obtained. The presence, or otherwise, of boron at the surface and in the bulk of the samples was determined using a combination of analytical techniques.

X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) were used to examine the extreme surface (up to 3-5nm depth) of the samples. Dynamic Secondary Ion Mass Spectrometry (DSIMS) was used to analyse the surface (up to 100nm) and the bulk of the samples.

XPS measurements were performed using a Surface Science Instruments M-Probe spectrometer operating at a base pressure of $3x10^{-9}$Torr. The samples were irradiated with monochromatic X-rays (1486.6eV) using a spot size of 1000μm x 400μm. Survey spectra were recorded from which the surface chemical compositions were determined.

ToF-SIMS analyses were carried out using a PHI 7000 instrument with a reflectron analyser, a Cs^+ ion source (8 keV) and a pulsed electron flood source (50-70eV) for charge compensation. Spectra were collected from areas measuring ca. 0.3mm x 0.3mm.

DSIMS measurements were carried out using a Cameca IMS 4f instrument with source for O_2^+, O^- and Ar^+ ions from 5 to 17.5keV.

RESULTS AND DISCUSSION

VISCOSITY AND BREAK TEMPERATURE RESULTS

The commercial F-free trial flux based compositions shown that:

1) increasing B_2O_3 decreases viscosity (Figure 5a); and
2) increasing B_2O_3 decreases break temperature (Figure 5b, Table 1); a decrease in break temperature of about -42.5°C per % B_2O_3. This compares with a value of –20K per % B_2O_3 derived from literature data for T_{crys}. Sridhar et al.(19) were unable to derive a value for the effect of B_2O_3 on T_{br} since they only studied one flux containing B_2O_3 (resulting in an increase in T_{br}, which is contrary to the experimental results presented here).

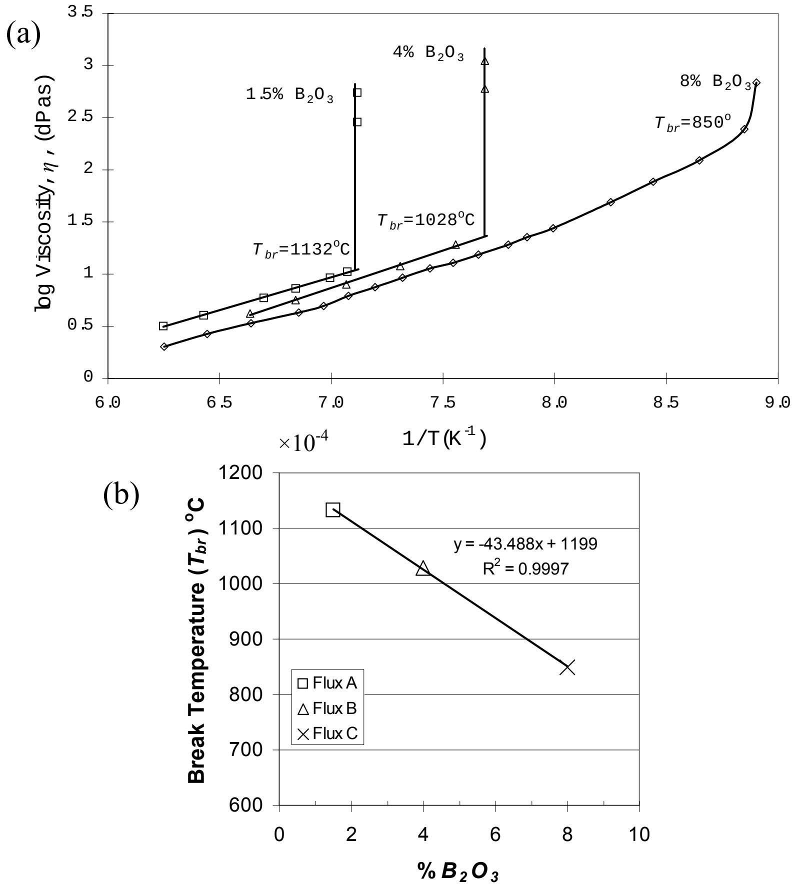


Figure 5. (a) Log_{10} viscosity versus inverse absolute temperature for fluxes A, B and C (b) Break temperature vs. % B_2O_3 fluxes A, B and C

Table 1. Measured fluoride-free flux break temperatures

Flux	Break Temperature (T_{br})
Flux A (1.5% B_2O_3)	1132°C
Flux B (4% B_2O_3)	1028°C
Flux C (8% B_2O_3)	850°C

CRYSTALLINITY RESULTS

F-free fluxes can produce crystalline slag films. Flux A (1.5% B_2O_3) produced a slag film with 52% crystallinity, whereas Flux C (4% B_2O_3) produced a completely glassy film.

REFORMULATED FLUX

The conventional fluorine-containing flux viscosity at 1300°C was supplied by Sidenor. The flux was found to be 100% glass by the Li tes$^{t(23)}$. This flux contained 1.82% F and 6.17% Na_2O. This composition was used as the starting point for the reformulated flux; F was then removed, B_2O_3 introduced at 1.11% and Na_2O was allowed to vary to match the original target viscosity. The Iida viscosity-temperature-composition model were used to calculate the amount of Na_2O which would give the required viscosity at 1300°C of 12.7 dPa.s. The reformulated mould flux presented a viscosity at 1300ºC of 13,18dPa.s as described in Figure 6.

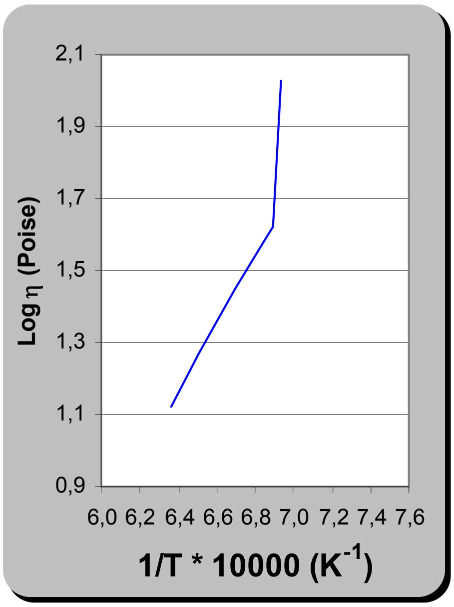


Figure 6. Viscosity curves for re-formulated F-free flux

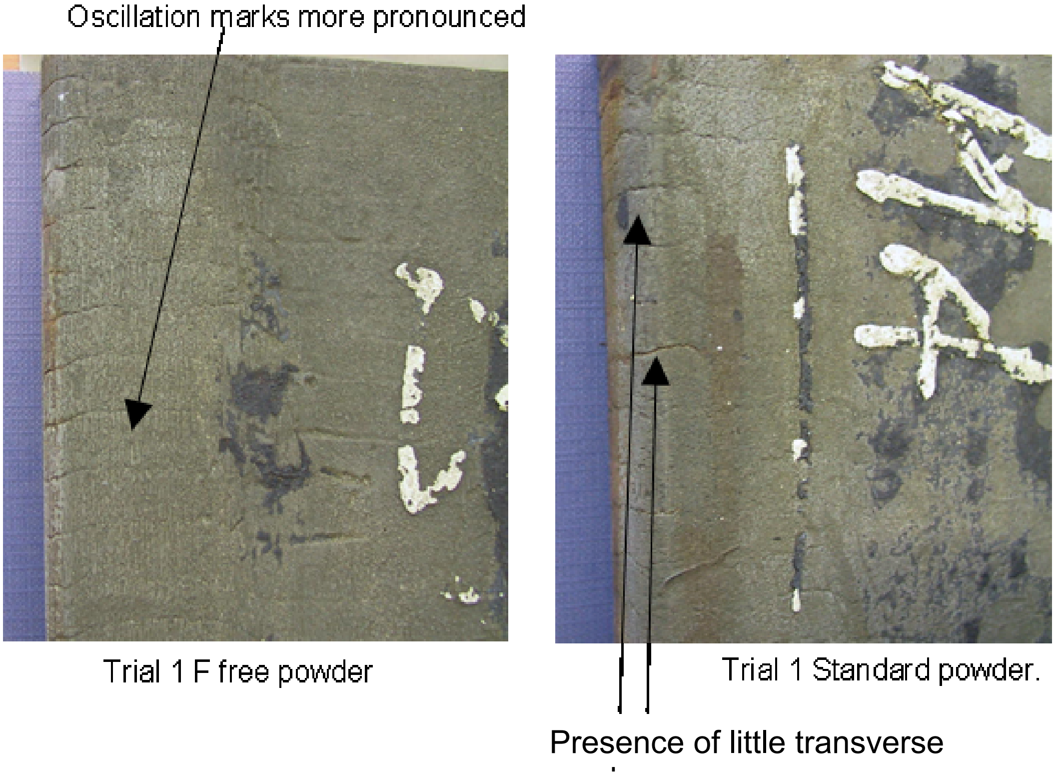
Plant Trial

A series of three plant trials were performed using the F^- containing mould flux and then replacing it with the F-free flux (Table 2). Carbon steel grades 42MoCr4E, 40CrNiMo7 and 42CrNiMo4E were cast in trials 1, 2 and 3 respectively. Bllets of section size of 185 mm square were cast at casting speeds of 1.25 - 1.50 m/min. Heats corresponding to the trial 1 was the fourth in a sequence of four heats (4/4); trial 2 was 1/3 and trial 3 was 3/3.

Table 2. Data from operational trials

Trial	Strand	Section (mm)	Flux	Steel Grade	Length (m)	Cast time (h)	Speed (m/min)	Q (kg/min)	Q (Kg/m^2)
1	5	185 x 185	F containing	42MoCr4E	79.1	0.042	1.35	0.076	0.078
1	6	185 x 185	F containing	42MoCr4E	37.4	0.019	1.43	0.129	0.126
1	6	185 x 185	F free powder	42MoCr4E	51	0.024	1.50	0.085	0.076
2	6	185 x 185	F containing	40CrNiMo7	52.7	0.034	1.25	0.074	0.093
2	6	185 x 185	F free powder	40CrNiMo7	46.4	0.026	1.25	0.055	0.059
3	6	185 x 185	F containing	42CrNiMo4E	48.3	0.024	1.43	0.048	0.045
3	6	185 x 185	F free powder	42CrNiMo4E	37.2	0.017	1.50	0.044	0.040

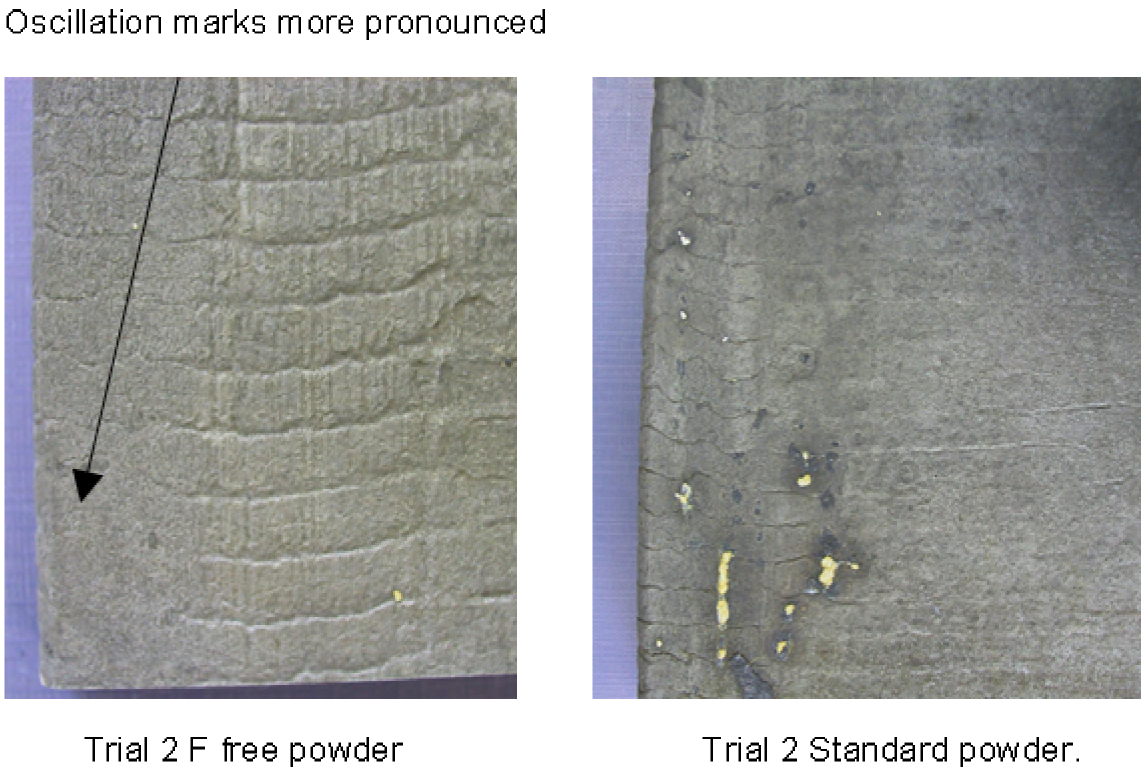
Initial results from the trial indicate that there were no visible cracks in the cast product from the F^{-}free flux (there were some minor crack in the F^{-}containing cast product (Figure7) and surface hot quality (particularly oscillation mark characteristics) appeared generally the same as that cast with the conventionally cast product (with occasionally some deeper oscillation marks (Figure 8)). No problems have been reported during rolling. Mould telemetry did not change when the F^{-}free flux was used. The casting manager reported satisfaction with the products performance. Interesting, the powder consumption fell during the F^{-}free casts (Table 2), however this effect cannot be said to be certain as the system may not have reached steady state.



Trial 1 F free powder

Trial 1 Standard powder.

Figure 7. Photograph of billet surface after casting showing oscillation marks and transverse cracks



Oscillation marks more pronounced

Trial 2 F free powder

Trial 2 Standard powder.

Figure 8. Photograph of billet surface after casting showing pronounced oscillation marks on F-Free cast product.

In summary, there was no reduction in performance when moving from F-containing to F-free fluxes in these trials.

B-pickup Experimental Results

Analysis using XPS and ToF-SIMS showed that the level of boron at the surface was (i) below the detection limit of XPS (i.e. less than 0.1 atomic %), (ii) was trace only and (iii) comparable for both control and trial samples.

DSIMS profiling indicated that at depths of 100nm boron is present at levels of 0.1-0.2 atomic % in both the control and trial samples. In the bulk, boron is present at less than 10ppm and is a similar level in both the control and trial samples.

CONCLUSIONS

Fluoride has been successfully removed from a conventional billet flux and substituted with a combination of B_2O_3 and Na_2O to match the viscosity trend against temperature of the original flux. Three steel grade were successfully cast as 185 mm square billets.

FURTHER WORK

The next step for this work is to reformulate slab powders. Conventional fluxes for low carbon slabs have a low crystalline fraction in the solid slag layer(26), so could be well suited to fluoride replacement. However, unlike billet fluxes both the break temperature and crytallinity would have to be considered in addition to the viscosity.

This will require development more advanced models for break temperature and crystallinity.

Acknowledgemets

The authors would like to gratefully acknowledge Dr. Z. Li and Miss Y. Su of Imperial College London are also acknowledged for their help with practical work. Mr T. Mallaband is also acknowledged for supplied the commercial trial fluoride-free flux composition. Professor T. Iida and Dr. O. Kita are gratefully acknowledged for their viscosity calculation.

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