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The use of thermal analysis in the determination of the crystalline fraction of slag films

K.C. Mills[a], L. Courtney[a,1], A.B. Fox[a,*], B. Harris[b], Z. Idoyaga[c], M.J. Richardson[d]

[a]*Department of Materials, Imperial College STM, Prince Consort's Road, South Kensington, London SW7 2BP, UK*
[b]*Corus Teesside Technology Centre, Eston Road, Grangetown, Middlesbrough TS6 6UB, UK*
[c]*Dpto. Electricidad y Electrónica, Facultad de Ciencias, UPV/EHU, 48 080 Bilbao, Spain*
[d]*Polymer Research Unit, University of Surrey, Guildford, Surrey, UK*

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Abstract

The horizontal heat transfer in the continuous casting of steel is exceedingly important since non-optimum heat transfer results in inferior surface quality of the product and process control problems. The horizontal heat transfer is controlled by both the thickness and the crystallinity of the solid slag film formed between the steel shell and the water-cooled, copper mould. This study is focused on the efficacy of thermal analysis techniques in measuring the fraction of glassy (or crystalline) phase present in the slag films. The glass fraction has been determined for several slag films using a variety of techniques. The results obtained are summarised and the problems encountered with thermal analytical techniques are outlined and discussed.

Keywords: Crystallinity; Thermal analysis; Continuous casting

1. Introduction

During the continuous casting of steel, molten steel is poured into a water-cooled copper mould. A thin shell of steel is formed by contact of the steel with the mould. The shell is withdrawn at a constant velocity and on leaving the mould it is further cooled by water sprays. It is subsequently bent and cut when the steel has completely solidified. Mould fluxes are added to the top of the mould to form a liquid slag, which infiltrates the mould/steel gap and thereby lubricates the shell and prevents it from sticking to the mould. The mould flux must also form a solid slag film providing the right level of horizontal heat flux between the shell and the mould.

The powder is placed on the top of the mould and its temperature increases as it progresses down the mould where carbon particles gradually burn off. It sinters and eventually forms a molten slag pool (Fig. 1). Most of the first molten slag to infiltrate into the channel between the mould and the shell solidifies against the mould as a glass except for a thin liquid slag which lubricates the steel. In time, the hotter regions of the solid slag film crystallise and the solid slag film contains two layers, a glassy layer on the mould side and a crystalline layer on the shell side adjacent to the liquid layer (Fig. 1).

* Corresponding author. Fax: +44-207-594-6758.
E-mail address: a.b.fox@ic.ac.uk (A.B. Fox).
[1] Present address: Department of Chemistry, University of Cardiff, Park Place, Cardiff CF10 3TB, UK.

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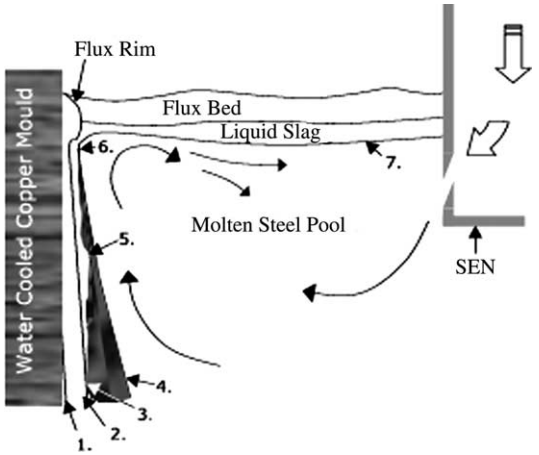

Fig. 1. Schematic diagram showing the various layers formed by the mould flux: (1) air gap; (2) solid slag layer; (3) contact resistance; (4) solidifying steel shell; (5) oscillation mark; (6) meniscus; (7) steel surface.

The horizontal heat transfer between the shell and the mould has a critical effect on process control. However, it is a complex process involving two conduction mechanisms, lattice (or phonon) conductivity (k_c) and radiation conductivity (k_r). In glasses k_r can make a major contribution to the total heat flux. Crystallites tend to scatter radiation so a crystalline layer causes a marked reduction in the radiation conductivity. Estimates of the contribution of k_r to the total conductivity (k_{eff}) for typical mould fluxes are frequently between 10 and 30% [1–3] but may be larger in certain cases. The overall thermal resistance (R_{Tot}) between the mould and shell is given by [1–3]

$$R_{Tot} = R_{Cu/sl} + \left(\frac{d}{k}\right)_{gl} + \left(\frac{d}{k}\right)_{crys} + \left(\frac{d}{k}\right)_{l} \quad (1)$$

where R is the thermal resistance, k the thermal conductivity, d the thickness of layer and the subscripts, l, crys, gl and sl refer to liquid, crystalline, glassy and slag, respectively, and Cu to the copper mould.

Cho et al. [4] reported that the interfacial resistance, $R_{Cu/sl}$ was (i) frequently the largest resistance term and (ii) increased with increasing crystalline fraction and increasing slag thickness. Thus the crystalline/glass ratio is very important in the control of the horizontal heat flux between steel shell and mould.

The horizontal heat transfer is important because certain serious problems in continuous casting are related to the magnitude of the heat transfer in the meniscus region of the shell. The heat transfer determines the thickness of the solidified shell. In medium-carbon (MC) steel (0.06–0.18% C) there is a 4% mismatch between the thermal shrinkage coefficients for δ-ferrite and austenite phases of iron This results in stresses in the shell and stress relief comes through *longitudinal cracking* of the steel shell. Longitudinal cracking is a serious problem in MC steels and the usual strategy adopted involves the reduction of these stresses by keeping the thickness of the shell to a minimum. This is achieved by reducing the horizontal heat transfer by increasing (i) the thickness of the solid layer and (ii) the crystallinity of the solid slag layer which reduces k_r and simultaneously increases $R_{Cu/sl}$ [4].

In contrast, *sticker breakouts* occur when the shell is not strong enough to withstand the ferrostatic pressure and the molten steel pours out of the mould. The strategy adopted here is to build a thicker shell; this is achieved by increasing the horizontal heat flux by (i) decreasing the thickness and (ii) increasing the glassy fraction (or reducing the crystalline fraction) of the solid slag layer.

Thus it is apparent that the amount of crystallinity developed in the slag film has a decisive effect on the horizontal heat transfer and, subsequently, upon the product quality and the process control. Despite its importance, there are no established methods for determining percentage of glass (or percentage of crystallinity) in a slag film. Susa et al. [5] used differential power scanning calorimetry (DPSC) to determine the percentage of glass in a slag film by measuring the stepwise change in C_p at the glass transition temperature (T_g) for the slag film and comparing it with that for a pure glass made from the parent mould flux. Courtney et al. [6] used differential thermal analysis (DTA) to measure the enthalpy of crystallisation, for both the slag film and pure glass. Watanabe [7] measured the percentage of crystallinity from the surface roughness developed in slag film. The percentage of glassy phase present has also been measured by microscopic examination of the various layers of the slag film and recently Riaz et al. [8] used X-ray diffraction (XRD) to determine the percentage of crystallinity in a slag film.

Thermal analysis is an attractive means of determining the percentage of glass in a slag film because the necessary equipment is available in many laboratories. Consequently, the principal aims of this work were (i) to measure the percentage of glassy phase present in a variety of different slag films taken from the mould and (ii) to compare the results obtained with various techniques and identify the problems encountered with different methods, especially those involving thermal analysis.

2. Experimental

The methods used here fall into three categories:

(1) Those where the percentage of glass in a slag film is measured by comparison of its properties with those of 100% glass samples.
(2) Those where percentage of crystallinity is measured by comparison of the properties with those of a pure crystalline material (usually cuspidine, $3CaO{\cdot}2SiO_2{\cdot}CaF_2$ which is nearly always present).
(3) Direct measurements where the percentage of crystalline phase present is measured by metallography.

2.1. Methods comparing slag film with pure glass

2.1.1. Change in C_p at glass transition temperature (T_g)

Glasses exhibit a marked change in heat capacity (ΔC_p) when passing through the glass transition temperature (T_g) from the glassy ($T < T_g$) to the supercooled liquid ($T > T_g$). Susa et al. [5] measured ΔC_p for a slag film and obtained the glass fraction by comparing it with ΔC_p for a pure glass prepared by rapid quenching the molten flux (i.e. parent mould flux):

$$\text{glass in slag film}\,(\%) = 100 \times \frac{\Delta C_p(\text{slag film})}{\Delta C_p(\text{pure glass})} \quad (2)$$

The same method was used here except that the pure glass was prepared by melting the slag film and rapidly quenching. In this way the effects of Al_2O_3, MnO pick up during the casting process could be taken into account. The heat capacities were measured using a Perkin-Elmer DPSC Model 2.

2.1.2. Enthalpy of crystallisation

When a glassy slag is heated above T_g, it tends to crystallise at some temperature. This crystallisation is an exothermic transformation and appears as a peak (or several peaks) in a DTA or DSC trace. The enthalpy of crystallisation (ΔH_{crys}) can be determined by measuring the area under the peak. Since there are no discernible differences in the chemical composition of the glassy and crystalline phases [9], the glass fraction in a slag film can be determined by comparing the (ΔH_{crys}) values for the slag film with that for a pure glass made from the same slag:

$$\text{glass in slag film}\,(\%) = 100 \times \frac{\Delta H_{crys}(\text{slag film})}{\Delta H_{crys}(\text{pure glass})} \quad (3)$$

2.1.3. Thermal expansion change at T_g

The transition from a glass to supercooled liquid at T_g also results in an approximately three-fold increase in the temperature dependence of the thermal expansion coefficient (TEC) ($d\alpha/dT$) and thus the change in the value of $d\alpha/dT$ can also be used to determine the percentage of glass in a slag film (Eq. (4)). The thermal expansion of the slag film was measured as a function of temperature in a Netzsch 420 E dilatometer:

$$\text{glass in slag film}\,(\%) = 100 \times \frac{\{(d\alpha/dT)_{T>T_g} - (d\alpha/dT)_{T<T_g}\}_{\text{slag film}}}{\{(d\alpha/dT)_{T>T_g} - (d\alpha/dT)_{T<T_g}\}_{\text{glass}}} \quad (4)$$

2.1.4. XRD

XRD patterns for glassy phases do not exhibit the sharp peaks associated with crystalline phases but give a "bulge" or "bump". Recently, Riaz et al. [8] showed that the percentage of glass could be correlated with the area under this bulge (minus the background intensity). In slag films containing both glassy and crystalline phases, it was necessary to measure the areas under the peaks (due to crystalline phases) and the bulge (due to glass) [8]. They showed that

$$\text{glass in slag film}\,(\%) = 100 \times \left[\frac{\text{total area} - \text{area under peaks}}{\text{total area}}\right] \quad (5)$$

Table 1
Chemical compositions of slag films (mass%)

Slag	SiO_2	Al_2O_3	CaO	MgO	FeO	MnO	BaO	F	Na_2O/K_2O	Comments
DA96A	34.6	8.5	38.7	0.4	0.6	2.9		5.2	8.1	
DA96B	35.3	7.7	38.0	0.9	0.8	2.7		4.9	8.9	
DA96C	35.8	8.6	38.5	0.4	0.8	3.1		5.0	8.3	
DA96D	36.0	8.7	38.2	0.4	0.7	1.2		4.3	8.1	
DA96E	36.2	8.2	38.4	0.4	1.3	1.0		5.0	8.0	
DA96F	37.2	8.9	37.4	0.4	0.6	1.2		4.6	8.4	
C126A	36.8	17.3	23.8	10.4	1.4	3.3		0.6	4.0	
C126ABA	42.4	12.5	21.6	3.6	0.8	0.2	7.5	2.3	7.9	Mould flux component + 4% Al_2O_3
C126D	42.5	11.3	14.2	3.2	1.2	0.6	15.4	2.6	9.7	Mould flux component + 4% Al_2O_3
STH12	36.6	18.6	27.9	3.3	1.4	2.6	12.0	0.1	5.1	
GR32	32.2	15.5	34.4	3.2	0.6	1.2		7.1	1.2	
C411	30.1	22.0	27.7	13.6	0.4	2.9		0.4	1.4	

where total area means the area under peaks plus area under bump between 22.5 and 37.5° and area under peaks means the area under peaks due to crystalline phases.

2.2. Methods comparing slag film with crystalline material

Riaz et al. [8] also used the XRD intensities of the peaks from crystalline materials to determine the percentage of crystalline phase by comparing these intensities with those for pure cuspidine ($3CaO{\cdot}2SiO_2{\cdot}CaF_2$). Cuspidine is nearly always present in slag films taken from the continuous casting mould. The cuspidine was synthesised by Prof. Nagata and Dr. Watanabe (Tokyo Institute of Technology).

$$\text{crystalline phase in slag film (\%)} = 100 \times \frac{I_{\text{peak 1}}(\text{slag film})}{I_{\text{peak 1}}(\text{cuspidine})} \quad (6)$$

2.3. Metallography

Rectangular slag film samples (ca. 20 mm × 5 mm × 2 mm) were carefully machined from strips of slag film. They were placed and secured with double-sided tape in an upright position (at right angles to the mould wall) in the plastic mould for cold mounting and were subsequently mounted with resin and hardener. Once dried, the mounted samples were ground on SiC paper and fine-polished first with 5 μm Al_2O_3 paste and finally with 1 μm diamond spray. The samples were etched with 2.5 vol.% HF in distilled water for 2 s. The etched samples were observed in an optical transmission microscope under normal and polarised mode to reveal the glassy and crystalline areas. In some cases the crystalline phase occurred in patches and it was necessary to obtain an average value for the slag film.

3. Slag films

The slag films were obtained at the end of the casting sequence by allowing the level of the steel in the mould to drop. The films were then detached from the mould wall. Their compositions are given in Table 1.

4. Results and discussion

Values of the percentage of glass phase present in a number of slag films were determined using various techniques; the results are given in Table 2. It should be noted that the liquid layer forms a glass on quenching. Thus the values cited 'cf. glass (%)' refer to the glass + liquid layers. Only the metallographic technique is capable of differentiating between the glass and quenched liquid layers.

Table 2 shows that, although there is broad agreement (within uncertainty bounds of ±10%) between the results obtained with the different techniques, there are some cases where values diverge significantly and

Table 2
The percentage of glass present in slag films taken from the mould

Sample	DPSC	DTA (Imperial College STM)		DTA (Corus TTC)	Metallography	XRD		TEC
		ΔH_{crys}	ΔC_p	ΔH_{crys}		cf. glass (%)	cf. crystallinity (%)	
DA96A		100	≈90					
B		42, 30	≈30, 40		62[a]	56[a]	61[a]	
C		(30?)			39[a]	50[a]		29
D		100	87					
E		100	≈70					
F		36			61[a], 32, 22	54[a]	55[a]	
C126A		(≈90)[b]		100	99[a]	98[a]	94[a]	
ABA		(45)		(21)	97[a]	97[a]		
D		82–100		55–100[b]	93[a]	93[a]		
STH12	(70)			95, 100[c]	92[a]	99[a]	88[a]	
GR32	(94[d])			(55)[b]	85			
CSM	(75)	91		(31)[b]				
C411				100 (70)[b]	100			

[a] [8].
[b] Baseline problem.
[c] Melting of the sample affects determination of area corresponding to crystallisation.
[d] Baseline may be affected by crystallisation affecting ΔC_{pT_g}.

it is therefore necessary to examine the reasons for these discrepancies. The problems with the individual techniques are discussed below but there are some general causes of scatter in the values, namely:

(1) The sample masses tend to be small (ca. 40 mg) and the slag films may not be homogeneous.
(2) The heat transfer in the corner of the mould is different to that in the centre of the mould face, which results in a thicker slag film, and possibly a different ratio of glass/crystalline phases; thus the percentage of glass may depend upon the location of the sample.
(3) The glass → crystalline transition may be incomplete for the heating rate selected.

4.1. TEC measurements

The slag film tended to collapse at temperatures above T_g because the supercooled liquid phase has little mechanical strength. Some values were obtained for $(d\alpha/dT)_{T>T_g}$ but there was no certainty that the maximum value of $(d\alpha/dT)_{T>T_g}$ had been attained. Thus, although the value obtained by this technique for DA96D was in reasonable agreement with the other values (Table 2) the method is not considered very suitable for measuring the glassy fraction in slag films.

4.2. DPSC measurements

The results obtained with this technique were found to be reproducible. Problems were only encountered:

(a) when T_g was higher than 727 °C, the maximum temperature for the DPSC or
(b) where the C_p values at temperatures above T_g may have been affected by baseline drift at the end of the run as a consequence of the sample crystallising (an exothermic event). The effect of crystallisation can be clearly seen as the dramatic decrease in C_p above 950 K (677 °C) with increasing temperature in Fig. 2. The heat given out at the end of the experiment could affect the reliability of the C_p values recorded. This problem may be overcome by extending the isothermal period at the end of a run (to allow crystallisation to go to completion) or by terminating the run at a lower temperature, before the onset of crystallisation.

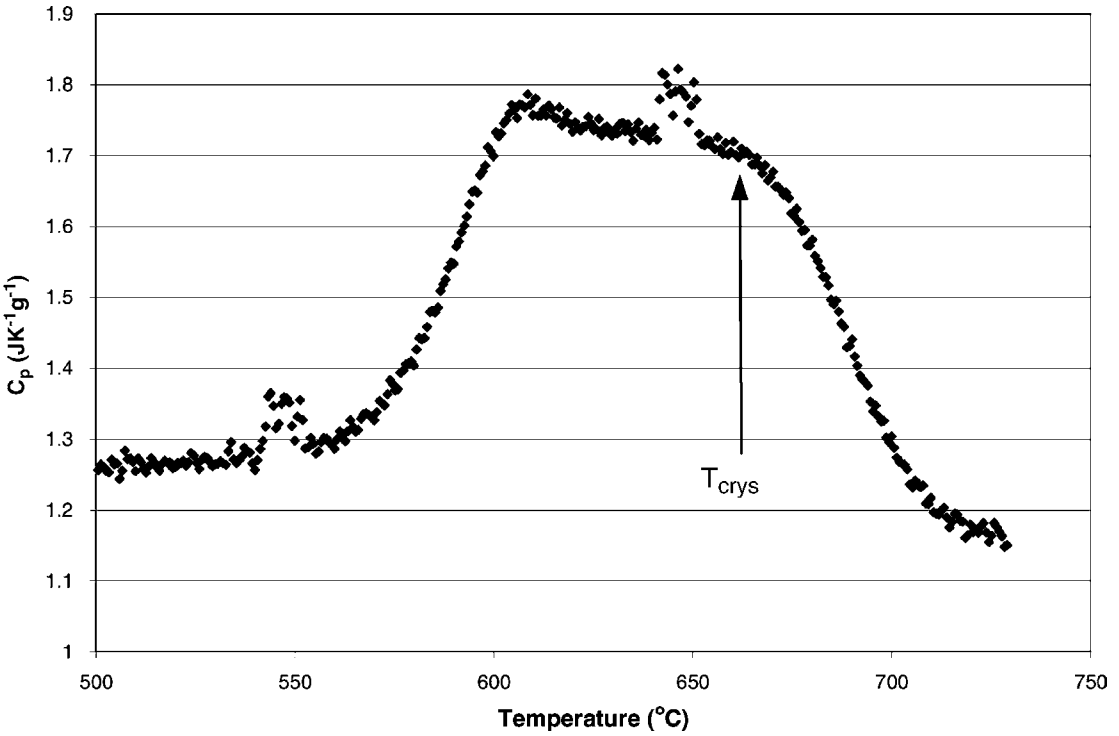

Fig. 2. Heat capacity of slag film GR32 determined by DPSC showing the apparent rapid decrease in C_p due to the exothermic crystallisation process (>950 K or 677 °C), which affects the reliability of the C_p values obtained.

4.3. DTA measurements

The results obtained with DTA methods tended to be more vulnerable to uncertainty than those obtained with DPSC for the following reasons:

(a) In principle, the percentage of glass could be determined by measurements of (ΔC_{pT_g}) but in practice, there is usually less control than in DTA experiments. Consequently, the results cited in Table 2 should only be regarded as rough indications of the percentage of glass in the slag film.
(b) Large changes in baseline can make it difficult to determine the area under the peak (ΔH_{crys}) as can be seen in Fig. 3 (we have noted that large baseline shifts tended to be more prevalent with smaller samples).
(c) Melting may occur before crystallisation is complete making the determination of ΔH_{crys} both difficult and unreliable (Fig. 4).

Fig. 5 shows a case where either baseline shifts or, more probably, melting of the sample, leads to uncertainty in the determination of the area that should be ascribed to crystallisation. As a result there is 50% uncertainty in the value of percentage of glass.

4.4. Metallographic measurements

The results of the metallographic examination are prone to the following sources of error:

(a) The section examined corresponds to a very small mass (<1 mg) and may not be representative of the entire slag film.
(b) In predominantly glassy materials the distribution of the crystalline phase can be very patchy and it is difficult to quantify the amount of crystalline material present (Fig. 6).
(c) In samples with well-developed crystalline layers an intermediate (glass + crystalline) layer is frequently encountered: it is difficult to allocate

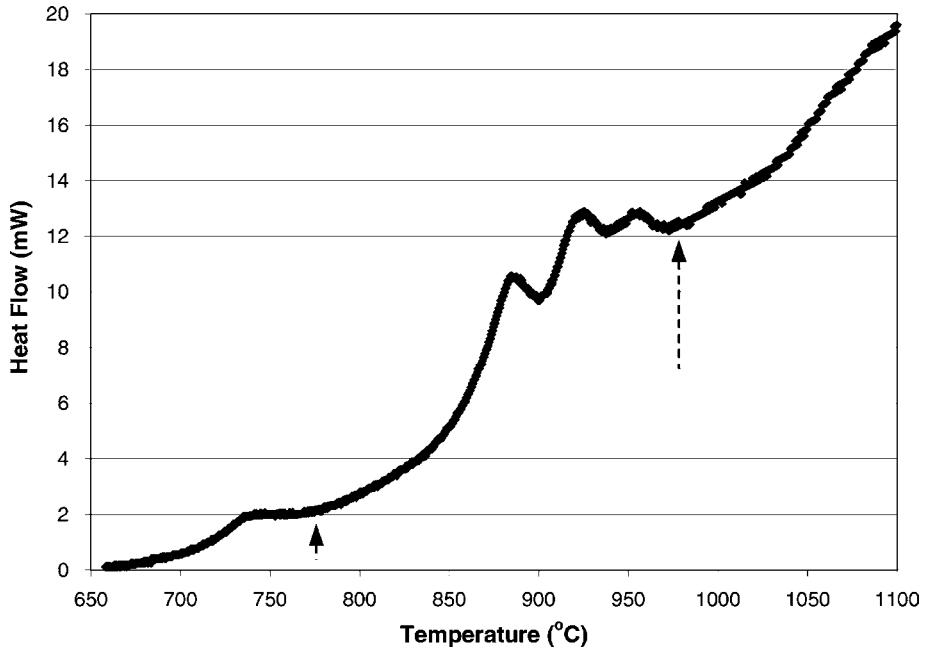

Fig. 3. DTSC trace for the slag film formed when using flux C126VID showing the difficulties in obtaining a reliable baseline in the crystallisation range (>800 to ca. 980 °C) when there is a marked shift in baseline (sign of the ordinate in Figs. 4 and 5 has been reversed so that thermal events have the same sign as those of Fig. 3).

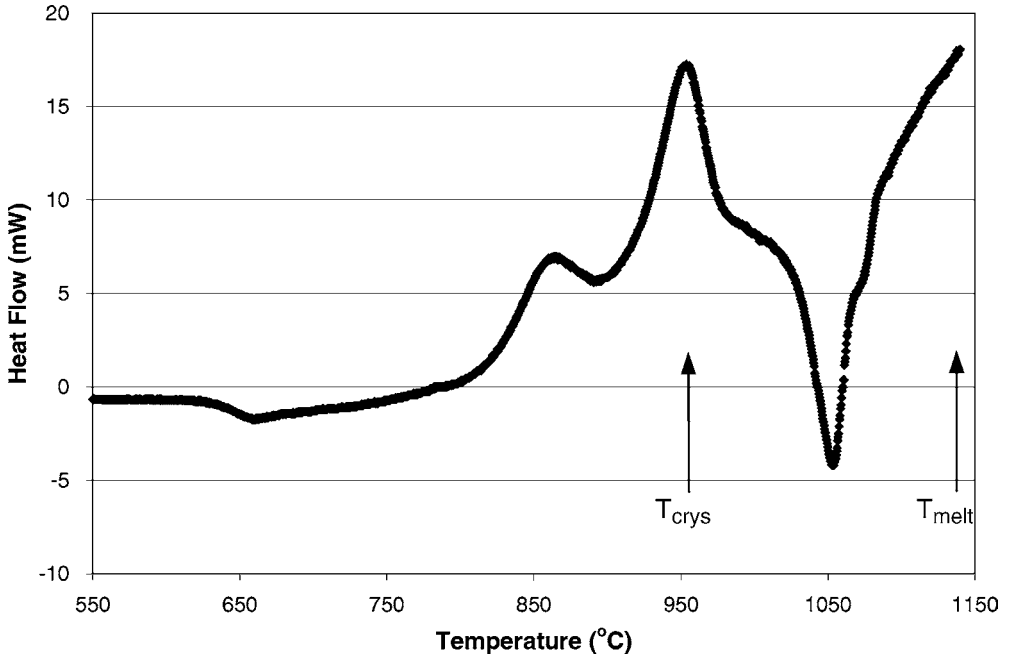

Fig. 4. DTSC trace for slag film formed when using mould flux STH12 showing a "valley" (due to crystallisation) and a peak (at 1050 °C), possibly due to melting which leads to uncertainty in the area determination.

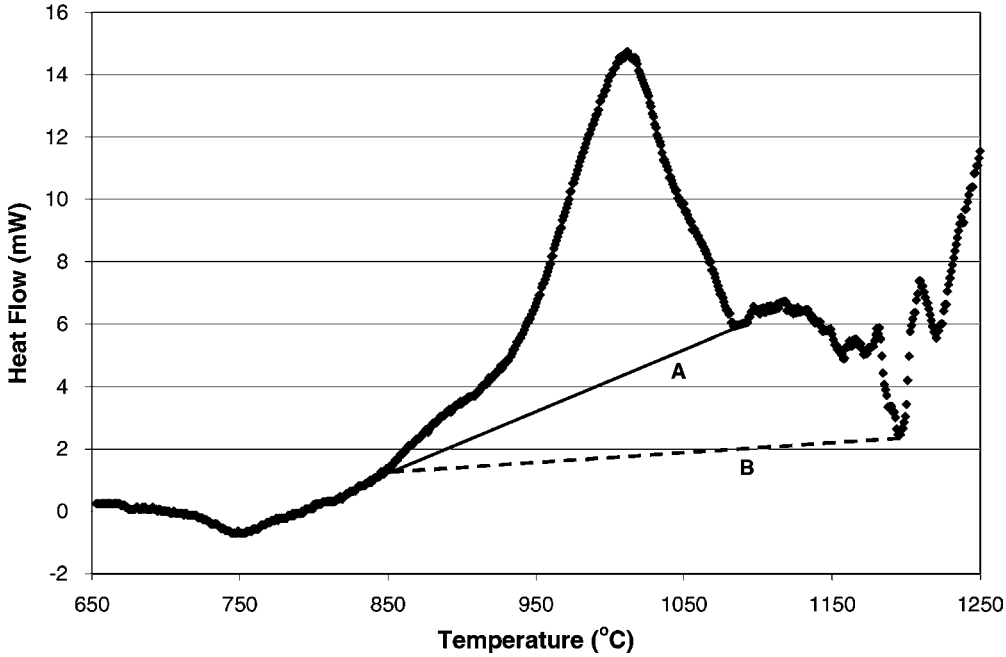

Fig. 5. DTA trace showing the large difference in areas depending upon on the baseline extrapolation (A or B) used.

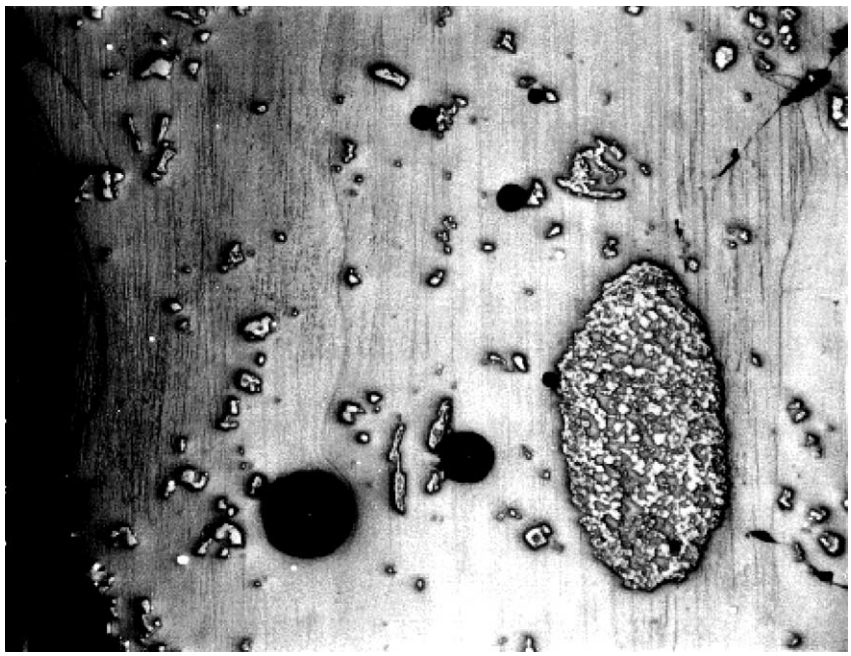

Fig. 6. Metallographic section of slag film C126D showing the patchy nature of the crystalline phase.

the contents of the intermediate layer to percentage of glass and percentage of crystalline materials.

4.5. XRD methods

Riaz et al. [8] have made measurements on the some of the slag films shown in Table 2. The method involving comparison with cuspidine assumes:

(a) that the prime crystalline phase is cuspidine (which would not be the case when using fluoride-free mould fluxes);
(b) that the cuspidine is 100% crystalline.

The advantages and disadvantages of the various methods are outlined in Table 3. In general, DPSC produces reliable results but there are cases where difficulties are encountered: these may be overcome at the expense of an increased time scale for the experiments. DTA results are more prone to more uncertainty. It is our view that there may be problems with all the current methods. To have confidence in the final values, tests should always be carried out using two or more techniques. One additional problem has not been mentioned, viz. material has been assumed to be amorphous or crystalline with no intermediate state. The equivalence of results using Eqs. (2) and (3) demands this. Some covalently bonded organic polymers do not fit this model [10] but results of Table 2 show that it is adequate for the inorganic glasses discussed here.

4.6. Effect of composition of chemical composition on percentage of glass

Mould fluxes contain several components. It is difficult to carry out numerical analysis on percentage of glass as a function of chemical composition since there are not enough data to obtain constants (in terms of mole fraction, x) for each component. However, it has been shown [11] that mould powder compositions can be represented by a pseudo-ternary consisting of the following:

- x‘‘CaO’’ $= x(\mathrm{CaO}) + x(\mathrm{MgO}) + x(\mathrm{FeO}) + x(\mathrm{MnO}) + \cdots$;
- x‘‘$\mathrm{SiO_2}$’’ $= x(\mathrm{SiO_2}) + x(\mathrm{Al_2O_3}) + x(\mathrm{TiO_2})$;
- x‘‘2NaF’’ $= x(\mathrm{CaF_2}) + x(\mathrm{Na_2O}) + x(\mathrm{K_2O}) + x(\mathrm{Li_2O})$.

The ‘‘$\mathrm{SiO_2}$’’ components are network formers, whereas the other two components are network breakers. Consequently it would be expected that the percentage of glass would tend to increase as the composition approaches the ‘‘$\mathrm{SiO_2}$’’ corner. The results are shown in Fig. 7 and it can be seen that the results are in agreement with this proposition.

Table 3
Advantages and disadvantages of the various methods

Method	Sample mass (mg)	Advantages	Disadvantages
DPSC	20–100	Gives reproducible results for percentage of glass	No use where $T_g > 1000$ K Crystallisation can interfere with baseline Glass → crystalline phase transformation possibly incomplete
DTA	20–100	Apparatus is widely available	Subject to baseline movements The onset of melting can interfere with determination of ΔH_{fus}
TEC			Specimen collapses above T_g making it difficult to determine if $d\alpha/dT$ attains steady value
Metallography	<1	Differentiates between liquid and glassy phases	Section equivalent to very small specimen mass Intermediate zone between glass and crystal difficult to allocate
XRD	40	Requires much less time than other techniques	Assumes cuspidine is present Assumes cuspidine sample is 100% crystalline

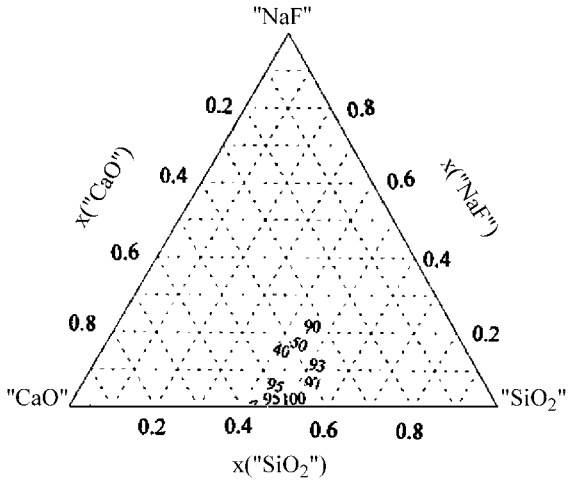

Fig. 7. The percentage of glass in slag films plotted on a pseudo-ternary diagram ''SiO_2'' + ''CaO'' + ''NaF''.

5. Conclusions

1. Thermal analytical techniques provide reliable values for the glass fraction in slag films formed in continuous casting moulds but care must be taken when there is a large change in baseline or if either crystallisation or melting of the sample cause uncertainties in baselines.
2. TECs are not recommended for measuring the glass fraction in slag films due to the mechanical collapse of the sample at temperatures above T_g.
3. The uncertainties in the measurements of the glass fraction are of the order of $\pm 10\%$ which may, in part, be due to inhomogeneities in the slag film.
4. It is recommended that values of the glass (or crystalline) fraction should be determined by two or more methods.
5. The glass fraction was found to be dependent upon composition increasing with increasing SiO_2 content.

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References

[1] A. Yamauchi, K. Sorimachi, T. Sakuraya, in: Proceedings of the Fourth International Conference on Metallurgical Slags and Fluxes, Sendai, 1992, Iron and Steel Institute of Japan, Tokyo, 1992, p. 415.
[2] H. Shibata, in: Proceedings of the Fifth International Conference on Molten Slags, Fluxes and Salts, Sydney, Australia, January 1997, Iron Steel Society, Warrendale, PA, 1997, p. 771.
[3] R. Taylor, K.C. Mills, Ironmaking–Steelmaking 15 (1988) 187.
[4] J.W. Cho, T. Emi, H. Shibata, M. Suzuki, ISIJ Int. 38 (1998) 844.
[5] M. Susa, K.C. Mills, M.J. Richardson, R. Taylor, D. Stewart, Ironmaking–Steelmaking 21 (1994) 279.
[6] L. Courtney, S. Nuortie-Perkkio, C.A.G. Valadares, M.J. Richardson, K.C. Mills, Ironmaking–Steelmaking, 2002, in press.
[7] K. Watanabe, Tetsu-to-Hagane 83 (2) (1997) 115.
[8] S. Riaz, Z. Idoyaga, K. Nagata, Proc Mills Symposium, to be held London Aug 2002, in press.
[9] N. Machingawuta, Continuous casting mould fluxes: constitution and properties, Report, Department of Materials, Imperial College, London, September 1987, p. 11.
[10] V.B.F. Mathot, Calorimetry and Thermal Analysis of Polymers, Carl Hanser, Munich, 1993 (Chapter 5).
[11] K.C. Mills, Ironmaking–Steelmaking 15 (1988) 175.