

THE CRYSTALLIZATION OF SLAG FILMS FORMED IN CONTINUOUS CASTING

L. Courtney^{a)}, S. Nuortie-Perkkiö^{a)}, C.A.G. Valadares^{b)}, M.J. Richardson^{c)}
and K.C. Mills^{a)}

a) Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London, SW7 2BP, UK.

b) Usiminas, CEP 31.3310-260, Ipatinga, MG, Brazil.

c) Polymer Research Center, University of Surrey, Guildford, Surrey, GU2 5XH, UK.

ABSTRACT

A slag film is formed in the channel between the mould and shell during the continuous casting of steel, and the amount of crystalline material in the slag film has a significant effect on the heat transfer between the steel shell and the mould. Various techniques to measure the degree of crystallization of these slag films have been examined in this investigation. The ratio of (% crystallized / % glass) phases has been determined for various slag films taken from the mould when casting different steel grades; these showed that the glassy fraction varied between 0 and 100 %. These results are discussed.

Crystallinity in Mould Slag Films

1. INTRODUCTION

In the continuous casting of steel, satisfactory casting can only be achieved if the mould flux performs well. There are several key steps a mould flux must carry out, and it is essential that it must perform well at each of these stages.¹ Failure to perform well at any one stage could result in surface defects in the cast product or process control problems. One of the key functions that the mould flux must provide is that uniform, horizontal heat transfer between the newly-formed steel shell and the water-cooled copper mould is at the optimum level.¹

Mould fluxes are fed onto the top of the mould, where they form a bed containing various layers (powdered, sintered, mushy and liquid) as can be seen from Figure 1. During the first moments of casting, liquid slag infiltrates into the channel between the steel shell and the copper mould and solidifies against the mould wall forming a glassy slag. There is a large temperature gradient across the slag film and the hotter regions of the slag start to crystallize. Thus the slag film formed in the shell/mould gap contains three regions: (i) a glassy phase adjacent to the mould, (ii) a crystalline phase, and (iii) a liquid layer in contact with the steel shell, as shown in Figure 1. Typically, the solid slag has a thickness of 2-3 mm and the liquid a thickness of 0.1 to 0.3 mm.

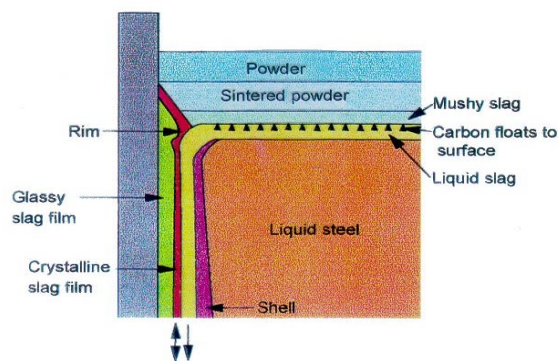


Figure 1. Schematic representation of the various flux layers formed in the mould.

The horizontal heat transfer is complex since it involves two mechanisms, lattice conduction and radiation conduction.^{1, 2} In the glassy phase the radiation conduction at high temperatures can be several times the magnitude of that for the lattice conduction. However, crystallites will scatter the infra-red radiation and thereby reduce the magnitude of the radiation conductivity. So the

formation of a crystalline layer in the slag film causes a significant reduction in the radiation conductivity.^{3, 4}

Control of the horizontal heat transfer is essential for satisfactory casting performance. In medium carbon (MC) steels (0.07 – 0.18 % C) there is a 4 % mismatch in the thermal shrinkage coefficients of the δ and austenite phases, and consequently, stresses are created in the steel shell which can only be relieved by the formation of longitudinal cracking. The strategy adopted to minimize cracking is to minimize the stress by producing a shell which is both thin and uniform. This is accomplished by reducing the horizontal heat flux by producing a thick slag film, with a significant crystalline layer.⁵

In contrast, high carbon (HC) steels ($C > 0.4$ %) have poor mechanical strength, and to avoid sticker breakouts (where molten steel pours from the mould), it is necessary to form a thick shell. Consequently, a high horizontal heat flux is required, which is obtained by producing a thin, glassy slag film.^{5, 6} Thus the degree of crystallinity developed in the slag film is important in controlling the horizontal heat flux. Given this, it is surprising that few methods have been developed for measuring the degree of crystallinity in a slag film.

The objectives of this investigation were (i) to look at the different methods for measuring the degree of crystallinity and, (ii) to measure the crystallinity of different slag films.

2. METHODS OF MEASURING CRYSTALLINITY

There are several methods which can be used to measure crystallinity. These can be classified as:

- (a) *direct* methods, where the amounts of crystalline and glassy phases are measured directly
- (b) *comparative* methods, where property measurements are carried out on a glass (or totally crystalline material) and the percentage glass (or crystalline) phase present is determined from the ratio of the property measurements.

2.1 Materials

Slag films were obtained from several steel plants throughout the world. The chemical compositions of these slags are given in Table 1.

Table 1. Manufacturer data for chemical compositions of powders resulting in the formation of slag films.

Mould Flux	Mass Percent								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	FeO	F	BaO	C Total
SA	32.8	4.2	39.7	10.2	7.0	0.7	8.1	—	
LXA	36.6	6.6	36.7	—	8.5	—	5.6	—	3.64
C126 VI/D	33	11	5	3	7.5	<1	<0.5	12	18.5
C126 VI/A	33	23	6.4	3.8	—	0.2	1.8	—	19.7

The pure glasses were obtained by heating the slag films to 1400 °C in a Pt crucible, and then quenching the crucible in water.

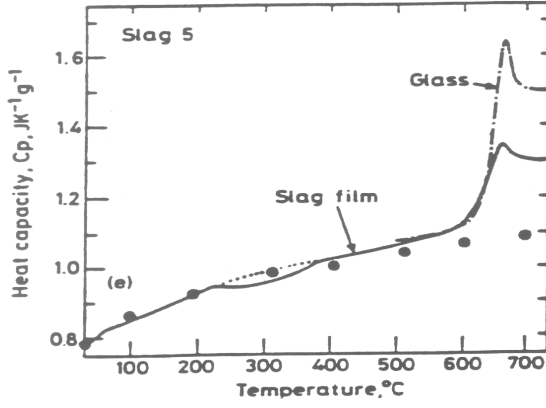
2.2 Comparative Methods

There are several potential comparative methods available, and the principals underlying these methods are outlined below.

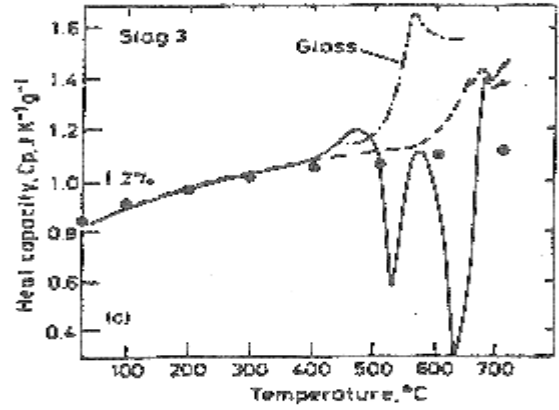
2.2.1 Heat Capacity Measurements

When a glass is heated, there is a stepwise change in the heat capacity (ΔC_p) at the glass transition temperature (T_g), where the glass transforms into a supercooled liquid. This can be seen in Figure 2. Thus, the amount of glass phase can be determined from Equation 1, where the ΔC_{pT_g} values are determined for the slag film and the pure glass prepared from the slag film.⁷

$$\% \text{Glass} = 100 \times \frac{\Delta C_{p_{T_g}} (\text{slag film})}{\Delta C_{p_{T_g}} (\text{pure glass})}$$



(a)



(b)

Figure 2. (a) Heat capacity (as determined by DPSC) as a function of temperature showing (a) the step-like increase in Cp at Tg and, (b) the exothermic peak due to crystallization.

In previous investigations⁷ the pure glass was prepared by pouring the molten casting flux onto a copper plate. However, the mould flux composition changes during the casting operation through the pick up of Al_2O_3 , MnO_2 etc. Consequently, it is better that the glass should be prepared from the slag film. Unfortunately, in many cases there was little slag film available, which made glass preparation difficult.

The measurements were carried out in a Perkin-Elmer Differential Power Scanning Calorimeter Model II (DSC), (denoted as DPSC). Measurements were made on (i) the empty pans, (ii) the pans filled with a sapphire sample, (iii) the pans filled with a slag sample. Typical results are shown in Figure 3. The method provided reproducible results. The major problems with this method were minor uncertainties with the extrapolation of the baseline and problems with obtaining a pure glass sample.

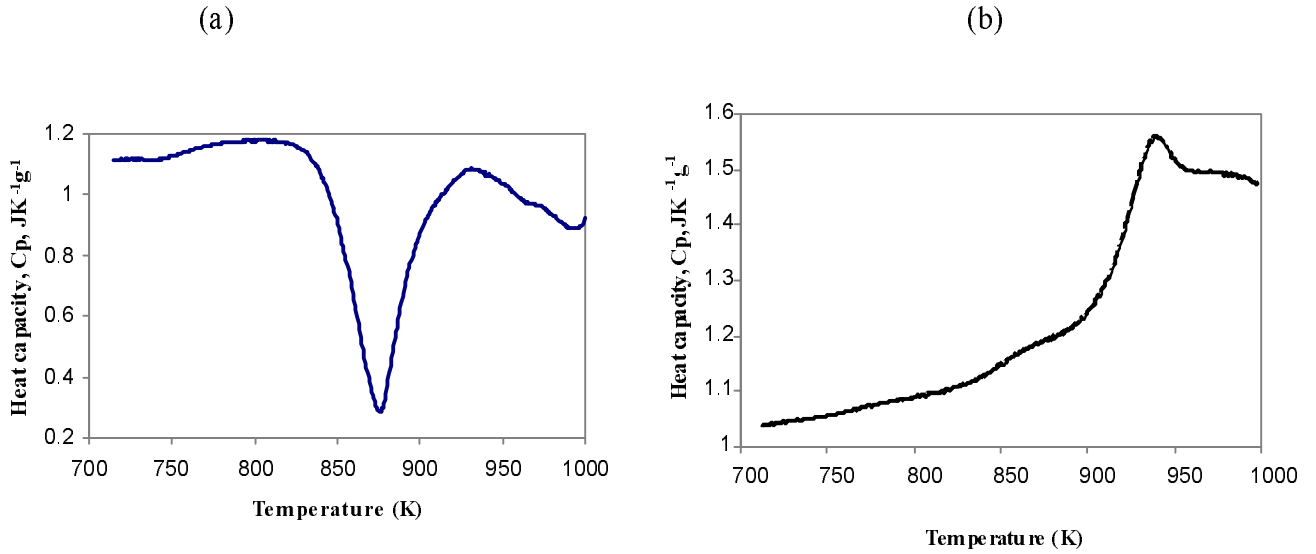


Figure 3. Heat capacity as a function of temperature for slag SA powder showing (a) the peak associated with enthalpy of crystallization and (b) increase in C_p (b).

2.2.2 Thermal Expansion Measurements

Another feature associated with the transition of a glass into a supercooled liquid at T_g is that there is a three-fold increase in the thermal expansion coefficient (α). Consequently, the % glass can be determined by the change in thermal expansion coefficient at T_g , as demonstrated in Figure 4.

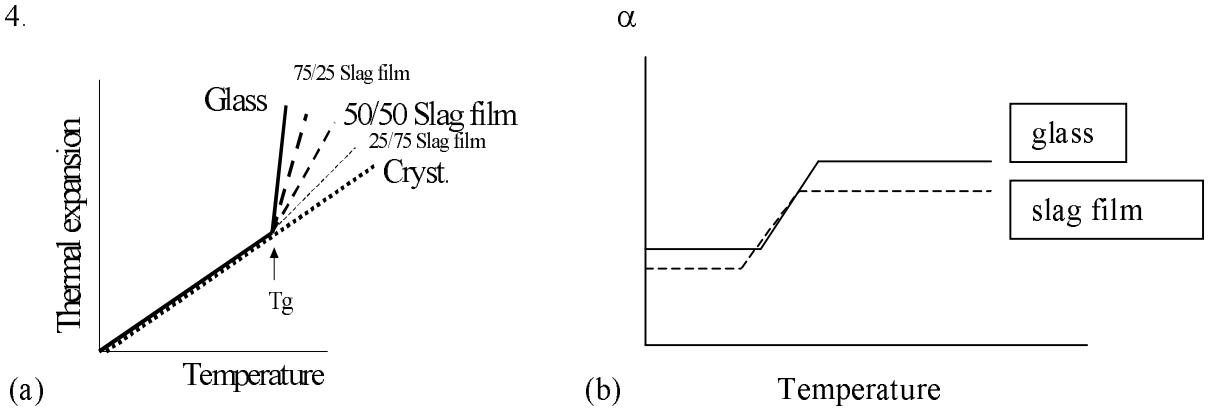


Figure 4. Change in (a) expansion, and (b) thermal expansion coefficient (α) of a glass with increasing temperature.

The thermal expansion measurements were made on a Netzsch 420 E High Temperature Dilatometer, and preliminary measurements were determined on (i) a pure glass (casting flux), and (ii) a crystalline material produced by annealing for 16 hours at 900°C. The results are shown in Figure 5, and indicate that the $\alpha_{\text{cryst}} > \alpha_{\text{glass}}$ for temperatures below T_g , but there was an abrupt

increase in α at T_g . The sample collapsed at slightly higher temperatures as it became a supercooled liquid.

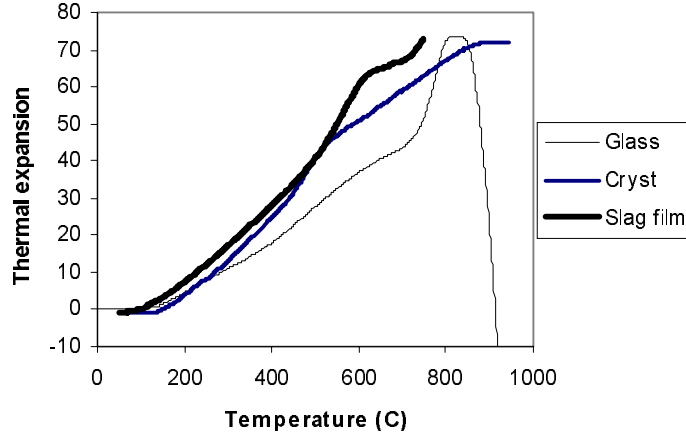


Figure 5. Thermal expansion coefficient for the slag film, crystalline and glassy samples of slag PS4 as a function of temperature.

Measurements were carried out on the slag film LXA-DA0096 C and on a glass prepared by pouring a melt (of the mould flux + 2 % Al_2O_3) onto a metallic plate. The results are shown in Figures 6a and 6b. The percentage glass was calculated using Equation 2.

$$\Delta\alpha = \Delta \frac{\left(\frac{dL}{dT}\right)}{dT} = \left[\frac{\left(\frac{dL}{Lo}\right)}{dT} > Tg - \frac{\left(\frac{dL}{Lo}\right)}{dT} < Tg \right] \quad (2)$$

Where L = length, and Lo = original sample length.

It can be seen from Figure 5 that

- (i) There is some variability in α for the temperature range below T_g .
- (ii) There are few values of α for $T > T_g$ due to the collapse of the sample.
- (iii) On the basis of these results, % glass = $[0.4/1.5 \times 100 \text{ \%}] = 26.7 \text{ \%}$

It is not known whether the α value obtained for temperatures above T_g were the maximum (steady state) values because of the collapse of the sample. For this reason the thermal expansion method is not recommended.

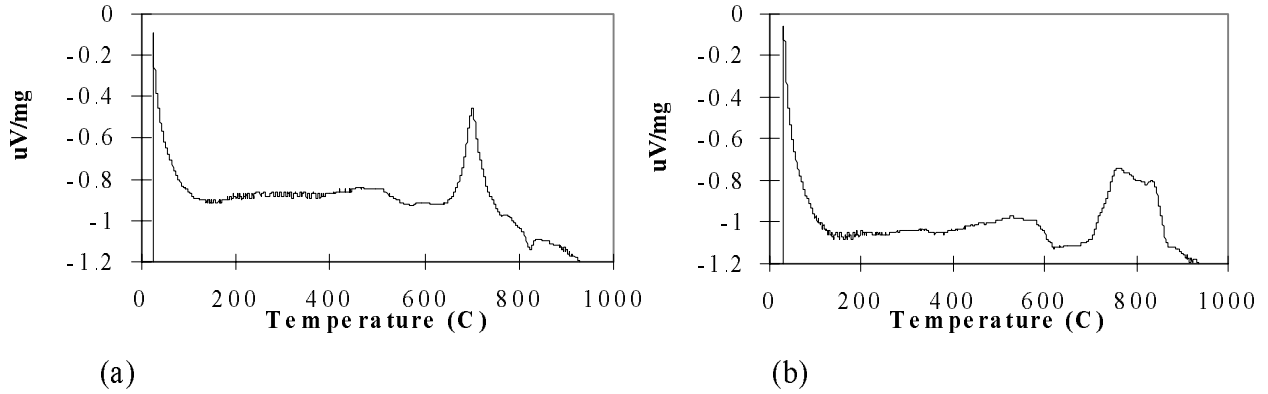
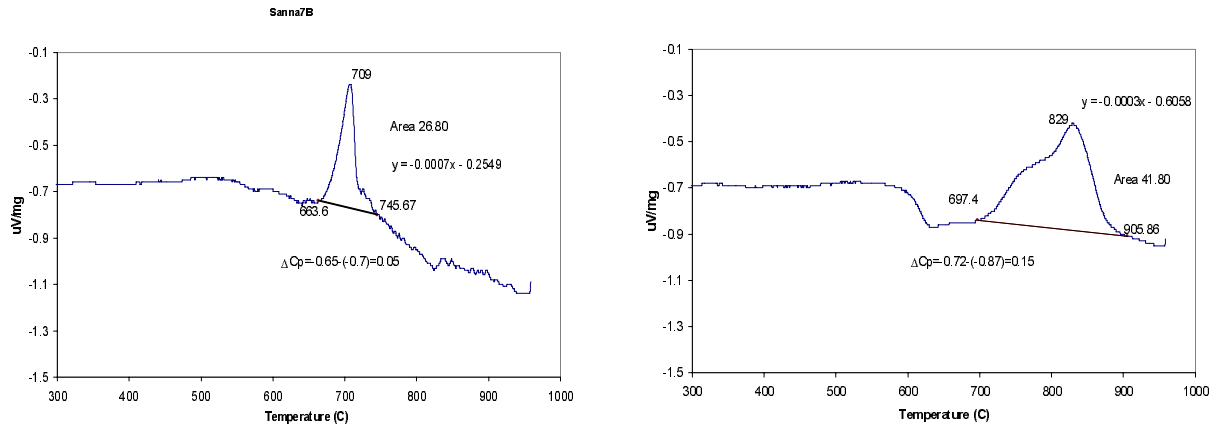


Figure 6. Thermal expansion coefficient as a function of temperature for (a) slag film, and (b) glass made from mould flux + 2 % Al_2O_3 .

2.2.3 Enthalpy of Crystallization

It can be seen from Figure 2b that there is an exothermic transition for the slag film just above T_g ; this is associated with the enthalpy of crystallization, ΔH^{cryst} . The percentage glass in a slag film can be determined by measurements of ΔH^{cryst} for both the slag film and the pure glass derived from it. Unfortunately, not all crystallization processes in mould fluxes are completed within the temperature capabilities (727°C) of the Perkin-Elmer DSC or DPSC. Consequently the following measurements were carried out using a Differential Thermal Analysis (DTA) at a heating rate $10^\circ\text{C min}^{-1}$. Typical DTA traces are shown in Figures 7a and 7b for the slag film and the glasses produced from the slag film. The percentage glass can be determined from (a) the area under the crystallization peak, and (b) the step-decrease which is associated with ΔC_{pT_g} , as shown in Figure 7.



(a)

(b)

Figure 7. DTA traces for (a) slag film and (b) glass for slag DA0096B as a function of temperature showing the exothermic peak due to crystallization.

The results obtained using the measurements of ΔH^{cryst} were reasonably reproducible. Furthermore, results on a Differential Temperature Scanning Calorimeter (denoted DTSC) at Corus Teesside Technology Center (TTC) were found to be in good agreement with those results obtained at Imperial College for temperatures above the crystallization temperature. The main uncertainty lies in the extrapolation of the baseline. It was observed that the baseline tended to decrease markedly with temperature in the DTA at Imperial College, whereas the equivalent baseline was reasonably steady in the DSC traces obtained at Corus TTC. Consequently, it would appear that these measurements should preferably be carried out using high temperature DTSC rather than DTA.

In general the step-decrease in the trace was relatively small in magnitude even for the glass (which is associated with ΔC_{pT_g}) and thus the measurements are prone to much higher uncertainties than those obtained (a) from ΔC_{pT_g} in the Perkin-Elmer DSC, and (b) from ΔH^{cryst} measurements.

2.2.4 X-ray Diffraction (XRD) Measurements

There are two approaches which can be taken involving the comparison of the XRD intensities of the slag film with either (a) the intensity of the crystalline phase, or (b) the intensity of the glassy phase. Preliminary measurements were carried out on (i) a pulverized slag film, (ii) a crystalline slag film given a further crystallization treatment of 7 days at 900°C, and (iii) a glass prepared

from the slag film. The results obtained for the intensities of the main peaks recorded for the slag film (A) (shown in Figure 8) and the crystallized sample (B) resulted in a crystalline fraction of > 100 %. One possible reason for this is that the crystallized sample was not fully crystallized.

Furthermore, a comparison of XRD intensities of the main peaks shown in Figure 8 for the slag film (A) with that of the glass (C) gave variable percentage crystalline results for the different peaks, with values ranging from between 33 and 86 % crystallinity (or 14 and 67 % glass).

It was decided that the most appropriate method was to obtain a standard sample of cuspidine, $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$, and to mix this with a glass phase in the proportions (% cuspidine : % glass) of 100 : 0, 75 : 25, 50 : 50, 25 : 75, 0 : 100, and determine the XRD intensities. The amount of crystalline, or glass, phase present could then be determined by comparison of the cuspidine intensities in the slag film with those in the standard samples. Unfortunately, we have not been able to obtain cuspidine in a pure form, and we have been unable to obtain satisfactory separation of the cuspidine from the gangue in a mineralogical sample we purchased.

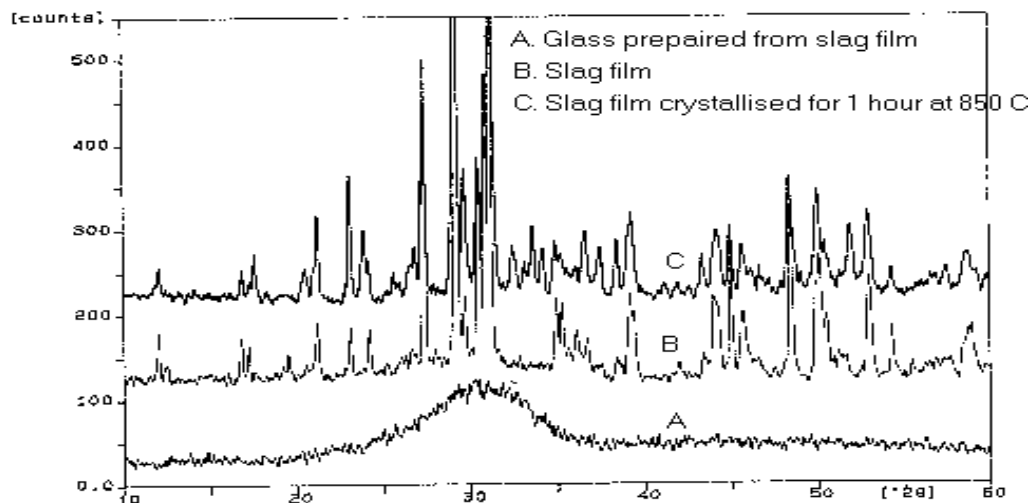


Figure 8. XRD intensities for (a) a glass prepared from the slag (b) slag film, and (c) a slag film crystallized for 1 hour at 850°C and furnace cooled.

3. MEASUREMENTS ON SLAG FILMS

The results obtained on different slag films are given in Table 2.

Table 2. Percentage glass in slag films.

	DPSC	DTA / DTSC		Comment	Metallography
	ΔC_{pTg}	ΔH^{cryst}	ΔC_p		
SA					
Powder (1)	15%	15% 12% 10%	Not Discernable	Thin slab powder	
Lump (2)	25%				
Slag Film		0%	0%	Rim sample	
LXA					
DA 96E		33% 42% (c)	100% 52-78% (c)	Slag film close to meniscus	
DA 96A		100%	87%	Liquid mould powder slag	
DA 96A		>100%	90%	From top of mould	
DA 96B		41% 30.5% (b)	~30%, 40% (b)	Slag film close to meniscus	
DA 96C		~25%(a) 30.5% (b)	Not discernable	Slag film 300mm from meniscus	
DA 96F		~30%(a)	Not discernable	Slag film 300mm from meniscus	29.5 + 2.3 = 31.8%
Metallurgica					
Y		8.8%	~10%	Thin slab plant B; 0.55% C; cap off after 4 heats; east broadface	
	Difficult to interpret west broadface				
X		25-30%	Difficult	Thin slab plant A, LC grade-cap off after 11 heats	
BST					
1423/TS/	Traces difficult to interpret				
SL/1/					
16571/M/					
28404/M/					
Sidenor					
C126VI/A		~30% (a)	Difficult to discern	Billet casting	
C126VI/ABA		~45% (a)	Difficult to discern	Billet casting	
C126 VI/D		82 – 100 %	Difficult to discern	Billet casting	~100%
CSM		90 – 95 %		LC steel casting	

- (a) Baseline problems
- (b) Carried out on different DTSC
- (c) As (b) but no value for glass, assumed same as glasses for DA96B and C

It should be noted that the results obtained by ΔC_{pTg} using DPSC and ΔH^{cryst} in DTA or DTSC are more reliable than those obtained by ΔC_{pTg} using DTA. Inspection of Table 2 indicates that:

- (i) the glassy phase in the sample taken from the liquid is 100 % glassy (see LXA - DA0096A), as might be expected.
- (ii) For LXA, the slag film taken close to the meniscus (DA0096B and E) there was about 40 % glass phase compared with 30 % glass in samples taken from 300 mm below the meniscus (DA0096C and F). (It is not known whether this is significant given the uncertainties in the measurements).
- (iii) Slag films from thin slab casters (SA, X and Y) tend to contain little glass phase, and the crystallization appeared to take place at lower temperatures in these samples.
- (iv) The slag rim samples contained no glassy phase even in samples 30 mm from the rim.

3.1 Metallographic Determination

The slag film was mounted in epoxy resin and polished to 1 μ m and then etched with 5 % aqueous HF. The samples were then viewed with an optical microscope and a scanning electron microscope. The amount of the glass, crystalline and glassy phases were determined by measuring the distance covered by the individual layers and dividing by the total distance for all three layers.

The principal advantage of this method is that it permits a measurement of the liquid layer, in contrast to the other methods which include the liquid layer in the glassy fraction. The main sources of uncertainty arise from (i) the occurrence of a transition zone of (glass + crystalline) phases in some samples, and (ii) the small area viewed may not be representative of the whole. It can be seen from Table 2 that the results obtained by micrographic examination are in good agreement with the results obtained by DTA.

Sidenor kindly provided us with a large slag film sample (about 100 x 80 mm) taken from the corner region of the mould when billet casting with powder C126 VI/D. A series of specimens were taken from this sample to identify whether (i) there was any substantial inhomogeneities in the slag film, and (ii) the crystallinity of the slag film in the corner was different to that on the mould faces. The results are presented in Table 3, and it can be seen that:

- (i) The slag film contained very little crystalline phase; this was confirmed by metallographic analysis which revealed a glass matrix with a few crystallites scattered within it.
- (ii) There were no consistent differences between the slag films from the faces and the corner
- (iii) The uncertainties in the measurements of glass percentage are probably $< \pm 10 \%$.

Table 3. The percentage glass in slag films, as determined by DTA, for specimens at different locations.

Location	Corner	Face 1			Face 2
Sample No.	1.1, 1.2	2.1, 2.2	4.1, 4.2	5.1, 5.2	3.1, 3.2
% Glass	100, 83	100, 93	100, 90	100, 88	100, 80

The very glassy nature of the slag film is consistent with the manufacturers value for the viscosity (η) of 35.0 dPas at 1300°C and the high SiO₂ content of this powder (Table 1). The casting speed (V_c) used was 1.3 m min⁻¹ so one would predict a viscosity at 1300°C of 2 dPas using the rule of $\eta V_c = 2.5$ dPas (m min⁻¹).⁸ However, since the powder consumption demands for billet casting are not stringent, steelmakers frequently use high-viscosity billet powders to combat problems with slag entrapment and / or SEN erosion. The very glassy slag film is the result of using a high viscosity mould flux.

4. DISCUSSION

It is apparent that there is reasonable agreement between the results obtained metallographically and those derived by comparative methods. The metallographic technique has been shown to produce reliable results, and it has the advantage of differentiating between the glassy and liquid layers. The ΔC_{pTg} obtained by using DPSC were also very reliable; the major problem being the production of a pure glass by quenching, when only a little slag film is available. Probably the best approach to the production of a pure glass in these circumstances is to use the mould flux with some modification for the amount of Al₂O₃, MnO₂ *etc.* picked up in casting.

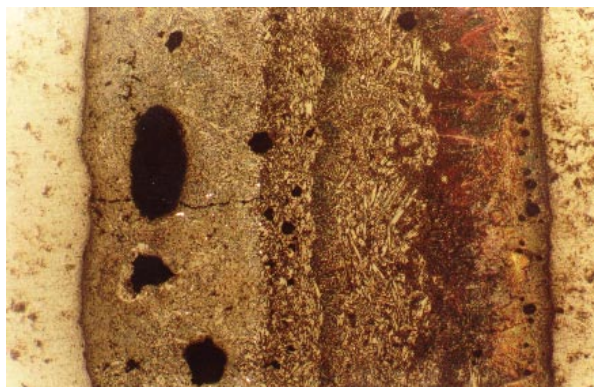


Figure 9. Micrograph of slag film DA0096F.

The measurement of ΔH^{crys} using DTA can provide accurate values of the percentage glass in a sample, but we frequently experienced uncertainties associated with how to extrapolate the base line in order to determine the area under the peak of the DTA trace. However, measurements of ΔH^{crys} using DTSC allowed much more reliable predictions of the base line. Thus the use of DTSC will probably make a significant improvement in the reliability of this technique.

The measurement of percentage glass by thermal expansion coefficient measurements did provide a reasonable value, but is not recommended since the thermal expansion coefficients in the supercooled liquid region can not be determined with confidence because of the collapse of the sample.

The X-ray method is an attractive method for determining the percentage glass since it is rapid, but we were unable to pursue this because we were unable to obtain pure cuspidine to make up our reference samples.

5. CONCLUSIONS

1. There is reasonable agreement between the percentage glass values obtained metallographically with values determined by measuring ΔC_{pTg} and ΔH^{crys} .

2. It is recommended that ΔH^{crys} measurements be carried out using DTSC rather than DTA instruments to minimize uncertainties in base line extrapolations in determining the areas under the peak (*i.e.* ΔH^{crys})
3. Although thermal expansion measurements gave reasonable values for the percentage glass, it is not recommended because the true value for the thermal expansion coefficient may not be obtained at temperatures $>T_g$, due to the collapse of the sample.
4. Examination of a large slag film revealed few significant differences in the percentage glass in different locations of the slag film.

6. ACKNOWLEDGEMENTS

The authors wish to thank Juha Perkkio, Sam Lee, John Sutcliffe, Seung-Taek Oh (Imperial College, London) and Era Kapilshrami (KTH, Stockholm) for their help with the practical work. We also thank Juan J. Laraudogoitia (Sidenor, Spain), Vince Ludlow, Scott McKay (Corus, TTC), Tim Mallaband (Metallurgica, UK) and Dr. Masayuki Kawamoto (SMI, Japan) for providing slag film samples. We also acknowledge funding from the European Coal and Steel Community (ECSC) via Corus TTC, and the Engineering and Physical Sciences Research Council (EPSRC).

7. REFERENCES

- 1 K.C. Mills, Review of ECSC-funded research on mould powders, EUR 13177, ECSC, Luxembourg, 1991
- 2 M.S. Jenkins, Ph.D. Thesis 1998, "Heat Transfer in the Continuous Casting Mould" Monash University, Clayton, Victoria, Aus.
- 3 H. Shibata *et al.* *Proc. 5th Intl. Conf. Molten Slags, Fluxes and Salts*, Sydney Aus. Jan 1997 publ. ISS, Warrendale 771-776
- 4 M. Kawamoto *et al.* Paper Presented Intl. Workshop "Thermophys. Data for the Development of Mathematical Models of Solidification" Gifu City, Japan Oct. 1995
- 5 K.C. Mills, *Proc. Alex McLean Symp.* Toronto, Canada July 1998
- 6 R. Bommaraju, *ISS AIME Steelmak. Conf. Proc.* 1997 74 131-146
- 7 M. Susa, K.C. Mills, M.J. Richardson, R. Taylor and D. Stewart *Ironmak. Steelmak.* 1994 21 279-286
- 8 S. Ogibayashi *et al.* *Nippon Steel Tech. Report* 1987 34 1-10
- 9 S. Sridhar, K.C. Mills, V. Ludlow and T. Mallaband *Proc. 3rd Europ. Conf. Continuous Casting* Madrid, Spain July 1998