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A test to determine crystallinity of mould fluxes

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A test has been devised that can predict accurately the % crystallinity developed in a slag film formed between the steel strand and the mould. The % crystallinity in the test samples was determined and compared with that for slag films formed in the mould when casting with that flux. There was good agreement between the % crystallinity in the test samples and the slag films. It was found that additions of TiO_2 and ZrO_2 had little effect on the amount of crystalline phase formed, but additions of CaO caused a dramatic increase in the amount of crystalline phase formed. Various parameters (which can be calculated from chemical composition of the flux) have been plotted against % crystallinty in the test samples. It was found that the modified (NBO/T) ratio provided the best relation with % crystallinity for the various parameters tested. The recommended relation is % crystallinity=141.1(NBO/T)-284.0.

Keywords: continuous casting, mould flux, slag film, crystallinity, chemical composition

Introduction

Mould fluxes play an important role in the continuous casting of steel[1]. Casting powders are fed continuously onto the top of the mould where they gradually heat up and eventually form a liquid flux pool. Molten flux then infiltrates into the gap between the shell and the mould. A considerable portion of the first liquid to enter the mould/shell gap freezes against the water-cooled mould to give a solid slag film (usually *ca.* 2 mm thick) leaving a thin liquid film (*ca.* 0.2 mm thick) against the shell. This liquid layer provides the required lubrication for the shell. The solid slag film controls the horizontal heat transfer between the shell and mould. The lubrication and the horizontal heat flux are the keys to the success of the continuous casting process and are the reasons why the performance of the casting flux is so important to the process.

The horizontal heat transfer is important especially when casting medium-carbon (MC) steels (0.06–0.18%°C), which are particularly prone to longitudinal cracking due to the mismatch in the shrinkage coefficients of the δ- and the γ- phases of steel. This mismatch results in stresses in the shell, which are relieved by longitudinal cracking. The stresses can be minimized by keeping the shell as thin and as uniform as possible i.e. by decreasing the heat flux. Control of the heat transfer is therefore essential to avoid longitudinal cracking.

There are two mechanisms involved in the heat transfer process, namely, lattice and radiation conduction. The latter is a process of absorption of radiant energy and its subsequent re-emission. In molten glasses >90% of the total energy comes from radiation conductivity (k_R) but it is decreased by (i) the presence of transition metal oxides e.g. FeO and (ii) by crystallites in solids, which scatter the photons. It has been reported that for the heat transfer in slab casting, only 10–30 % of the total conductivity arises from radiation conductivity. The overall thermal resistance between the shell and the mould (R_{eff}) can be represented as a series of resistances[2–7].

$$R_{eff} = R_{Cu/s1} + (d/k)_{gl} + (d/k)_{crys} + (d/k)_{liq} \quad [1]$$

where $R_{Cu/sl}$ is the thermal resistance at the Cu/slag interface, d thickness and k thermal conductivity. Subscripts *gl*, *crys* and *liq* refer to glassy, crystalline and liquid phases, respectively, and *Cu* to the copper mould. The radiation conductivity (k_R) can be represented in Equation [1] as a parallel resistance[8].

Recent work has shown that the two important terms are $R_{Cu/sl}$ and the resistance of the solid layer $\{(d/k)_{gl} + (d/k)_{crys}\}$. Furthermore, it has been shown that $R_{Cu/sl}$ increases as (i) the thickness of solid layer increases and (ii) the amount of crystalline phase in the slag film increases[6].

A model has been developed to predict the optimum flux composition in terms of the optimum lubrication (powder consumption) and horizontal heat transfer for the casting conditions and steel grade[9]. However, at the present time the heat transfer is calculated solely from the thickness of the slag film (which is represented by the break or solidification temperature). In order to incorporate the effect of the % crystallinity in the slag film, it is first necessary to derive a relation between % crystallinity (or % glass: % crystallinity + % glass = 100%) and chemical composition. It has proved exceedingly difficult to obtain sufficient slag films to establish such a relationship.

Consequently, the objectives of this study were:

- To develop a test that provides a reasonable measure of the % crystallinity in slag films taken from the mould
- To use the samples derived in the test (in view of the scarcity of slag films) to obtain a relation between chemical composition and % crystallinity.

Several such tests have been reported in the published literature[10–11] but it is essential that such tests give a similar value for the % crystallinity to that of the slag film. It should also be noted that the slag film may be present in the mould/strand gap for a considerable time. Thus some of the crystallization developed in the slag film may develop as a consequence of annealing in a temperature gradient: the hot face of the slag film (against steel shell) will be between the steel liquidus and 1150˚C[12], but there has been some dispute concerning the temperature of the slag film on the mould side ranging from 300˚C lower down to the mould[13] to above 600˚C[14–16] although the temperature in the hot face of a copper plate slab mould is estimated between 260˚C and 110˚C[15,17].

It should also be noted that mould fluxes contain about 10 chemical components. Consequently, a large number of experiments are required to establish any relation between % crystallinity and % component through data analysis techniques. For this reason we have tried several parameters (which can be calculated from the chemical composition) to obtain a reliable estimate of the % crystallinity. In order to identify such parameters, it is necessary to understand what factors affect crystallization (or glass formation).

In the case of glass formation various parameters have been used to represent the polymerization of the silicate structure. These range from simple relations for the basicity (e.g., V ratio = %CaO/%SiO_2) to relations such as the NBO/T (=number of non-bridging oxygen/number of atoms in tetragonal coordination e.g. SiO_2, Al_2O_3) which provide a measure of the structure or polymerization of the melt. Even the latter may be affected by components such as MgO and MnO, which have been reported to promote glass formation[18–19] despite the fact they are classified as network breakers.

Cuspidine ($3CaO{\cdot}2SiO_2{\cdot}CaF_2$) has been reported to occur in all mould fluxes containing fluorine[20]. Recently, Hanao *et al.*[21] suggested that the precipitation of cuspidine is the first phase to be formed during the quenching of molten mould fluxes and these cuspidine particles act as nucleation sites for crystallization. Consequently, the % crystallinity may be related to the amount of cuspidine in the sample.

It has also been suggested that ZrO_2 and TiO_2 also act as nucleating agents for crystallization[22]. It is thought that the solubility limits of these oxides are limited (about 2 and 10%, respectively) and they are precipitated on cooling and act as nucleation sites. Consequently, the effect of ZrO_2 and TiO_2 on the % crystallinity has also been studied using the method devised in this work.

Experimental

Materials

The 8 commercial mould fluxes used in this study were those for which slag films were available. Other mould fluxes were tested to increase the size of the database. The compositions are given in Table I. The fluxes tested were used for casting various steel grades in billet, bloom and slab casting. The compositions of the samples used in the study of the effect of CaO, ZrO_2 and TiO_2 additions (in the form of 1 micron powders) on the % crystallinity are given in Table II.

Data on % crystallinity

The % crystallinity (crystalline fraction) in the slag films shown in Table I was derived from the work reported by Courtney *et al.*[23] on the same slag films. They determined the % glass in the slag film by comparing the value of several properties of the sample with that of a glass made from the slag film by rapid quenching. The properties measured were (*i*) the change in heat capacity at the glass

Table I
Normalized chemical compositions (after the removal of C and CO_2) of mould fluxes (mass%) used in this study and the % crystallinity in slag films and test samples

	C/S	MgO	Al_2O_3	R_2O	Fe_2O_3	MnO	F	Film %crys	Test %crys	Stollberg %crys	Calculated %crys*
CA	1.25	1.62	4.31	5.39	1.08	0.54	9.70	85	80	10	92
CJ	0.91		2.84	13.46			9.28	30	15	0	46
GA	1.07	3.20	15.50	1.20	0.60	1.20	7.10	8	5	0	
MA	0.92	13.60	22.00	1.40	0.4		2.9	0	5	0	
NA	0.94	5.40	5.0	2.10			5.10		6	0	9
PA**	0.76	3.30	18.60	5.10	1.40	2.60	0.10	6	5	0	
PB	0.65	10.40	17.30	4.00	1.40	3.30	0.60	6	5	0	
PC	1.15		5.83	11.36	1.75	3.50	8.74		99	17	90
PD	0.98		3.44	14.03	1.15	0.12	8.87		87	14	72
PE	1.00		8.43	5.42	1.21	0.12	5.72		6		
SA	1.20	2.03	8.81	3.39	3.39	4.41	3.39		5		2
SB	0.84	0.67	10.00	6.00	3.33	6.67	4.67		5		
SC	1.11	0.58	4.06	4.64	0.58	5.80	4.93		5		4
SD	1.14	0.58	5.81	6.40	0.58		5.81		39	7	35
SE	0.87	0.55	13.26	2.21	6.63		3.87		9		
SF	1.04	0.83	6.65	7.20	0.55		6.65		12		8
SG	0.91	11.54	5.49	3.30	1.65		9.89		8		
TA	0.90	4.3	3.60	12.10			6.50	90	71	5	74
WA	1.0	0.70	4.13	12.85	0.57	0.12	6.89		71		63
WB	0.86	1.30	5.77	14.53	1.99	0.05	9.81		18		19
WE	0.820	1.50	5.75	15.24	2.30	0.12	10.07	40	35	0	30

Film %crys, Test %crys and Stollberg %crys are the % crystallinity of slag films, slag samples produced by the present method, and slag samples produced by Stollberg test in this work, respectively. *: Calculated %crys is the value calculated using Equation[5], the relation between % crystallinity and modified NBO/T obtained in this work for the mould fluxes of NBO/T >2.0. **: PA mould flux contains 12.0% BaO

Table II
Normalized chemical compositions and % crystallinity of mould flux CJ and with addition of CaO, TiO_2, and ZrO_2

	C/S	Al_2O_3	R_2O	F	TiO_2	ZrO_2	Test %crys
CJ	0.91	2.84	13.46	9.28			15
CJ+CaOI	1.08	2.67	12.63	8.71			48
CJ+CaOII	1.26	2.51	11.89	8.20			98
CJ+3%TiO_2	0.91	2.76	13.06	9.01	2.91		15
CJ+6%TIO_2	0.91	2.68	12.69	8.75	5.66		22
CJ+3%ZrO_2	0.91	2.76	13.06	9.01		2.91	21

transition, ΔC_{pTg} (*ii*) the enthalpy of crystallization on heating ΔH_{crys} and (*iii*) the change in thermal expansion at T_g. Measurements were also made using metallography and X-ray diffraction[24]. The values obtained using different methods show some variation, but most of the values (denoted as 'Film %crys' in Table I) have an uncertainty of *ca.* 10 %.

'Stollberg' test[10]

20 g of the decarburized mould flux was melted in a Pt crucible at 1300˚C for 20 minutes and poured into a copper crucible, which was immersed in cold water (<15˚C). The solidified sample was removed and sectioned, and the thickness of the crystallized layer was measured to calculate the % crystallinity.

Modified test

It was found that the % crystallinity in the Stollberg test samples (derived by quenching molten fluxes) was significantly lower than the measured values in the slag films (Figure 1). Consequently, the tests were modified as detailed below and in Figure 2.

- Mould powders were decarburized by heating at 650˚C for 16 hours in air
- 20g of the decarburized sample was placed in a Pt crucible and heated at 1300˚C for 20 minutes
- The molten flux was then poured into a stainless steel crucible at the desired temperature of 15˚C to 650˚C
- The sample and stainless steel crucible were then heated at the desired temperature for a period of 10 to 40 minutes to simulate the annealing of mould flux film between mould and steel shell
- The samples were cut and mounted in epoxy resin and polished to 1 μm and then etched with 2.5% aqueous HF. The samples were then observed with an optical microscope and a scanning electron microscope. The % crystallinity was determined by measuring the thickness of the crystallized layer
- Through preliminary experiments, a holding time of 20 minutes at 610˚C in stainless crucible is recommended.

Results and discussion

The results obtained with the modified test are described below.

Effect of annealing temperature and time on % crystallinity

The effect of annealing temperature for a fixed duration of 20 minutes is shown in Figure 3. It can be seen that % crystallinity increases steadily with increasing annealing temperature. The % crystallinity of the tested mould flux sample CA at the temperature of 600˚C to 650˚C is similar to that for the CA slag film. The effect of annealing time at 610˚C is shown in Figure 4 and it can be seen that the % crystallinity was not affected by the annealing time of 10 minutes to 40 minutes. Therefore, an annealing time of 20 minutes at 610˚C in a stainless steel crucible is recommended.

Temperature changes in the sample during testing

The tested sample was about 5.5 mm in thickness. The

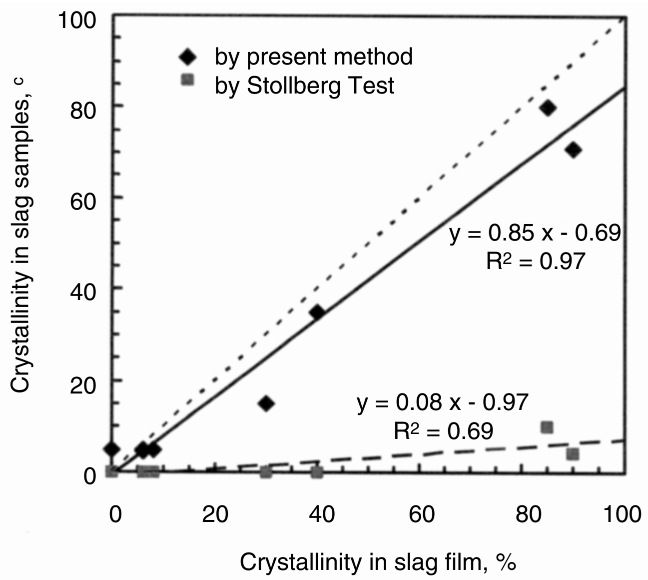

Figure 1. The % crystallinity in test samples as a function of % crystallinity in slag films

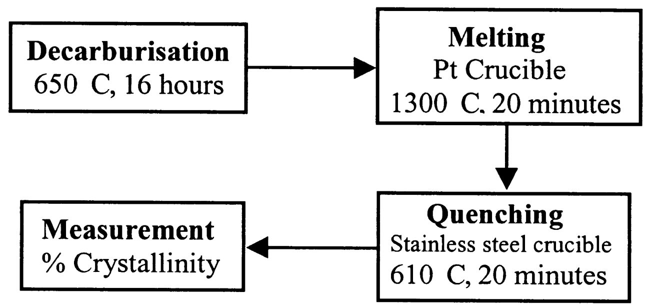

Figure 2. Experimental flow chart employed in this study

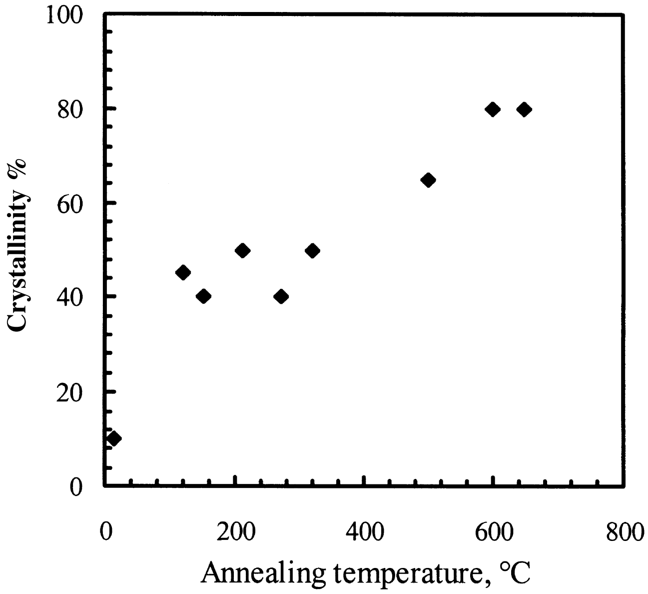

Figure 3. The % crystallinity in test samples of mould flux CA as funtion of annealing temperature. Holding time is 20 minutes

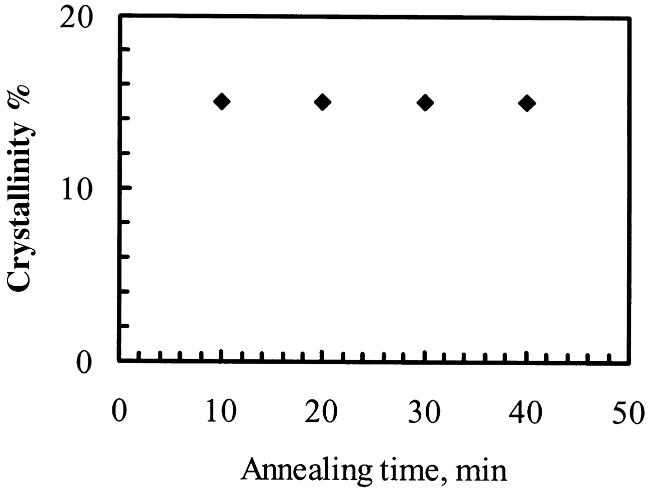

Figure 4. The % crystallinity in test samples of mould flux CJ as a function of annealing time at 610°C

temperatures of various regions of the sample were monitored by placing three K-type thermocouples in the stainless steel crucible in the positions of 0.5 mm, 2.5 mm and 4.5 mm from the inner bottom of the stainless crucible and denoted as bottom, middle and upper, respectively. The results are shown in Figure 5. The temperatures increase dramatically after pouring the molten flux into the crucible, but after holding for about 10 minutes, the temperature in the slag sample remains at 610°C.

Comparison of test results with % crystallinity in slag films

The results obtained for the % crystallinity in the slag films (x-axis) are compared with the values obtained with the test samples (y-axis) in Figure 1. It can be seen from this figure that:

- There was good agreement with the % crystallinity in the test samples with that measured in the slag films; the test slightly underestimates the % crystallinity
- The % crystallinity in the Stollberg test samples in this work is significantly lower than that measured in the slag films.

Effect of ZrO_2, TiO_2 and CaO additions on the % crystallinity

Additions of 3% ZrO_2 to flux CJ resulted in a small increase in the % crystallinity (Table II), whereas additions of 3% TiO_2 resulted in no increase in % crystallinty, and 6% additions caused only a small increase in crystallinity. However, additions of 4% and 8% CaO brought about large increases in the amount of the crystalline phase.

Rocabois *et al.*[25] also found that TiO_2 and ZrO_2 additions in Al_2O_3-CaO-SiO_2-Na_2O-CaF_2 liquids containing less than 30% SiO_2 did not cause a significant increase in the formation of the crystalline phase to be formed (cuspidine), but did increase the growth rate of the particles. There was evidence of nucleation of some cuspidine crystals on ZrO_2 particles. They concluded that crystallization occurred by homogeneous nucleation and diffusion-controlled growth.

The increased crystallization caused by CaO additions is not surprising since it is known that increased basicity, as represented by (%CaO/%SiO_2) causes increased crystallinity[18,26]. This ratio has been used as a simple measure of the depolymerization of the melt.

Relations between % cystallinity and parameters representing composition

Parameters representing depolymerization

It was noted above that the (%CaO/%SiO_2) ratio has been used as a measure of the depolymerization of the melt and it was also noted that increases in this ratio are accompanied by increases in the amount of crystallinity. Various other parameters have been proposed as a measure of the depolymerization of the melt and these have been plotted against the % crystallinity in the test samples.

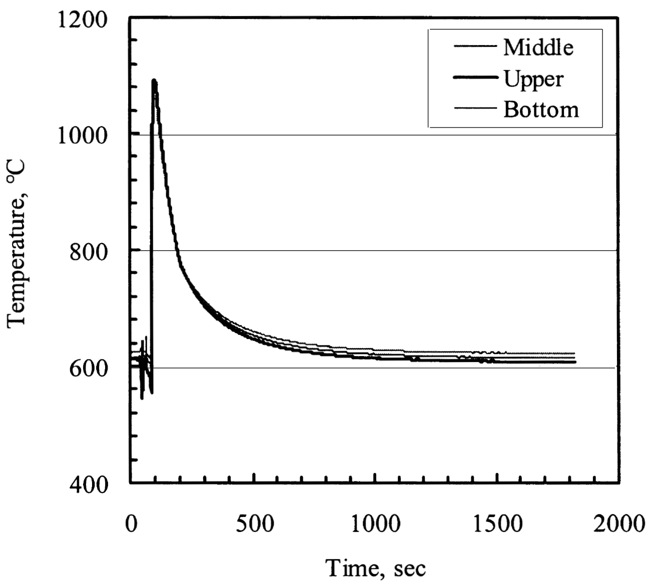

Figure 5. Temperature distribution in the slag sample of mould flux CJ during test. Bottom 0.5 mm, Middle 2.5 mm, and Upper 4.5 mm from the inner bottom of crucible

In this work, the % crystallinity of mould fluxes has been plotted as a function of three parameters, namely, (i) the oxygen to silicon mole ratio (O/Si or O/Si)[27], (ii) mole ratio[28], and (iii) NBO/T[29]. But it was found that in these relations the results for mould fluxes SA, SC, SG etc. exhibit low % crystallinity values which diverge from the bulk of the data.

This low % crystallinity in the test samples SA, SC and SG may be associated with the high MnO contents in mould fluxes SA and SC and high MgO content in SG. The % crystallinity of mould fluxes decreases steeply when the MgO content is >5%, and it will be less than 10% if the MgO content exceeds 7% or so[18]. It is also known that the crystallinity of mould fluxes increases with increasing MnO content for %MnO<4%, but obviously decreases with increasing MnO content above 4% MnO. It can be concluded that MgO or MnO promote glass formation if the MgO content exceeds 5–7% or MnO exceeds 4%.

Modified O/Si ratio

The modified oxygen to silicon (mole) ratio (O/Si) is calculated by the following formula. It is considered that the glass network cannot be formed if (O/Si)>3[27].

$$O/Si = \frac{n_{CaO} + n_{MgO} + n_{MnO} + n_{BaO} + 2n_{CaF_2} + n_{Na_2O} + n_{K_2O} + 3n_{Fe_2O_3} + 2n_{SiO_2} + 3n_{Al_2O_3} + 2n_{TiO_2} + 3n_{B_2O_3}}{n_{SiO_2} + 2n_{Al_2O_3} + n_{TiO_2} + 2n_{B_2O_3} \left(+n_{MgO} + n_{MnO}\right)} \qquad [2]$$

where n = mole number of the component in the mould flux. The bracket in the denominator means it will be included into the denominator if MgO is larger than 7.0% and or MnO is larger than 4.0%.

Figure 6a shows that:

- any mould flux with the modified O/Si ratio <3.1 is glassy. The % crystallinity increases with increases when the modified O/Si ratio is >3.1
- there is a reasonable amount of scatter in the plots.

Modified mole ratio

Neumann *et al.*[28] suggested mole ratio to express the crystallization ability of mould fluxes, that is a modification of the basic/acidic oxide mole ratio where fluorine appears in the numerator with the network breaking components. In this work, this ratio is modified as:

$$\text{Mole ratio} = \frac{n_{CaO} + n_{BaO} + n_{CaF_2} + n_{Na_2O} + n_{K_2O} + n_{Fe_2O_3}\left(+n_{MgO} + n_{MnO}\right)}{n_{SiO_2} + n_{Al_2O_3} + n_{TiO_2} + n_{B_2O_3} \left(+n_{MgO} + n_{MnO}\right)} \qquad [3]$$

The bracket in the denominator/numerator means it will be included into the denominator if MgO is larger than 7.0% and or MnO is larger than 4.0%, otherwise it will be included in the numerator.

Figure 6b shows that:

- the % crystallinity of mould fluxes exhibits a good relationship with the modified mole ratio
- below the critical value of 1.1 for the modified mole ratio, the slag samples are completely glassy (very low % crystallinity)
- above this point, the % crystallinity increases linearly with increasing modified mole ratio

- the slope of this curve is a little steep, which means the calculated % crystallinity will be very sensitive to small changes in chemical compositions.

NBO/T ratio

The NBO/T ratio, i.e. the number of non-bridging oxygen per tetrahedrally-coordinated atom, has been adopted to represent the degree of depolymerization of silicate slags[29]. In this work, this index is calculated as follows:

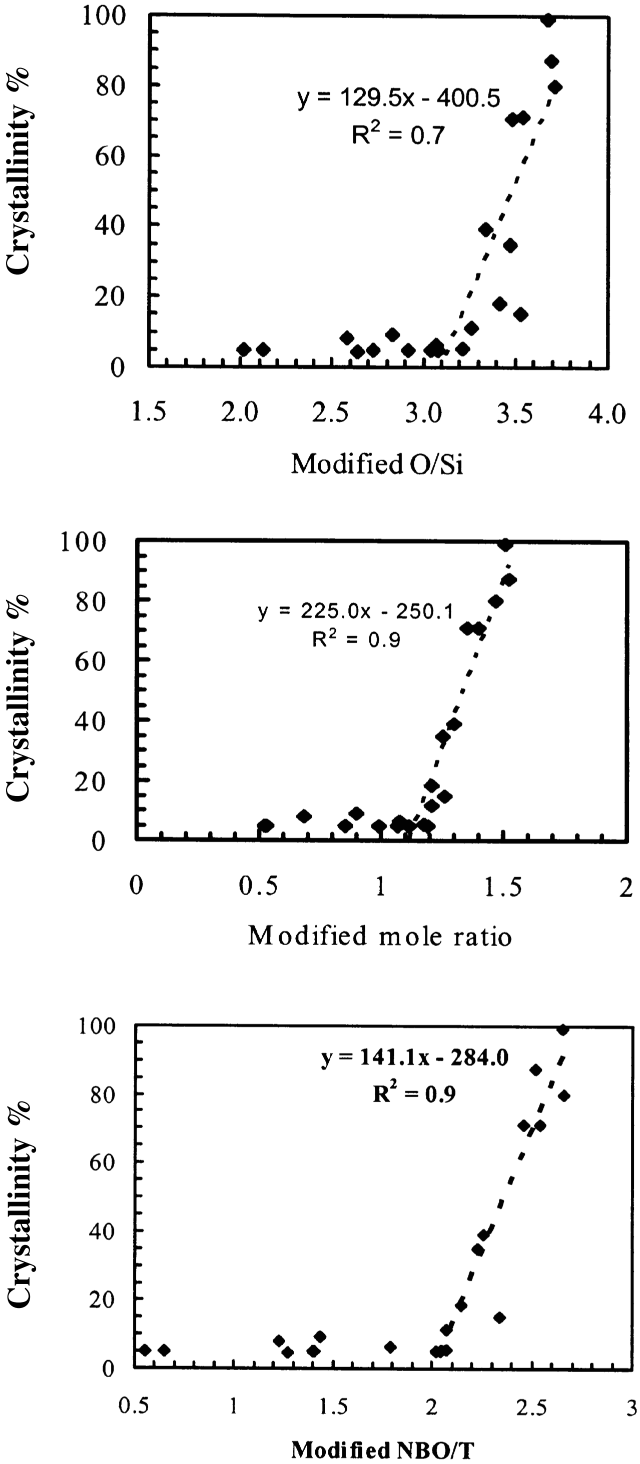

Figure 6. The % crystallinity as a function of parameters representing depolymerization. a: modified O/Si ratio, (b): modified mole ratio and (c:) modified NBO/T ratio

$$NBO/T = \frac{\begin{array}{c}2x_{CaO} + 2x_{BaO} + 2x_{CaF_2} + 2x_{Na_2O} - \\ 2x_{Al_2O_3} + 6x_{Fe_2O_3} + \left(2x_{MgO} + 2x_{MnO}\right)\end{array}}{\begin{array}{c}x_{SiO_2} + 2x_{Al_2O_3} + x_{TiO_2} + 2x_{B_2O_3} + \\ \left(x_{MgO} + x_{MnO}\right)\end{array}} \quad [4]$$

where x = mole fraction of the component in the mould flux. The bracket in the denominator/numerator means it will be included into the denominator if MgO is larger than 7.0% and/or MnO is larger than 4.0%, otherwise it will be included in the numerator.

Figure 6c shows that:

- there is a good relationship between the % crystallinity and the modified NBO/T
- the critical point occurs at NBO/T=2.0. Below this critical point, the slag samples are completely glassy (very low % crystallinity), whilst above this point, the % crystallinity increases linearly with increasing the modified NBO/T
- the recommended equation to calculate the % crystallinity is:

$$\%\text{ crystallinity} = 141.1(NBO/T) - 284.0 \quad [5]$$

The calculated % crystallinity using Equation [5] for the mould fluxes with the modified (NBO/T)>2.0 is given in Table I.

Parameters representing % crystallinity

The maximum amount of cuspidine % was obtained by calculating the maximum mass amount of cuspidine that could be formed in 100 grams of mould flux. In mould fluxes there is usually sufficient SiO_2 present so the mould fluxes can be divided into CaO excess (CaF_2 insufficient) and CaF_2 excess (CaO insufficient). The maximum mass amount of cuspidine is calculated according to the insufficient component (CaF_2 or CaO). It is possible that crystallization is affected by whether there is an excess of CaF_2 or CaO, and so these have been plotted by different symbols in Figure 7. It can be seen that there is a reasonable relation between the parameter and % crystallinity for those samples where there is an excess CaF_2 but more work is required to determine any relation for those fluxes with an excess of CaO.

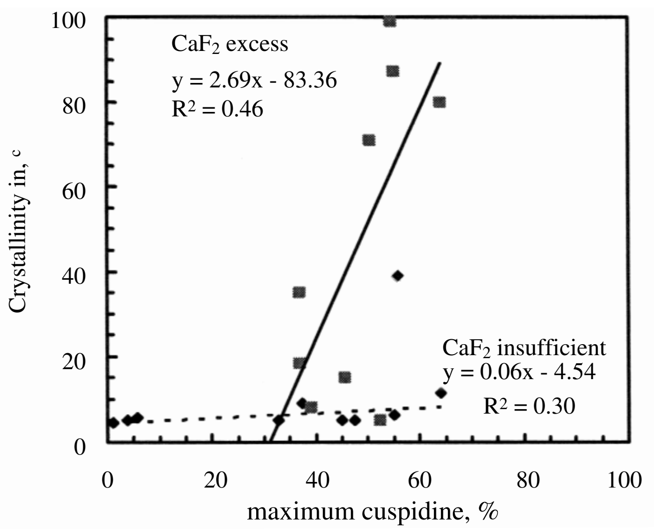

Figure 7. % crystallinity % as a function of maximum calculated cuspidine amount

Therefore for the various parameters tested, the most reliable estimates of the % crystallinity are obtained using modified NBO/T.

It should be noted that the slag films may not be homogeneous. The methods used to measure % crystallinity use very small samples and thus local inhomogenities may result in variations in % crystallinity in the slag film. Furthermore, the crystal fraction in the slag films would be expected to vary with position in the mould, namely (i) in the corners where there is stronger heat extraction (particularly in billets)) and (ii) with distance from the meniscus. All of these points suggest that there will be uncertainties associated with the measurement of the % crystallinity in addition to any systematic errors arising from the measurement method. Thus the results reported here will be prone to some uncertainty but should allow the % crystallinity to be taken into account in development of the model for selecting mould flux composition.

Conclusions

- A test has been devised that provides a good measure of the % crystallinity found in slag films taken from the mould
- Additions of ZrO_2 and TiO_2 did not result in any significant increase in crystallinity
- The parameter NBO/T was found to be the most suitable of the various parameters tested to derive the % crystallinity from the chemical composition. The recommended equation to calculate the % crystallinity for the mould fluxes with the modified (NBO/T)>2.0 is: % crystallinity = 141.1(NBO/T)-284.0.

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