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CRYSTALLIZATION OF MOULD POWDERS USED IN THE CONTINUOUS CASTING OF STEEL

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Mould powders used in the continuous casting of steel play an important role in the heat transfer and lubrication between the liquid metal strand and mould. A range of industrial fluxes was investigated, each sample being decarburized and milled prior to DTA. On heating, the powders undergo silicate crystallization producing exotherms in the range 600°–1000°C, before melting. The activation energy of crystallization (E_a) was determined from the peak shifts of each flux heated at different rates, and ranged from 100–450 kJ/mol. E_a values increased with flux viscosity and decreased with basicity, suggesting that DTA can be applied to mould powder evaluation for use in continuous steel casting.

Keywords: activation energy of crystallization, DTA/TG, mould powders

Introduction

Mould powders are glasses formed from oxides, silica and fluoride that can be represented by a pseudo-ternary system, SiO_2–CaO–NaF. The SiO_2 (SiO_2, Al_2O_3) component, termed the network former, is modified by CaO (CaO, MgO, Fe_2O_3), while NaF (CaF_2, Na_2O, K_2O) contributes fluidizing properties to the glass. The powders are used in continuous steel casting where they provide lubrication between mould and metal strand and create a thermal barrier that regulates the heat transfer from strand to mould [1, 2]. The incidence of longitudinal cracking in steel, for example, has been associated with heat transfer characteristic of the slag layer. In general, the surface quality of continuously cast steel is influenced by heat transfer, melting and viscosity behaviour of mould powders.

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Decarburization

The samples contained about 2% carbon which was removed prior to crystallization studies in order to ensure compositional stability during DTA analysis. The as-received powder was placed in an alumina boat and heated in a muffle furnace for 16 hours in air at 650°C.

Melting and casting

The decarburized powder was melted in a platinum crucible at 1400°C using a resistance-heated Lucifer furnace. Each sample was held at this temperature for 40 min prior to casting in a 250°C preheated brass mould. To prevent devitrification of the glass a brass cap was placed on the mould immediately after casting. The cooled cast product was milled to –53 μm prior to DTA analysis.

Freshly prepared powders were used since DTA/TG suggested that carbonation could occur in aged samples. In the latter, the glass transition was replaced by an endotherm associated with a weight loss of 2–4%.

Table 1 Composition of mould powders following decarburization

Composition	MP1	MP2	MP3	MP4	MP5
Total C	0.02	0.03	0.02	0.02	<0.02
SiO_2	35.0	38.6	36.4	37.0	39.9
CaO	37.6	27.9	37.8	35.8	41.1
Al_2O_3	2.6	5.1	6.3	6.4	6.5
Fe_2O_3	0.22	0.4	1.1	0.4	0.5
Na_2O	11.2	12.8	6.3	5.9	0.5
MgO	0.88	2.3	0.19	2.5	2.9
BaO	—	5.7	—	5.6	3.3
K_2O	0.31	—	0.22	—	—
MnO	0.03	—	0.04	—	—
TiO_2	—	—	0.21	—	—
CaF_2	8.9	8.6	4.9	4.8	2.9
η(Poise, 1300°C)	0.71	2.8	4.1	5.0	11.0
BI	1.82	1.65	1.44	1.59	1.32

Table 1 gives the composition following decarburization of five different mould powders. Also indicated are their corresponding viscosity [3] values (at 1300°C) and calculated basicity index, BI. The latter was calculated [4] using the expression

$$BI = \frac{1.53\% CaO + 1.51\% MgO + 1.94\% (BaO + Na_2O) + 1.53\% CaF_2}{1.48\% SiO_2 + 0.10\% Al_2O_3}$$

DTA/TG analysis was performed using a Rigaku Denki Thermoflex 1500 system. Sample masses of about 40 mg were heated in Pt cups to 1200°–1300°C in static air. Variable heating rates (5 to 40 deg/min) were employed. Crystalline phases were identified using a Siemens D500 diffractometer.

Results and discussion

The DTA curves of the powders revealed glass transitions followed by several crystallization exotherms in the range 650°–1000°C (Fig. 1). Frequently two exotherms were observed but MP3 produced only one broad peak and MP5 produced three.

Generally the first peak was most prominent. Crystallization was followed eventually by melting which sometimes occurred in several stages before the liquidus was formed. The latter occurred at about 1150°C.

The compositions of the crystalline phases produced at high temperature were variable and consisted of complex oxo- and oxyflurorosilicates. In agreement with Hiromoto *et al.* [5] cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$) was always observed in the crystalline fluxes, and pectolite ($Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$) usually encountered. However, species such as gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), pseudo-wol-

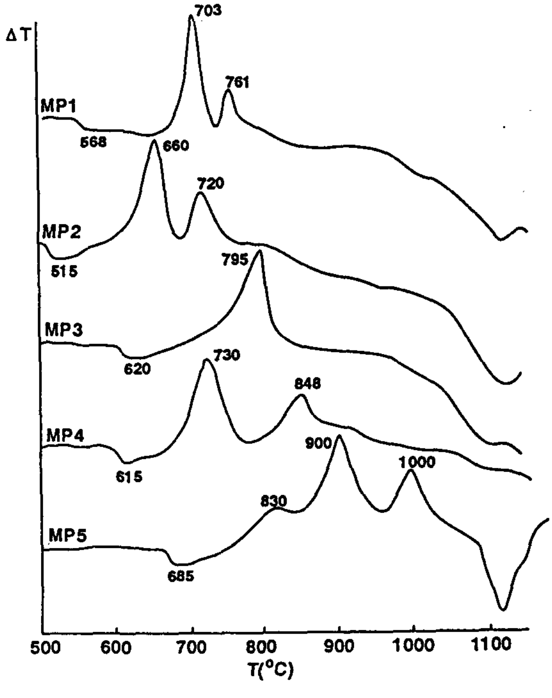

Fig. 1 DTA curves of industrial mould powders (heating rate 20 $deg \cdot min^{-1}$)

lastonite ($CaO \cdot SiO_2$) and $Na_2O \cdot CaO \cdot SiO_2$, occurred only in some compositional ranges.

Glass transition temperatures (T_g) were observed between 500°–690°C (Fig. 1) and tended to increase with sample viscosity. As shown in Fig. 2, T_g decreased with NaF content of the powders, a relationship reported [6] for many fluorosilicate glasses. Crystallization followed T_g by about 80°–120°C, and the crystallization temperature T_c showed a tendency to increase with increasing viscosity of the molten flux. Conversely T_c decreased with % Na_2O, which influences the flow characteristics of the melt.

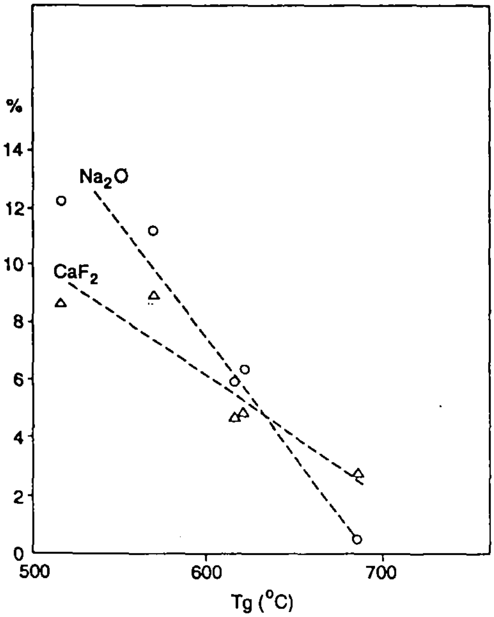

Fig. 2 Plot of T_g (°C) *vs.* %Na_2O and % CaF_2

Using the T_c value of the dominant exotherm from the DTA curve at different heating rates for each powder, the energy of activation for crystallization, E_a, was determined from the relationship,

$$\log h = -\frac{E_a}{2.303RT_c} + C$$

where h is the heating rate [7]. A typical plot is shown in Fig. 3. E_a values were calculated from the gradients of such lines and fell in the range of 100–450 $kJ \cdot mol^{-1}$. Bulk crystallization might be expected to dominate the nucleation growth of powders with lower E_a values. Fluxes possessing high E_a, however, are likely to demonstrate diffusion-controlled crystal growth from nucleii at the glass surface.

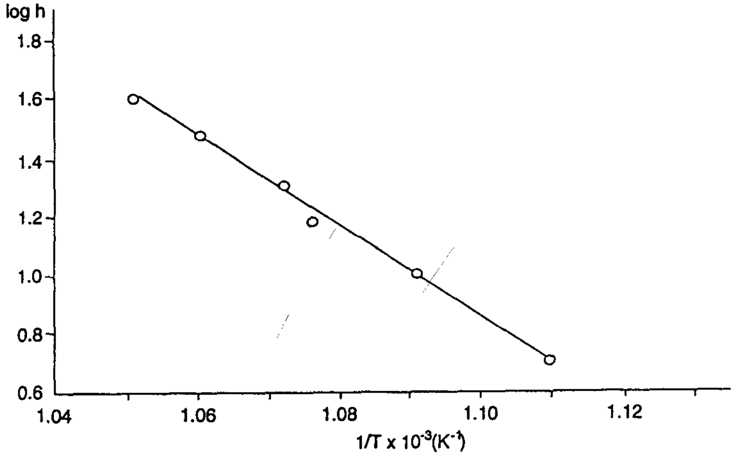

Fig. 3 Plot of log *h* *vs.* $1/T_c$ (MP2)

The E_a values mirror the viscosity values of molten flux measured at 1300°C, and, as indicated by Fig. 4, increased essentially linearly over the range 0.7 to 6 poise. A gradual deviation was apparent at high viscosities. A 15-fold increase in viscosity yielded a 4-fold increase in activation energy. Moreover, the basicity index (BI), a measure of alkaline oxides in relation to silica/alumina, gave a plot (Fig. 4) in which high flux basicity resulted in facile crystallization and low E_a

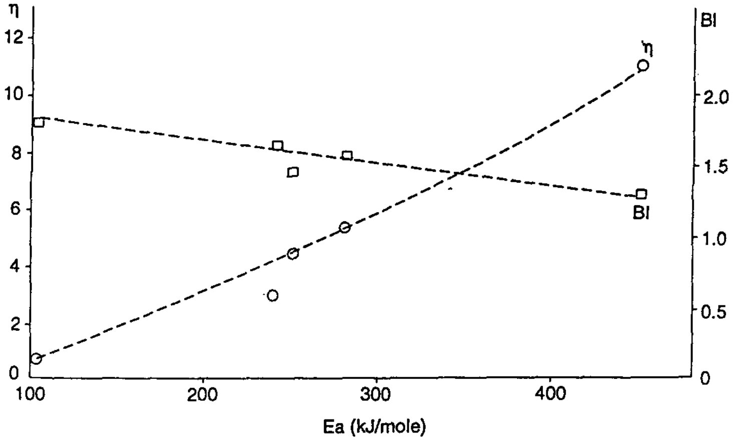

Fig. 4 Relationship between E_a, mould powder viscosity (1300°C) and basicity index (BI)

values. However, BI values were found not to be particularly sensitive to changes in E_a.

The tendency of a flux or mould powder to precipitate a crystalline phase depends on its E_a value, which relates physically to the viscosity and basicity of the material. On a molecular basis this can be attributed to NaF and the length of the silica chains in the pre-crystalline structure. At low basicity, long silica chains are favoured and occur in melts of high viscosity. Sodium content is relatively low. Conversely, high basicity favours short-chain sodium silicates which crystallise relatively early and at lower temperatures.

The apparent relationships between viscosity, BI and E_a imply that DTA can be used to compare, at least approximately, the fluid properties of a given mould powder at high temperature (where η is measured). Additional data would be necessary to improve the usefulness of the curve in Fig. 4.

Finally, because of the high thermal gradient across the flux film between liquid strand and mould wall used in continuous casting, the crystallization on cooling is also of major concern. Preliminary work has shown that devitrification from the melt occurs between 1000°–1100°C. Therefore the controlled cooling of mould powders using DTA warrants separate study.

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Zusammenfassung — Abdeckpulver beim kontinuierlichen Gießen von Stahl spielen eine bedeutende Rolle beim Wärmetransport und beim Schmieren zwischen dem flüssigen Metallstrang und der Form. Es wurde eine Reihe von Industrieflußmitteln untersucht, wobei jede Probe vor der DTA entkohlt und gemahlen wurde. Beim Erhitzen unterliegen die Pulver vor dem Schmelzen einer Silikatkristallisation, was im Bereich 600°–1000°C zu exothermen Peaks führt. Die Aktivierungsenergie E_a der Kristallisation liegt im Bereich 100-450 $kJ{\cdot}mol^{-1}$ und wurde bei jedem Flußmittel anhand der Verschiebung der Peaks bei verschiedenen Aufheizgeschwindigkeiten ermittelt. Die Werte für E_a steigen mit der Flußmittelviskosität und sinken mit der Basizität, was zeigt, daß DTA zur Bewertung von Abdeckpulvern für das kontinuierliche Gießen von Stahl angewendet werden kann.