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Fundamental investigations for the design of fluorine free mold powder compositions

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Abstract

The influence of the CaO/SiO_2 ratio on flux viscosity at 1300°C, break temperature and crystallization was investigated.
The thermo-chemical software FactSage was used for the calculation of the viscosity, the equilibrium phase content and the liquidus temperature. Based on these results, two sample series with 8.8 wt% TiO_2, 5 wt% B_2O_3 and CaO/SiO_2 ratios from 0.8-1.2 were manufactured. Series M1 contained Li_2O which was replaced by a higher content of Na_2O for F-free mixtures in series M2. The viscosity and break temperature were determined through rotational viscometry, the crystallization temperature and crystalline fraction by a so called Furnace Crystallization Test, a macro style differential thermal analysis which enables a mineralogical investigation of the samples afterwards.
The experiments exhibited that the break temperature, the liquidus temperature and the crystalline fraction rose with increasing C/S ratio while the viscosity decreased for both sequences.

Introduction

Commercial mold powders are synthetic slags that usually contain SiO_2, CaO, Na_2O, CaF_2, C, etc. [1,2,3]. Fluorine is an essential component to decrease liquidus temperature and viscosity of the mold slag, and it further promotes the crystallization of the slag film through the formation of cuspidine [1,4,5]. However, fluorine is undesirable concerning health and environmental issues. Fluorine emissions may bring about corrosion and the acidification of cooling water [6]. Thus the investigation of mold powders without fluorine has become a research area of interest.
It is noted that flux components as B_2O_3, TiO_2, Li_2O and Na_2O are, to some extent, alternatives to fluorine on decreasing melting point and viscosity [7,8,9,10].
In this study the influence of the CaO/SiO_2 (C/S) ratio on flux viscosity at 1300 °C, break temperature and crystallization of laboratory slags, situated in the CaO-SiO_2-Al_2O_3-Na_2O-B_2O_3-system was investigated.

Experimental

Chemical Composition

The thermo-chemical software FactSage was used for the calculation of the viscosity, the equilibrium phase content, and the liquidus temperature. From these calculations two series of samples with chemical compositions given in Table I followed.

Table I. Chemical composition (mass%) of the samples investigated

	CaO/SiO_2	$CaO+SiO_2$	TiO_2	Na_2O	B_2O_3	MgO	Al_2O_3	Li_2O	FeO
M1	0.8-1.2	68	8.8	8.0	5.0	4.5	3.5	1.2	1.0
M2	0.8-1.2	68	8.8	9.2	5.0	4.5	3.5	-	1.0

Sample Preparation

The mixtures were made from purified oxides and carbonates (reagent grades with at least ≥98 % purity). $CaCO_3$, Na_2CO_3 and Li_2CO_3 were added to provide CaO, Na_2O, Li_2O respectively and Fe_2O_3 was added as a source of FeO. For decarburization the samples were annealed within ceramic containers in a high temperature chamber furnace at 700 °C for 12 hours. Subsequently the samples were melted in covered platinum crucibles at 1400 °C in a preheated chamber furnace for 15 min, afterwards poured into a steel mold and quenched to room temperature with cold water to obtain glassy pieces. Finally the samples were ground into powder and split up for the consecutive tests.

Inclined Plane Test

Determining the ribbon length of a viscous fluid after pouring on an inclined plane is a relatively simple, practical rheometric test [11]. Slags with lower viscosities will produce a longer ribbon, if the samples' solidification temperatures are equal or in the same range. Thus, the Inclined Plane Test was used in this study to roughly evaluate the viscosities of fluxes at 1300 °C. 15 g of a sample were put into a platinum crucible and liquefied at 1490°C in a high temperature chamber furnace for 15 min. Then the platinum crucible with the molten slag was removed and quickly inserted into a cylinder-shaped container. The mold slag was poured out immediately to let the slag flow down the plane and cool at ambient temperature, whereas the temperature of the slag upon impinging was controlled by a thermocouple and averaged 1300 °C. Finally the length of solidified specimen was measured.

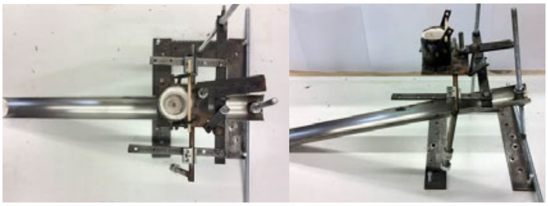

Figure 1. The device for the Inclined Plane Test.

Rotational Viscometry

The dynamic viscosities and the break temperatures of the sample fluxes were evaluated with a commercial high temperature rotational viscometer. The crucible as well as the rotor were made of platinum. 27 g of the sample were heated within 30 min to 1400 °C and measured at a cooling rate of 10 °C/min. During the experiment the furnace chamber was purged with argon.

Furnace Crystallization Test

The Furnace Crystallization Test (FCT) is a sort of a big scale differential thermal analysis and was performed in a high temperature chamber furnace as shown in Figure 2. A sample weight of 27 g was put in one platinum crucible and the equal mass of alumina was used as a reference material in a second crucible. The crucibles were heated up to 1350 °C and held for 15 min to ensure that the powders became completely liquid and then the furnace was allowed to cool to room temperature at a cooling rate of 10 °C/min. The temperatures of the F-free mold powder and the alumina were measured with type S thermocouples and recorded via a data logger at intervals of 30 s.

Figure 2. Set up of the Furnace Crystallization Test.

After this procedure, the crucible was turned upside down to retrieve the solidified specimen, which was cut across the platinum wire into two pieces. One half was crushed into powder and analyzed by X-ray diffraction (XRD), the other part was polished for reflected light microscopy and scanning electron microscopy (SEM) investigations.

Simultaneous Thermal Analysis

Simultaneous thermal analysis (STA) measurements were carried out in order to determine the liquidus temperature and the crystallization temperature of the specimens. 80 mg mixture were put into a platinum crucible together with a platinum loop with a diameter of 2 mm to enhance crystallization. The crucible was covered with a platinum lid during the measurement process. The measurement was performed with a heating rate of 20 °C/min and a cooling rate of 10 °C/min, the sample chamber was purged with nitrogen.

Results and Discussion

Viscosity

The results of the rotational viscometry at 1300°C are given in Figure 3a; they are somewhat lower than those predicted by FactSage with the data available at the beginning of 2015. The ribbon length from inclined plane test as function of basicity (C/S) is shown in Figure 3b. As expected, both methods exhibit that the viscosities of the fluxes at 1300°C decrease with the increase of basicity and mixtures with Li_2O have lower viscosities than mixtures without Li_2O. CaO, Na_2O and LiO_2 all act as network modifiers within the silicate structure. In M2 1.2mass% Na_2O are replaced by 1.2 mass% Li_2O. Due to the lower molecular weight of Li the molar amount of Li_2O is more than double of the Na_2O reduction and thus increases the available network modifiers. Due to the viscosity decrease with rising C/S ratio only the samples with basicities ranging up to to 1.1 remain glassy during the Inclined Plane Test. Mixtures with C/S of 1.2 have a higher crystallization tendency, and the cooling rate was too low to prevent the samples from crystallizing at the surface.

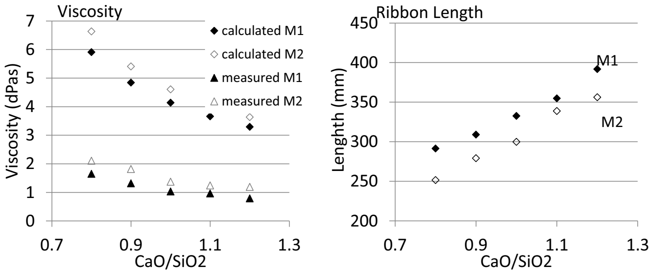

Figure 3. Viscosity at 1300°C (a) and the ribbon lengths (b) of different F-free mixtures after Inclined Plane Test in dependency of basicity (C/S).

Solidification

Solidified samples after the Furnace Crystallization Test are pictured in Fig. 4. The black parts of the specimen are glassy while the yellow ones contain crystal phases. For mixtures with C/S of 0.8 crystal phases formed only along the platinum wire. For a ratio of 0.9 this crystalline mass slightly increased. With a value of 1.0 it could be observed that the interface of the samples became yellow, which indicated that a lot of crystals were formed around the surface, but still a large amount of glass phase existed inside the samples. For C/S of 1.1, just small amounts of glass phase appeared in the middle of the samples and no glass phase could be observed with C/S=1.2. Therefore, it can be concluded that the tendency for crystallization increases with increasing slag basicity. Due to the fact that the amount of crystals within samples of series M1 and M2 and a basicity of 0.8, 0.9 and 1.0 was that small, no crystal phase could be precisely identified through XRD. In Figure 5 XRD patterns of series M2 are given. For C/S of 1.1 and 1.2 combeite ($NaCaSiO_4$), perovskite ($CaTiO_3$), nepheline ($(Na,K)AlSiO_4$) and a calcium borate silicate ($Ca_{11}B_2Si_4O_{22}$) could be determined in both series.

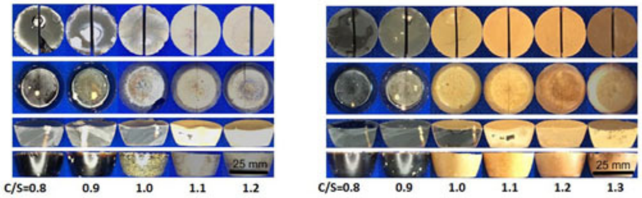

Figure 4. Samples after FCT test M1 left, M2 right.

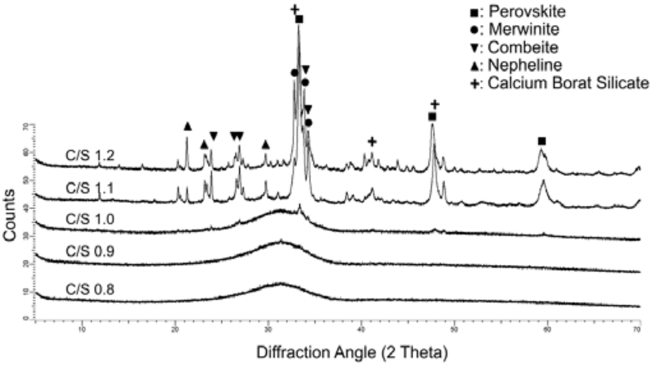

Figure 5. X-ray diffraction spectra of series M2 after Furnace Crystallization Test.

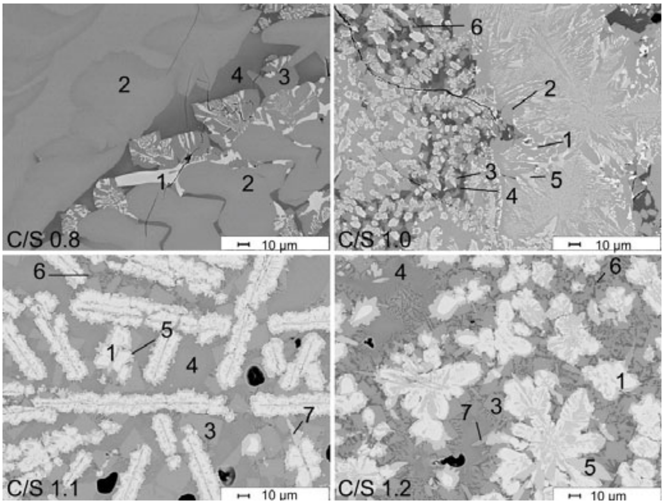

Figure 6. Back scattered electron images of series M2 after FCT. Phases: perovskite ($CaTiO_3$) (1), wollastonite ($CaSiO_3$) (2), combeite ($NaCaSiO_4$) (3), amorphous phase (4), calcium borate silicate $Ca_{11}B_2Si_4O_{22}$ (5), nepheline $(Na,K)AlSiO_4$ (6) and merwinite ($Ca_3MgSi_2O_8$)(7).

Microstructure

As mentioned before, with M1 and M2 C/S 0.8, 0.9 and 1.0 some crystals appeared in the thermocouple area since heterogeneous nucleation occurred at the platinum wires. In both series for C/S of 0.8 and 0.9 wollastonite ($CaSiO_3$) was formed first and became the main crystalline phase, followed by perovskite, the brightest phase visible in Fig 6. Finally trigonal combeite crystallized. For samples with a C/S ratio of 1.0 perovskite became the first phase to form and $Ca_{11}B_2Si_4O_{22}$ and nepheline were formed additionally.

Raising the C/S ratio to 1.1 led to a drastic change in the crystal formation. In Fig.6 perovskite is now visible as large dendroid crystals surrounded by merwinite and $Ca_{11}B_2Si_4O_{22}$. Moreover $Ca_{11}B_2Si_4O_{22}$ became the main crystalline phase, combeite and some nepheline formed additionally. Large merwinite crystals grew in contact with the platinum wire. Wollastonite could not be observed any more. Finally, raising the C/S ratio to 1.2, perovskite and $Ca_{11}B_2Si_4O_{22}$ increased their size, as can be seen from Figure 8. Again combeite appeared around the perovskite and $Ca_{11}B_2Si_4O_{22}$ is framed by nepheline and merwinite.

The increase of the crystalline portion and the crystal size is caused by the function of CaO as a network modifier, which weakens the glass structure. On the other hand lower viscosities promote diffusion processes and therefore crystal growth. Since the amount of TiO_2 is > 6.7%, perovskite was always present in line with Xin [10].

Melting and Solidification

As can be seen from Fig. 7 the impact of the C/S ratio on the liquidus temperatures, as measured by STA exceeds the FactSage prediction (which was not performed with a database optimized for the boron containing compositions). Furthermore, in accordance with [12] substitution of Na_2O for LiO_2 led to an increase of the liquidus temperature.

To determine the crystallization temperatures, the FCT and STA were applied and their results compared in Fig.7. The FCT results display only a slight increase of the crystallization temperature with rising C/S ratio, whereas the STA temperature values are lower for C/S of 0.8 to 1.0 and much higher for C/S above 1.0. The reason for this discrepancy is the characteristic of each method. Whereas with the FCT the thermocouple, which promotes crystallization, is inserted into the sample, the thermocouple of the STA is located under the crucible. In the first case only a small area around the thermocouple is measured, where crystals always form first, while with the STA the whole sample mass may contribute to the measurement. STA measurements represent a higher undercooling thus leading to lower results. If crystallization occurs in the bulk volume, temperature results of both methods are similar. On the other hand, due to the higher sensitivity of the STA device very small peaks of first crystallization, most likely from perovskite, which are not the main peaks, could be detected. These peaks are not visible in the FCT curves. The lower viscosity and therefore faster diffusion processes in the liquid of the samples with LiO_2 may also be the reason why the crystallization temperatures of M1 were higher than those of M2.

Fig. 8a displays selected curves from which it can also be deduced that more than one crystal phase has formed during the viscosity measurement in some cases, especially with the samples of C/S ratio of 1.1 and 1.2. But in these two cases the crystallization of the first precipitating phase had an insignificant impact on the viscosity curve progression. This was the reason why for Fig. 8b not the first but the break temperatures with the most distinguished rise in viscosity, so to say the main break temperatures, were chosen. From this it follows that, in accordance with the crystallization temperatures, the samples with Li_2O show the higher break temperatures and that the main break temperature will rise with increasing C/S ratio as long as the main break temperature is the first break temperature.

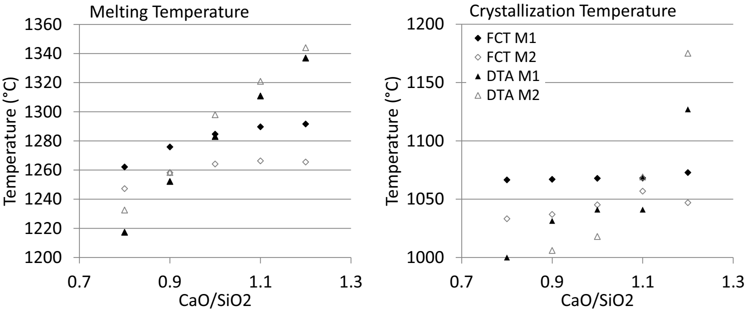

Figure 7. Melting (a) and b) Crystallization temperatures (b) received from STA and Furnace Crystallization Test.

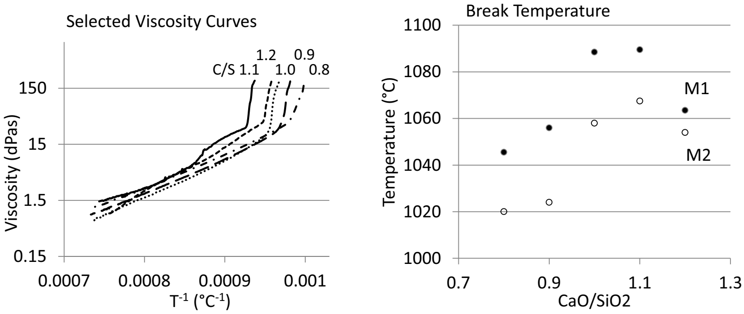

Figure 8. Selected viscosity curves of M1 (a) and main break temperatures (b).

Conclusion

From this work can be concluded that a rise of the C/S ratio leads to an increase of the melting and crystallization temperatures. Furthermore the amount of crystal portion formed can be controlled by the CaO/SiO_2 ratio. Especially the amount, the shape and the size of perovskite correlate positively with the CaO/SiO_2 ratio. For a C/S ratio of 1.0 to 1.2 perovskite supports heterogeneous nucleation of other phases. Additional crystalline phases form dependent on the CaO/SiO_2 ratio. LiO_2 enhances crystallization due to its action as a network modifier.

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