EFFECT OF Al_2O_3 AND CaF_2 ON THE SOLIDIFICATION OF MOULD SLAGS AND THE HEAT TRANSFER THROUGH SLAG FILMS

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ABSTRACT

A basic investigation was done for the solidification of mould slags and its impact on the heat transfer through mould slag films. The crystallization behaviour of synthetic mould slags was analyzed using the Single and Double Hot Thermocouple Technique (SHTT and DHTT) while applying temperature profiles characteristic for continuous casting moulds. The impact of Al_2O_3 *and* CaF_2 *addition was quantified for different slag basicities from the molten state down to 800°C. The start temperature of crystal formation and the evolution of crystal growth are strongly dependent on these additions and can be related to the three-phase diagrams. Both components increase the crystallization tendency and promote crystal formation even in areas of the slag film with very high cooling rates. Nevertheless there are differences in the impact and the crystallization rate.*

Temperature-Time-Transition (TTT) diagrams for various slag compositions were developed for continuous cooling procedure and the effect of cooling rate on crystallization behaviour was investigated. In DHTT mode with given temperature gradient the heat transfer properties of slag depending on the crystallized fraction is shown.

INTRODUCTION

The properties of mould slags largely control the continuous casting process and affect the steel quality. Especially the heat transfer from the strand into the mould depends on the behaviour of mould slags [1, 2, 3, 4, 5]. The formation of crystals in the gap between mould and strand decreases the overall heat transfer rate which can be beneficial for the casting of peritectic steel grades. On the other hand this can be a problem when casting steel grades where bulging is a problem and the strand shell must be very thick. Additionally the increasing trend to high-speed casting demands high heat transfer rates. Also sticker breakouts have been related to a higher crystallized fraction in mould slags which increase viscosity and friction forces [6, 7].

It is commonly accepted that a higher amount of crystalline phases (mould slag with higher crystallization temperature at a given cooling rate) in mould slag film decreases the overall heat transfer rate through the slag layer. This is attributed to the scattering of the heat radiation by the crystal edges as well as the formation of pores and a rough surface on the mould side. The heat radiation is reflected to the strand in spite of being transferred to the mould through glassy layers.

There are some methods to investigate mould slag solidification phenomena like differential thermal analysis or slag casting into moulds and analysis at room temperature. Nevertheless a direct observation of the samples is necessary to understand the formation and transformation of crystals at high temperatures. Additionally the onset of crystallization is a function of the cooling rate which cannot be varied with these methods too much. In most cases the improvement of mould powders is based on experience and viscosity measurements are often the only source of interpretation. The double-hot-thermocouple-technique used in own investigation combines precise experimental conditions with the direct observation of the sample.

As systematic studies on simple slag systems are rare [8, 9, 10, 11, 12], an own investigation of the solidification behaviour of slags from CaO-SiO_2 slags to complex slags with Al_2O_3 and CaF_2 additions has been performed.

EXPERIMENTAL SETUP

An experimental setup for the investigation of slags in molten and solid state was constructed which works according to the double-hot-thermocouple-technique (DHTT) [8]. A schematic view is given in Figure 1. With this technique it is possible to determine accurately and fast temperature-time-transition (TTT) diagrams of slags.

The facility consists of a vacuum chamber with two water-cooled inserts left and right. Both of them hold a thermocouple with 0.5 mm diameter at their tip. The method makes it possible to measure the temperature with a thermocouple while it is heated simultaneously. This is managed by a complex electronic circuit which separates both electronic signals. The power input to heat the thermocouples is controlled by a PID controller independently for left and right side. The temperature signal is used as input for a computer program which manages the control especially the time-dependent temperature course. The temperature measurement is calibrated by measuring the melting point of pure salts as Na_2SO_4, K_2SO_4 and CaF_2. The maximum working temperature of the system is 1700°C. Usually the light emission of the sample and the thermocouples is sufficient to observe the sample down to 900°C. With an additional light source from below transparent samples can be observed down to room temperature. When free cooling is applied it is possible to achieve cooling rates of more than 50 K/s. As real cooling rates in continuous casting are in the range from less than 1 K/s to 100 K/s [13, 14, 15] this methods covers a wide range of industrial situations.

The chamber is filled with inert gas to protect especially non-oxide components like CaF_2 or NaF. The sample size is very small (diameter < 2 mm). Only several mg of slag are needed in order to melt the sample properly and to reduce inhomogeneous composition. On the other hand attention has to be paid to the evaporation of slag components like CaF_2 which can change the composition of small samples very fast.

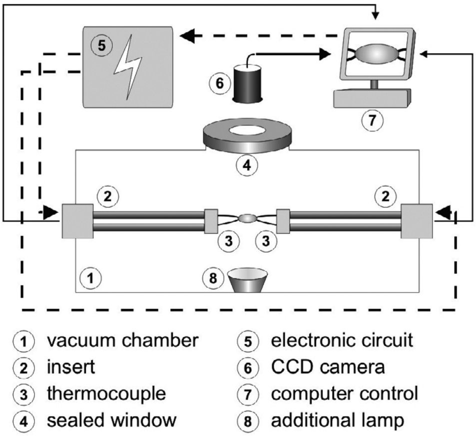

Figure 1: Schematic view of double-hot-thermocouple-technique

There are two experimental modes for this method. The single-hot-thermocouple-technique (SHTT) is mainly used for observation of solidification behaviour of slags without temperature gradients. The sample is placed on one thermocouple tip and heated and cooled at the desired rates. This mode is suitable for fast and reproducible experiments for slags which are to be compared under equal conditions (e.g. continuous cooling and isothermal holding).

The double-hot-thermocouple-technique (DHTT) is used for solidification experiments with given temperature gradients. In this mode the slag sample is placed between the tips of both thermocouples. Both sides can be controlled independently and mould-like temperature gradients or heat peaks can be applied.

In order to directly observe the behaviour of the sample the vacuum chamber has a sealed window on the top. A CCD camera system with a magnifying lens records a video stream during the experiment. A later examination of the experiment is thus easily possible. For an exact analysis of the solidification behaviour of slags with this method a high contrast between liquid (or glassy phase) and crystalline phases is necessary. Fortunately most slags are transparent (except higher amount of FeO and MnO) while the precipitating crystals are opaque. In this way a good distinction between both fractions is possible through image analysis.

EXPERIMENTAL PROCEDURE

The investigated slags (see Table 1) were mixed from pure components, premelted in carbon crucibles and poured into a mould. They were powdered and mixed again. Small portions of powder were pressed to samples which were placed on the thermocouple tips.

After sealing the vacuum chamber, it was evacuated and filled with argon. The thermocouples were heated shortly to maximum temperature and cooled immediately. This created a thin slag layer in the sample which could attach to the thermocouple to fix the sample and ensure a proper temperature measurement. The thermocouple (or both in DHTT mode) was then heated to a temperature 50 K above the theoretical melting temperature according the Slag atlas [16].

The samples were hold at this temperature for 1 min in order to destroy any remaining solids but not longer to limit the loss of volatile CaF_2. After homogenization the sample was cooled at the desired cooling rate (two different cooling rates for DHTT mode) until 800°C.

Table 1: Composition of synthetic mould slags (mass%)

Slag	basicity CaO/SiO_2	CaO	SiO_2	Al_2O_3	CaF_2
CS1	1.0	50.0	50.0		
CS3	1.2	54.5	45.5		
CS5	0.8	45.5	54.5		
CS3_A5	1.2	51.8	43.2	5	
CS3_A10	1.2	49.0	41.0	10	
CS3_F5	1.2	51.8	43.2		5
CS3_F10	1.2	49.0	41.0		10
CS3_F15	1.2	46.3	38.7		15

For a rough characterization of the solidification behaviour of the samples it is sufficient to analyze the video file in normal or slow mode. The temperature of beginning crystallization can be easily detected when first crystals appear. A glassy solidification can only be qualitatively detected by sudden changes in the light diffraction. However as glasses do not have a defined solidification temperature these processes could not always be quantified.

Image analysis was applied to detect the evolution of crystal growth. A software measures the area occupied by crystals which gives the crystallized fraction.

RESULTS AND DISCUSSION

Effect of Basicity on Solidification Behaviour

Three slags (CS1, CS3, CS5) have been prepared for the investigation of the effect of basicity on the solidification behaviour in SHTT mode (see Table 1). They have been selected in order to systematically investigate the slag system of mould slags beginning with basic compositions. The samples have been melted, homogenized and cooled at a constant cooling rate of 10 K/min until 800°C had been reached. As these slags have high melting temperatures (1460 to 1530°C) in some cases longer holding at 50 K above the melting temperature was necessary in order to readily melt the whole sample.

The solidification temperature could not be measured as no opaque crystals formed even at this very low cooling rate. According to the two-phase-diagram first pseudo-wollastonite ($CaO{\cdot}SiO_2$) crystals at temperatures below 1540°C should appear. However in the experimental trials of slags CS1, CS3 and CS5 no crystals were visible. This might be because of the transparent nature of this kind of crystal or limited diffusion processes. A high viscosity at lower temperature limits the diffusion of crystal components to such an extent that it might be too slow to form this kind of crystal.

Effect of Additional Components on Solidifcation Behaviour

Two slags with Al_2O_3 (CS3_A5, CS3_A10) and three slags with CaF_2 (CS3_F5, CS3_F10, CS3_F15) have been prepared for the investigation of the effect of slag additions on the solidification behaviour in SHTT mode (see Table 1). CaF_2 is a slag component which reduces viscosity of a mould slag. Al_2O_3 is a component of usual raw materials used for mould powder preparation. Furthermore its amount increases during continuous casting due to the entrapment of alumina inclusions in the mould slag.

The samples have been melted, homogenized and cooled at a constant cooling rate of 10 K/min until 800°C had been reached. The slags containing CaF_2 have melting temperature between 1400°C and 1500°C, while the slags containing alumina melt at temperatures between 1350 and 1400°C. All samples were heated to temperatures 50 K above their melting points. As these slags tend to have a lower viscosity than the CaO-SiO_{2}- mixtures gas bubbles hardly occurred in the sample. The formation and growth of the crystalline fraction in the slag CS3_A5 is shown in Figure 2. The crystallization started slowly at about 1280°C. With decreasing temperature the rate of crystallization increased especially below 1240°C.

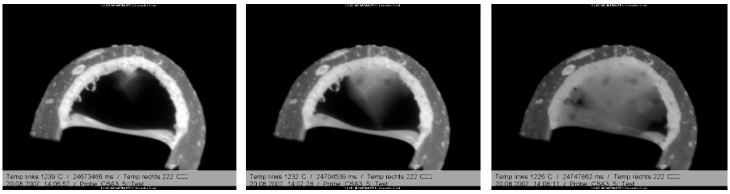

Figure 2: Course of solidification of slag CS3_A5 (left to right: 1239 / 1232 / 1226°C)

The start temperatures of crystallization have been measured and are shown in Figure 3 depending of the amount of CaF2 and alumina additions in the slag.

While the addition of 5 mass% Al_2O_3 to base slag CS3 promoted crystallization and opaque crystals were clearly visible, the addition of 10 mass% decreased the start temperature of crystallization which usually indicates a lower crystallization tendency. Nevertheless both slags (CS3_A5, CS3_A10) crystallized completely at 10 K/min. The reason for this behaviour is not yet completely clear. As no crystals formed in the base slag CS3 it is supposed that the crystals belong to the gehlenite type ($2CaO \cdot SiO_2 \cdot Al_2O_3$ / Tmelt < 1540°C). It seems possible that in the slag CS3_A5 both types of crystals (pseudo-wollastonite and gehlenite) form, while pseudo-wollastonite is the first to appear at higher temperatures. Its composition corresponds to the slag composition except alumina. Gehlenite having another composition might need more undercooling and appears at slightly lower temperatures. The consecutive formation of different crystals has been also found by other researches [17]. In the slag CS3_A10 the alumina content is higher promoting the formation of gehlenite while the formation of pseudo-wollastonite is suppressed. As a result the start of crystallization is at lower temperatures.

The opposite behaviour was detected in slags containing CaF_2. If CaF_2 is added the crystallization starts at higher temperatures which indicates a higher crystallization tendency (see Figure 3). The usual crystal in these slags is cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$ / Tmelt = 1407°C). With higher amount of CaF_2 the slag composition is closer to the crystal composition of cuspidine which facilitates its formation.

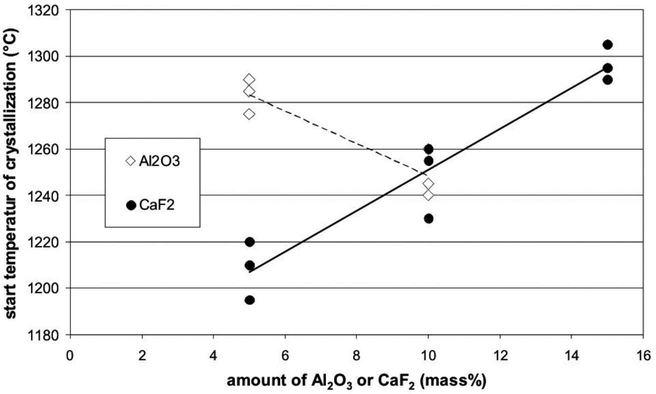

Figure 3: Effect of Al_2O_3 and CaF_2 additions on start temperature of crystallization

Effect of Cooling Rate on Solidifcation Behaviour

Two slags with higher alumina (CS3_A10) and CaF_2 contents (CS3_F10) have been cooled at various cooling rates between 10 K/min and 500 K/min. As a result temperature-time-transition diagrams (TTT) have been constructed which show the evolution of the crystalline fraction with time. The temperatures where 50% and 100% of crystalline fraction appeared were analyzed using image analysis. The results are shown in Figure 4 and 5.

The start temperature decreases with increasing cooling rate in all cases. This is in accordance with typical nucleation and growth from an undercooled melt where each phase formation needs time for necessary diffusion of the components. The same is valid for the temperature of a certain crystallization degree. At high cooling rates (more than 100 K/min) the samples did not crystallize completely down to room temperature as the diffusion was too slow at lower temperatures (lower than 1000°C).

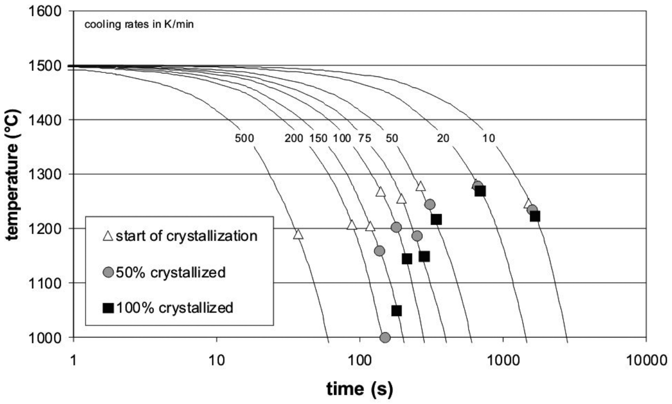

Figure 4: Time-temperature-transition-diagram for mould slag with Al_2O_3 addition (slag CS3_A10)

While the slag with alumina (CS3_A10) tends to form crystals even at 500 K/min, glassy solidification takes place in slag CS3_F10 at cooling rates of more than 200 K/min. The very close composition of CS3_A10 to gehlenite might be the reason for this behaviour. Thus less diffusion transport of slag components is necessary to form gehlenite and the crystal formation takes place even at high cooling rates.

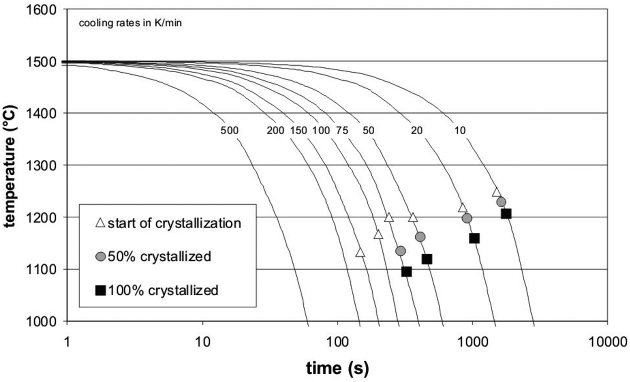

Figure 5: Time-temperature-transition-diagram for mould slag with CaF_2 addition (slag CS3_F10)

Effect of Temperature Gradient on Solidification Behaviour

In order to investigate the solidification behaviour of slag under industrial conditions the DHTT mode was applied for some slags. The cooling regime was adjusted to the conditions in the continuous casting mould. The sample was molten between both thermocouples at 1600°C. After homogenization one thermocouple representing the cold side of the slag film was quenched to 700°C and cooled at 8 K/s to 350°C. This simulates the cold side of the mould slag layer when it is first quenched during mould contact and then continuously cools down. Because of the formation of an air gap the slag does not reach the temperature of the mould hot face. The other thermocouple representing the hot side of the slag film was cooled at 8 K/s down to 1100°C to simulate the continuous cooling of the mould slag in contact to the steel strand. The distance between the thermocouples was about 1 mm. An example is shown in Figure 6.

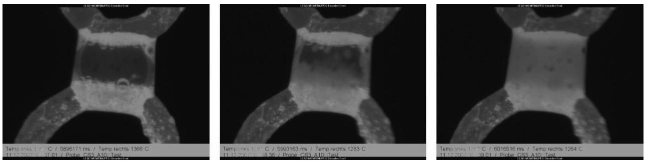

Figure 6: Course of solidification of slag CS3_A10
(left to right: 1360 / 1280 / 1260°C)

The slags start to crystallize at lower temperatures in comparison to the SHTT mode. This is due to the rapid cooling which prevents fast diffusion processes. No visible glassy layer was found on the cold side like it was expected. The crystallization started just at the thermocouple tip of the cold side. A crystallization front grew towards the hot side while a small portion remained liquid (or as glass) until the temperature of the hot side was below about 1300°C.

A slight difference was found when comparing slags with alumina and CaF_2 additions. Slags containing alumina showed a lower crystallization tendency in DHTT mode compared to SHTT mode. The crystal growth was more slowly and often not completed down to room temperature. The reason for this discrepancy is not yet clear. Obviously the higher cooling rates in DHTT mode suppressed sufficient diffusion for the precipitation of gehlenite, while cuspidine precipitated in all experiments.

Heat Transfer through Mould Slags

As heat transfer is strongly dependent on the temperature gradient as well as the heat resistance of the slag film in the mould, additions of Al_2O_3 and CaF_2 have a considerable impact. Experiments were started to measure the heat transfer through slag films using the double-hot-thermocouple-technique which principle is similar to the laser-pulse technique. Previous investigations have shown the applicability of DHTT for the measurement of the thermal diffusivity of B_2O_3 [18, 19]. For this type of experiments both thermocouples are used in DHTT mode and heated to a certain temperature. On one side a temperature pulse of e.g. 100 K is applied while the other thermocouple records the temperature response. This response can be used to evaluate the heat transfer through the slag and to calculate its thermal diffusivity. For this purpose suitable reference values as well as an estimation of the apparatus constant are necessary.

Preliminary experiments with slag CS3_A10 at two different states showed marked differences in heat transfer. In case A the temperature peak was applied immediately after cooling the sample from 1600°C to 1300°C. Under these conditions the sample was glassy at 1300°C and contained less than 20% of crystalline fraction at the end of the temperature rise. In case B the same sample was hold 5 minutes at 1300°C before applying the temperature rise and therefore it was completely crystallized. The temperatures profiles at 1300°C of both cases after a temperature peak rise up to 1500°C on the hot side are shown in Figure 7 for a distance of 1 mm between the thermocouples.

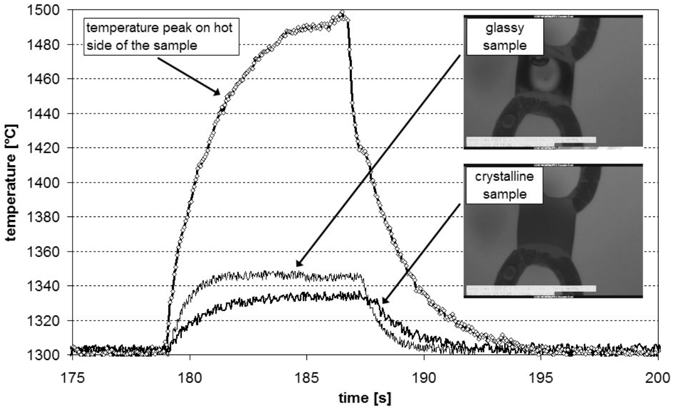

Figure 7: Temperature profile on the cold side at 1300°C after temperature peak to 1500°C on hot side for CS3_A10 (case A: glassy sample, case B: crystalline sample)

It can be seen in Figure 7 that the heat transfer through the fully crystalline sample is retarded and the maximum temperature is lower. Heat radiation is reflected at the crystals edges while in the glassy sample heat radiation and heat conduction are both on a high level. In effect one slag can have quite different thermal diffusivities depending on its thermal history and therefore on the state of crystallization. Actually further experiments are performed to analyze this behaviour.

CONCLUSIONS

Slag mixtures of CaO and SiO_2 with additions of Al_2O_3 and CaF_2 have been investigated. Their solidification behaviour together with a possible formation of a crystalline fraction was analyzed using SHTT mode under different conditions. The basic slags of CaO and

SiO_2 did not show a macroscopic precipitation of crystals. This might be due to the high viscosity of these slags which suppresses diffusion processes which are necessary for crystal formation. Another reason might be the transparent nature of pseudo-wollastonite which makes it hard to detect.

Slags with additions of Al_2O_3 and CaF_2 showed clear visible crystal precipitation. While the start temperature of crystal formation decreases with increasing alumina content, the opposite is valid for CaF_2. With respect to the three-phase diagram by addition of CaF_2 the chemical composition of the slag approaches the composition of cuspidine and its precipitation becomes favourable at higher temperatures. In the case of alumina addition pseudo-wollastonite forms at at higher temperatures followed by gehlenite. With increasing alumina content the precipitation of pseudo-wollastonite can be retarded and gehlenite appears first but at lower temperatures.

TTT-Diagrams of these slags have been developed. The cooling rate has a strong influence on the ability of slags to form crystals, its start temperature and the crystallization rate. Slags were tested at different cooling rates. With increasing cooling rates the start of crystallization is moved to lower temperatures. At very high cooling rates (> 200 K/min) solidification was glassy in most cases or partly crystallized.

Solidification experiments with an applied temperature gradient typical for continuous casting showed a complete crystallization for slags containing CaF_2, while the crystallization tendency of slags with alumina addition was lower. The crystallization proceeded in most cases almost planar from the cold to the hot side of the sample.

DHTT mode was used to investigate the heat transfer through thin slag layers. For this purpose the temperature profile of the cold side thermocouple is recorded after a temperature peak on the hot side thermocouple was applied. Preliminary tests have shown that the same slag can have quite different heat transfer behaviour at the same temperature and only depending on its glassy or crystalline state.

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