New Mold Slag Compositions for the Continuous Casting of Soft Steels

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Several fluorine-free mold slag compositions have already been established in the literature. In all cases, the formation of a crystalline phase exhibiting behavior similar to that of cuspidine is emphasized to control horizontal heat transfer without influencing the lubrication performance for the casting of peritectic steel grades. In contrast, for casting soft steels, glassy solidification of the slag is required. Herein, different slag compositions involving the selected oxides are developed with the help of FactSage calculations. Mixtures of pure raw materials are melted at 1673 K and quenched to 295 K. It is observed that B2O3 increases the glass-forming ability of the slags. To obtain the glassy phase, the composition must satisfy the conditions Al2O3 : SiO2 < 0.9 and (CaO + MgO) < 30 wt%. For TiO2 content <10 wt%, glassy solidification is detected after quenching to room temperature. However, this phenomenon is not observed for slags with TiO2 content >15 wt%. Moreover, the addition of alumina and alkali oxides enhances crystallization. Based on these findings, promising mold slag compositions are designed and characterized in the laboratory using a furnace crystallization test, mineralogical investigations, and the single/double hot thermocouple technique. From the investigated mixtures, three compositions are suggested for use in continuous casting processes.

1. Introduction

Fluorine-containing mold fluxes are used for the continuous casting of steels because of their excellent performance in terms of lubrication and horizontal heat transport. Nevertheless, fluorine contributes to the corrosion of the continuous caster and is regarded as hazardous. Therefore, alternative mold slag compositions must be designed to fulfill the requirements needed for a successful casting process. These mold powders should exhibit low viscosity and control the heat transfer process in the mold.

One substitute for fluorine is TiO2, which is an amphoteric oxide. If added to mold fluxes, [TiO6] octahedral and [TiO4] tetrahedral structures are formed. Whereas [TiO6] octahedra form complex titanium silicate structures and increase the degree of polymerization and viscosity, [TiO4] tetrahedral monomers weaken the slag structure, resulting in a decrease in viscosity. Therefore, the impact on viscosity depends on the dominating effect, which further depends on the basicity of the slag. The addition of TiO2 promotes the formation of crystalline phase perovskite (CaTiO3) and calcium titanium silicate (CaSiTiO5) because of the reduced activation energy of crystallization. Both crystalline phases may contribute to controlling the horizontal heat transfer in the mold. Furthermore, it was observed that the increase in the TiO2 content first resulted in a decrease of the crystallization ability of a CaO–SiO2–B2O3 slag; further TiO2 addition increased the crystallization tendency. In addition to laboratory investigations, plant-scale trials have also been performed. Two fluorine-free mold powder compositions for casting two types of peritectic steel were used. In contrast to the results of Wang et al. promising results, including uniform melting behavior, no sticking, no thick slag rims, a heat flux value close to that of the fluorine-containing mold slag, and no significant surface problems on the slab, were obtained.

The network modifier Na2O may be used as a fluxing agent instead of fluorine and has also been shown to reduce the melting temperature of mold slags. Furthermore, it was found that with the addition of Na2O, the incubation time was reduced and the crystallization tendency increased. Shu et al. investigated the effect of the Na2O content on nonisothermal crystallization kinetics to adjust the crystalline fraction in fluorine-free CaO–Al2O3–SiO2-based mold slags with respect to the continuous casting of peritectic steels. It was shown that an increase in the Na2O content enhanced crystallization due to the depolymerization of the slag structure and decreased the effective activation energy for nonisothermal crystallization.

Another common fluxing agent that acts as a network former is B2O3. Depending on the basicity of the slag, [BO4] tetrahedrons and [BO3] trithedrons are formed. As the B2O3 content is increased, pentaborate groups form, which contribute to stronger networking of the silicate structure. Due to the decrease in the break temperature with the addition of B2O3 to a silicate slag,
the degree of superheating increases, resulting in a lowered viscosity at 1573 K. Simultaneously, the formation of crystalline phases with relatively low melting points, such as CaB2O4, is favored. Furthermore, a lower crystallization tendency of the mold flux is observed. Fourier transform infrared spectroscopy (FTIR) experiments revealed that this phenomenon was caused by a decrease in the liquidus temperature rather than structural changes.[17] Moreover, the effect of basicity on the structure and viscosity of boron-containing slags differs from its effect on F-containing slags. Zhou et al.[22–24] designed mold slag compositions for the casting of medium-carbon steels. They focused on the investigation of the crystallization behavior and compared positions for the casting of medium-carbon steels. They found that these slags show an increased crystallization ability compared to CaO–SiO2-based slags.[19,28] Moreover, the effect of basicity on the structure and viscosity of boron-containing slags differs from its effect on F-containing slags. Zhou et al.[22–24] designed mold slag compositions for the casting of medium-carbon steels. They focused on the investigation of the crystallization behavior and compared it to a conventional F-containing mold flux. It was found that for the F-free mold slags, the crystallization process took longer than in the F-containing mold slag and the crystals that were formed (Ca11Si4B2O22, Ca14Mg2(SiO4)8) were considerably smaller but closer to one another. Nevertheless, these minerals have been suggested to replace cuspidine in mold slags. In addition, the influence of the Na2O content on the crystallization behavior and heat transfer of the boron-containing mold fluxes was investigated. An increase in the Na2O content resulted in an increase in the crystallization temperature and a decrease in the incubation time. The heat transfer decreased at low contents (5–9 wt% Na2O) and increased for higher contents (11 wt% Na2O). This may be explained by the precipitation of different crystalline phases.[25] Industrial trials were conducted for billets and slabs with different slag compositions. In the case of billet casting, no cracks were observed on the product, but more pronounced oscillation marks could be detected.[26] For the casting of low-carbon steel, the F-free mold slag exhibited a similar melting performance, absorption ability for alumina, and slag pool thickness to the F-containing mold slag. The surfaces of the slabs were of good quality.[27]

During the development of mold slags for casting high-Al steels, it was found that these slags show an increased crystallization ability compared to CaO–SiO2-based slags.[19,28] Therefore, another approach to developing fluorine-free mold slags is based on the CaO–Al2O3–B2O3 system.[29] An increase in the B2O3 and Na2O contents resulted in a reduced liquidus temperature and viscosity. In contrast, an increase in the CaO/Al2O3 (C/A) ratio first increases both the liquidus temperature and viscosity, whereas a further increase results in a decrease in both properties.[30]

The casting of soft steels requires slags exhibiting mainly glassy solidification behaviors and providing appreciable steel lubrication. Moreover, these are unlike the slags investigated in previous studies. A viscosity of 0.3 Pa s at 1573 K is required, the liquidus temperature must not exceed 1523 K, and a temperature below 1433 K is favored. In this study, an approach to achieve proper slag compositions that fulfill these requirements is investigated and described. To achieve this objective, thermochemical calculations were conducted to gain suitable slag compositions. These were mixed from pure raw materials, melted, and quenched to investigate their glass-forming ability. If a primarily glassy phase was obtained, it was investigated in the laboratory with respect to its crystallization tendency and viscosity.

2. Experimental Section

2.1. Selection of Proper Slag Compositions

First, based on the characterization of different mold slags, possible oxides for the new slag compositions were selected: Na2O, K2O, CaO, MgO, TiO2, Al2O3, B2O3, SiO2, MnO, and Fe2O3. Calculations were performed using FactSage 7.2 software. In the program Fact-Optimal, different constraints, such as the maximum content of oxides and the range of the CaO/SiO2 ratio, were defined. Using this program, slag compositions with liquidus temperatures below 1473 K were designed. Next, the viscosities of these compositions at 1573 K were calculated using Fact-Viscosity. In the case of extremely high viscosity, the chemical composition was manually modified, such as by increasing the alkali content. Following this, the viscosity and liquidus temperature were calculated for the new slag composition. For any slag that met the requirements, a mixture of pure raw materials was prepared for quenching tests to investigate its glass-forming ability. For this test, each sample was melted in a platinum crucible at 1673 K in a preheated muffle furnace. Afterward, it was quenched to 295 K by pouring it onto a steel plate. Even at this high cooling rate, some of the samples crystallized completely, and these samples were not investigated further. In contrast, many samples showed either total glassy solidification or crystal formation only at the surface (see Figure 1). Based on these results, promising mold slag compositions were selected for further investigation with a focus on viscosity and crystallization behavior. Their compositions are listed in Table 1. The basicity, Bas, and theoretical optical basicity, $\Lambda_{th},$[31] were calculated according to the following equations

\[
\text{Bas} = \frac{N + K + C + M}{A + S + B}
\]

Figure 1. Slag samples after quenching from 1673 K to room temperature on a steel plate: a) sample 2, b) sample 5, and c) sample 4.
**Table 1.** Fluorine-free mold slag compositions.

| Component | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|-----------|----------|----------|----------|----------|----------|
| Na$_2$O   | 12.27    | 11.56    | 12.22    | 13.37    | 14.02    |
| K$_2$O    | 6.21     | 5.86     | 8.46     | 6.77     | 7.09     |
| CaO       | 26.66    | 31.2     | 29.7     | 25.11    | 25.23    |
| MgO       | 2.81     | 3.03     | 3.76     | 3.99     | 4.07     |
| Al$_2$O$_3$| 37.23    | –        | –        | 4.21     | 4.23     |
| SiO$_2$   | –        | 39.33    | 36.98    | 33.12    | 33.27    |
| TiO$_2$   | 8.5      | 9.02     | 9.4      | 11.85    | 12.09    |
| MnO       | –        | –        | –        | 0.78     | –        |
| FeO       | –        | –        | –        | 0.79     | –        |
| B$_2$O$_3$| 6.47     | –        | –        | –        | –        |
| C/S       | 0.72     | 0.79     | 0.79     | 0.76     | 0.76     |
| Bas       | 1.09     | 1.31     | 1.46     | 1.31     | 1.34     |
| Bas$_{rel}$| –        | 1        | 1.12     | 1        | 1.02     |
| $\Lambda_{th}$ | 0.675 | 0.704 | 0.722 | 0.721 | 0.721 |
| $\Lambda_{th,rel}$ | – | 1 | 1.031 | 1.024 | 1.024 |

In Equation (1), $N$, $K$, $C$, $M$, $A$, $S$, and $B$ are the contents of Na$_2$O, K$_2$O, CaO, MgO, Al$_2$O$_3$, SiO$_2$, and B$_2$O$_3$ in wt%, respectively. In Equation (2), $x_i$ is the mole fraction of component $i$, $n$ is the number of oxygen atoms of component $i$, and $A_i$ is the optical basicity of the oxide $i$. In addition, the ratios of these two values with respect to slag 2 are given: Bas$_{rel}$ and $\Lambda_{th,rel}$.

**2.2. Experimental Procedure**

Different setups were used to investigate the crystallization behaviors. The furnace crystallization test (FCT) is a large-scale differential thermal analysis (DTA) that is conducted in a muffle furnace. Two platinum crucibles, one containing the sample and the other corundum, were placed at the center of the furnace. Each crucible contained a type S (Pt/90 wt% Pt–10 wt% Rh) thermocouple, which extended from the furnace through corundum tubes and was connected to a data logger. The temperature in both crucibles and the furnace was recorded every 10 s. Therefore, exothermic or endothermic reactions taking place in the sample may be observed depending on the furnace temperature. The furnace was heated to 1673 K at a rate of 10 K min$^{-1}$ and held at the maximum temperature for homogenization. The furnace was then cooled to room temperature at a rate of 10 K min$^{-1}$. Due to the larger sample size than in standard DTA measurements, the chemical composition of the slag hardly changes during the dwelling time. Furthermore, the surface roughness of the platinum crucible does not influence the detection of the initial crystallization because the temperature is measured at the crucible center. This was confirmed by mineralogical investigations of the samples, which revealed crystal formation in contact with the wall of the crucible, whereas no further crystal growth was observed in the direction of the center. Furthermore, these samples were investigated using a scanning electron microscope that included energy-dispersive X-ray spectroscopy to identify the crystals formed during cooling (Table 2).

In addition, the slags were characterized using the single hot thermocouple technique (SHTT). Using this method, the crystallization behavior at high temperatures and the glass-forming tendency at low temperatures were investigated. Each sample was melted within a Pt-wire loop, stretched to a thin layer, and quenched to a selected temperature below the liquidus temperature. This temperature was maintained until the sample was completely crystallized or no further crystallization could be identified. Afterward, pictures of each sample were evaluated with respect to the crystalline fraction. Based on this evaluation, time–temperature transformation (TTT) diagrams were obtained.

The double hot thermocouple technique (DHTT) enables the observation of crystallization under near-service conditions. In this case, two Pt wires were used: one H-shaped wire for the hot side (1573 K) and one U-shaped for the cold side. At the H-shaped wire, the sample was melted at 1573 K and then stretched to a thin layer with the help of the U-shaped wire, representing the predefined temperature of the cold side (i.e., 873 K). Crystallization was recorded until the total slag film was crystallized or until no further crystallization was detected.

Viscosity measurements were conducted using the high-temperature rheometer FRS 1800 with a concentric cylinder type from Anton Paar. For each measurement, a platinum crucible was filled with 34 g of the quenched sample and transferred to the sample carrier. The sample within the rheometer was heated at a maximum heating rate of 1673 K, and the dwell time was adjusted to achieve homogenization. The rotor was immersed into the liquid slag and the rotation speed was set to 7.21 rpm. Then, the equipment was cooled at 5 K min$^{-1}$. The dependence of viscosity on temperature was recorded every 3 s until the torque value exceeded the measuring range of the device. Afterward, the viscosity curves were compared to the curves of the fluorine-containing mold slags already used for the continuous casting of soft steels.

**3. Results and Discussion**

**3.1. FCT Measurements**

Fluorine-containing mold fluxes used for the continuous casting of soft steels often tend to solidify to some extent in a glassy manner within the FCT crucible, despite the relatively low cooling rate of 10 K min$^{-1}$. This was also observed for some of the slag compositions investigated in this study (see Figure 2). Slag 1 formed two glassy phases: one continuous glassy phase containing crystalline areas, which in turn contained a further residual glassy phase. The sample of slag 2 revealed a significant vitreous fraction after FCT. Small amounts of a glassy phase were also observed in sample 3. In contrast, only crystalline phases were detected in slags 4 and 5.

The replacement of fluorine with TiO$_2$ results in the crystallization of perovskite as either the main or intermediate phase. It is also sometimes accompanied by a titanium-containing phase,
namely, calcium titanium silicate. The formation of further phases is influenced by the amount of oxides present. In particular, MnO and Fe$_2$O$_3$ appear to affect the phase composition even if they are only added in small amounts, as can be observed by comparing slags 4 and 5.

Comparing the exothermal peaks of the FCTs and the respective microscopic investigations, it appears that slags with a resid-

ual glassy phase tend to crystallize more rapidly within a smaller temperature range than those consisting only of crystals (see Figure 3). For slags 1 and 2, both demonstrated a glassy phase during cooling at 10 K min$^{-1}$, and an obvious exothermal peak could be distinguished. This indicates that crystal formation occurs only in a small temperature range. In contrast, for slags showing a marginal or no glassy phase, only small changes in the curves, which represent the temperature difference between the sample and reference, are observed. This indicates continuous crystal formation during cooling.

### 3.2. SHTT and DHTT

With the SHTT, only transparent or translucent slag films can be investigated. Slag 4, which contains small amounts of coloring oxides (MgO, Fe$_2$O$_3$), appeared slightly transparent if the slag film was very thin. Therefore, it could be investigated at temperatures below 1225 K. Conversely, at higher temperatures, light scattering did not allow a precise detection of the crystalline area due to the coloring oxides. In the case of slag 3, crystalline areas consisting of numerous small crystals were formed, and only a few areas showed crystallization on a larger scale. A quantitative evaluation of the slags that form very small single crystals is not possible because the crystalline areas cannot be well defined within the image obtained during the experiment. Furthermore, the start of crystallization cannot be determined because of the small size of the crystals. Nevertheless, at temperatures below 1073 K, no total crystallization of the slag film could be observed within the experimental time of 30 min. A representative picture of this slag at 873 K after a dwell time of 30 min is shown in Figure 4. Here, larger crystals are located at the upper right corner of the slag film, smaller crystals are located near the platinum loop, and the center remains glassy.

The TTT curves representing the start (0.5% crystalline fraction) and end (95% crystalline fraction) of crystallization for the other slags are summarized in Figure 5. For slags 2, 4, and 5, the nose temperatures are located between 1150 and 1200 K for the start and end of crystallization, whereas the nose temperatures of slag 1 are considerably lower due to the B$_2$O$_3$ content. Although this oxide is glass-forming, it also reduces the viscosity of the melt and enables material transport at lower temperatures. In addition, this phenomenon was enhanced by lowering the liquidus temperature.[17–21]

Because of the promising results of the SHTT measurements, wherein the total sample is quenched to defined temperatures, DHTT experiments, which enable the investigation of the crystallization behavior within a defined temperature gradient under near-service conditions, were conducted. Although no quantification of the crystalline fraction could be obtained for slag 5 due to the small crystal size, a rough estimation was possible. As shown in Figure 6, when the sample was in contact with the cold side (873 K), the slag solidified in a glassy manner. During the dwell time, no devitrification of this area was detected. However, the coloring oxides of slag 4 impede the investigation of this slag with the DHTT device. Due to light scattering, which increases from half the distance between the H- and U-shaped wires in the direction of the hot side, the distinction between liquid, crystalline, or possible glassy areas is impossible. Therefore, quantitative results could only be obtained for slags 1–3, as shown in Figure 7.

As shown in Figure 7, the crystallization behavior of these slags within the temperature gradient differs, although some exhibit similar behaviors. Slags 2 and 5 both demonstrate clearly visible glassy solidification in contact with the cold side for a temperature gradient of 1573/873 K. The crystalline fraction first increases in the direction of the hot side and then decreases. In the case of slag 1, the crystalline fraction close to the hot side is explained as follows: Within the slag film, several crystals precipitate and subsequently begin to grow to large sizes of $\approx$100 $\mu$m. In Figure 7b, it can be seen that the crystallization growth rate increases from the start of the experiment to a maximum and then decreases until it approaches zero. Marangoni convection crystals that formed at lower temperatures are transported throughout the area of the slag film where
the liquid phase is present. However, as the residence time at high temperatures is too low to melt these crystals, some amount of the solid phase is also present at temperatures above the melting point of the slag. In contrast, this phenomenon was not observed for slags 3 and 5. For these slags, the crystals are considerably smaller and can therefore be melted immediately on the hot side.

For slag 3, immediate crystallization is observed during the stretching of the slag film to a distance of 3 mm with the help of the U-shaped cold end, enhancing the precipitation of crystals in the melt. This resulted in the formation of a large amount of crystalline slag film at the beginning of the experiment. With increasing dwell time, solids are melted again close to the hot side. This can also be seen in Figure 7b, where the crystal growth rate shows a negative value, which decreases with time. In contrast, slag 2 forms a glassy area close to the cold side. Crystals precipitate within a smaller area and also in smaller
numbers. Thus, only a small liquefaction rate at the beginning is observed, as crystallization continues at the same time at lower temperatures.

### 3.3. Viscosity

In Figure 8, viscosity curves with respect to temperature for all slags, including two fluorine-containing mold slags, at cooling rates of 10 K min⁻¹ are displayed.

Slag 2 does not meet the desired viscosity value of <0.3 Pa s at 1573 K. To decrease the viscosity of this slag, the chemical composition was successfully modified (slag 3). As this decrease in viscosity favors crystallization, the break temperature, $T_{Br}$, is shifted to a higher temperature and the slope of the curve below $T_{Br}$ is drastically increased. This finding agrees with those obtained via the microscopic and DHTT investigations. Slag 1 shows a continuous increase in viscosity as the temperature decreases. Furthermore, the break temperature of this slag is weakly defined. This is related to the large extent of glassy solidification observed in this slag, which is in good agreement with the microscopic investigations of the FCT sample of this slag, as well as with reports from the literature.[17–21]

Figure 8 shows the large differentiation between the viscosity curve progressions for several newly developed slags compared to those of the mold slags. Similarities can only be observed for slags 4 and 5; the chemical compositions of these two slags differed only slightly (see Table 1). Nevertheless, it appears that the addition of only small amounts of Fe₂O₃ and MnO has a significant impact on lowering the viscosity of the resulting slag.

### 4. Conclusion

In this study, more than 50 slags related to the chemical compositions of the slags labeled 1 to 5 were investigated. Based on our observations, the following conclusions can be drawn. For glassy solidification to occur during the quench test, the ratio

Table 2. Phases after FCT.

| Glassy phase | Main crystalline phase | Secondary phases |
|--------------|------------------------|------------------|
| Sample 1    | +++ Calcium titanium silicate ($Ca_2(Si,Ti)SiO_6$) | Perovskite ($CaTiO_3$), combeite ($Na_2Ca_2Si_4O_9$) |
| Sample 2    | ++ Calcium titanium oxide ($CaTiO_3$) | Bredigite ($Ca_2Mg_2(SiO_4)_3$), combeite ($Na_2Ca_2Si_4O_9$), $Ca_2TiSiO_6$ |
| Sample 3    | + $Ca_2SiO_3$, bredigite $Ca_2Mg_2(SiO_4)_3$ | Sodium calcium silicate, perovskite ($CaTiO_3$) |
| Sample 4    | – Perovskite ($CaTiO_3$), $Ca_2SiO_3$ | Sodium titanium oxide ($Na_2TiO_3$), combeite ($Na_2Ca_2Si_4O_9$), kalsilite ($KAiSiO_4$), sanidine ($K(Na)Si_4Al_2O_8$), merwinite ($Ca_2Mg_2(SiO_4)_3$), potassium magnesium silicate ($K_2MgSiO_4$) |
| Sample 5    | – $Ca_2SiO_3$, Perovskite ($CaTiO_3$) | Combeite ($Na_2Ca_2Si_4O_9$), kalsilite ($KAiSiO_4$), sodium titanium oxide ($Na_2TiO_3$) |
must be lower than 0.9. At the same time, the slag must contain a sum of CaO + MgO below 30 wt%; only if the slag contains no Al2O3 it may be slightly higher. In all cases, the addition of even small amounts of B2O3, which acts as a glass former, increased the glass-forming ability of the slag. The addition of alumina to a slag requires the simultaneous increase of the alkali oxides to receive the desired liquidus temperature and viscosity at 1573 K. This results in an increasing crystallization tendency during quenching. This is also reported by and viscosity at 1573 K. This results in an increasing crystallization tendency during quenching. This is also reported by

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Conflict of Interest

The author declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

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