In situ observations and thermal analysis of Crystallization phenomenon in mold Slags

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Abstract

During continuous casting the crystallization behavior of a mold slag has decisive effects on the lubrication and heat transfer between mold wall and steel strand. By the means of the Double Hot Thermocouple Technique the crystallization kinetics of a mold slag could be studied in details for a wide temperature range. TTT and CCT diagrams have been obtained and the crystal morphology has been determined at different undercoolings or cooling rates. The crystalline phase has been determined using X-ray diffraction. Experiments with the presence of water vapor in the atmosphere were also conducted. The presence of water vapor increased the nucleation rate and crystal growth rate significantly when compared to experiments carried out in a dry atmosphere. Precipitation of solid crystals also occurred at a temperature above the equilibrium liquidus temperature (1260^{o}C) that is measured in a dry atmosphere. These results suggest that there is significant interaction between water vapor and liquid slags at high temperatures and that the phase diagram for these slags is very sensitive to the equilibrium partial pressure of water vapor in the surrounding atmosphere.

Keywords: *Continuous Casting, Mold Slags, Crystallization, and Double hot thermocouple, Differential-Thermal-Analysis*

1. Introduction

A fundamental understanding of the crystallization of slags under various thermal conditions is important for many steelmaking processes. In the continuous casting of steel, mold powder is added continuously to the top of the mold where it melts to a liquid slag. The slag is then subsequently withdrawn in the gap between the mold wall and the solidifying steel strand working as a medium for both lubrication and heat transfer. The slag film closest to the mold, which experiences the highest cooling rate freezes initially to a glassy layer whereas the slag film next to the strand remains liquid. Between these two layers crystals will precipitate. The presence of crystals has decisive effects on both the lubrication and the heat transfer between the mold and strand.

It is well known from classical nucleation theory that the onset of the formation of solid crystals in slags must be a function of cooling rate and that to determine the true crystallization behavior of a slag isothermal time temperature transformation diagrams (TTT curves) or continuous cooling transformation diagrams (CCT curves) must be constructed. The crystallization kinetics of a slag is determined by the kinetics of nucleation and growth.

Industrial observations have suggested that increased moisture content of mold powders can cause increase friction between mold wall and in some cases a dramatic increase in breakout frequency. There have been few studies on the effect of atmospheric conditions on the crystallization behavior of mold slags[1]. This paper will document the results of a series of experiments carried out in dry and humid atmospheres to test the sensitivity of slag crystallization behavior to the water content of the surrounding atmosphere.

2. Experimental

Ordway[2] and Welch et al[3] successfully developed the concept of the singe hot thermocouple technique dates back to the end of the nineteenth century and the hot thermocouple technique itself in the 1950's. The progress of electronic development has made the hot thermocouple method easier and more reliable to apply. In this study the Double Hot Thermocouple Technique (DHTT) developed by Kashiwaya et al[3] was employed. In the DHTT the sample is placed between two hot thermocouples where the sample stays due to capillary forces. An illustration of the DHTT can be seen in figure 1.

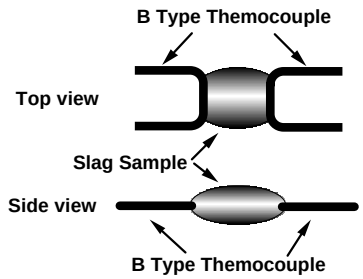

Figure 1. Illustration of the Double Hot Thermocouple Technique.

Due to the low mass of the system (sample and thermocouple), high heating and cooling rates can be easily obtained, which is very useful for determination of TTT diagrams where fast cooling rates are required. The experimental apparatus of the double hot thermocouple technique consists of an observation system and a thermocouple system. The observation system includes a microscope with 3CCD (Charge Couple Device) color video camera connected to a VCR (videocassette Recorder) to which the experiments are recorded. The thermocouple system includes the two thermocouples located in a reaction tube below the microscope and the sample is placed between the thermocouples. Each thermocouple is connected to a separate thermocouple controller. The thermocouple controller is a unique system to enable simultaneous measurement of temperature while heating a thermocouple. A computer controls two thermocouple enabling individual controls of temperature, heating and cooling rates of the thermocouples. The computer uses a Proportional and Integral (PI) Control program. The temperature measurement of the hot thermocouples was corrected by calibration with pure CaF_2, a material with a distinct melting point at 1418°C as described by Kashiwaya et al[4]. Figure 2 shows the setup of the experimental apparatus.

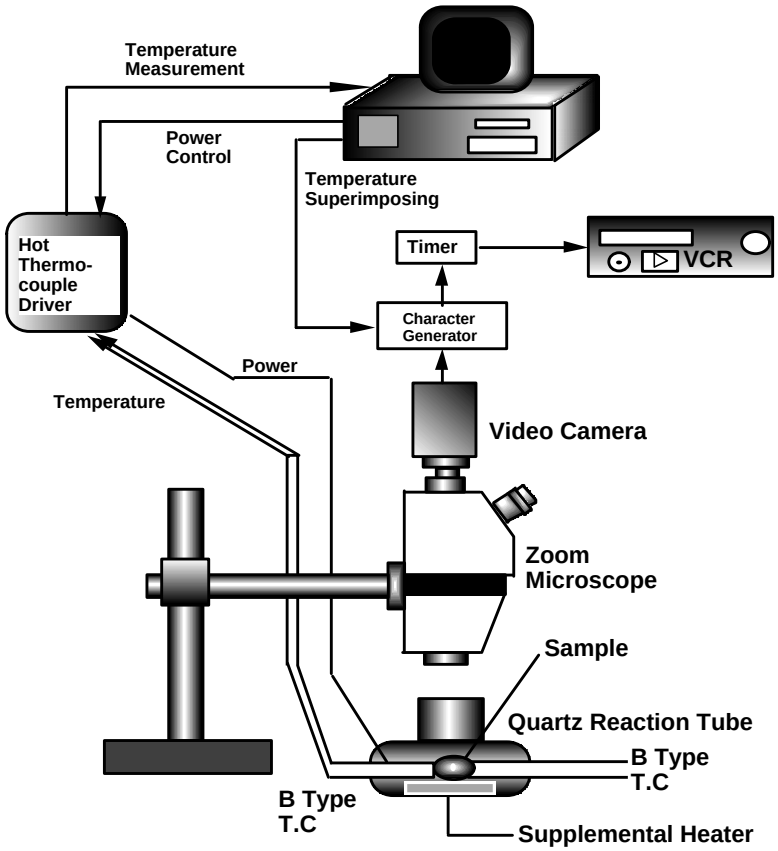

Figure. 2. Experimental apparatus of the SHTT/DHTT.

The water vapor was generated by flowing argon through hot water and subsequently through a condensation spiral tube, which was surrounded by constant temperature water. The spiral tube enabled excess water vapor absorbed in carrier gas to be eliminated by

condensation and allows the humidity of the gas to be accurately set and varied. Adjustment of the temperature of both the hot water and of the circulating water in the condensation spiral made it possible to control water content in gas phase. When the difference between the temperature of hot water and that in the condensation tube was less than 30°C, the desired water vapor partial pressure in equilibrium with the temperature of the condensation spiral was achieved for a flow rate range from 30 to 140 ml/min.

The slag sample was prepared by mixing individual pure oxides, which were then prefused in a platinum crucible and subsequently ground into fine powders.

3. Results and Discussion

Isothermal experiments, continuous cooling and differential continuous cooling (DCCT) experiments were performed for the sample with the composition shown in table 1. The DCCT is a novel technique based on the DHTT where one side of the thermocouple is initially quenched to a relatively low temperature (<700°C) at a high rate, 350°C/s while the other is cooled at a constant rate (1-15°C/s). A representative temperature profile for DCCT experiment can be seen in figure 3.

Table 1. Sample composition

Sample	Wt% CaO	Wt% SiO_2	Wt% Al_2O_3	Wt% Na_2O	Wt% CaF_2
	39.58	40.94	6.94	9.57	1.00

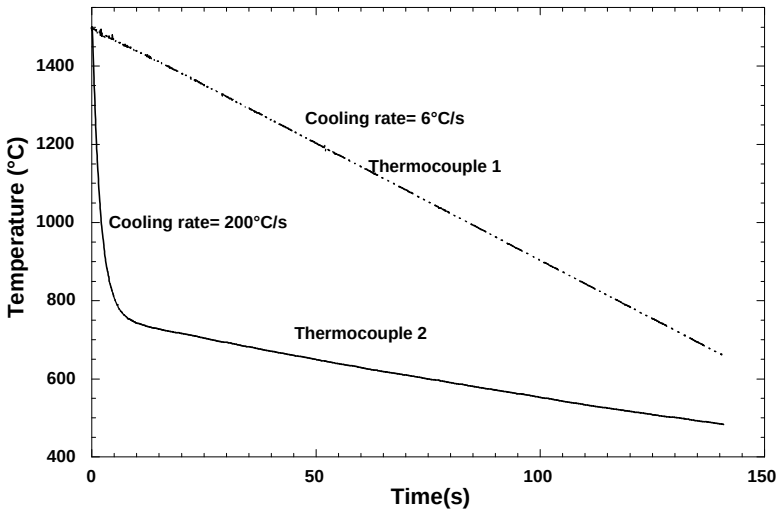

Figure 5. Temperature profile of differential continuous cooling experiment.

3.1 Isothermal Experiments

The isothermal experiments were carried out in a temperature range of 1260°C and 800°C. The time for the beginning of crystallization is defined as the time when the first crystal can be observed in the sample. The resolution of camera lens system allows observation down to approximately 0.5% crystalline fraction in the sample. Melting experiments were performed with a low heating rate to determine the solid and liquid temperature. It was found that the sample started to melt at 1160°C and became completely liquid at 1260°C. From this result it was concluded that a two-phase region exists between 1260-1160°C. Figure 4 shows the TTT-diagram for the onset of crystallization for the studied slag sample.

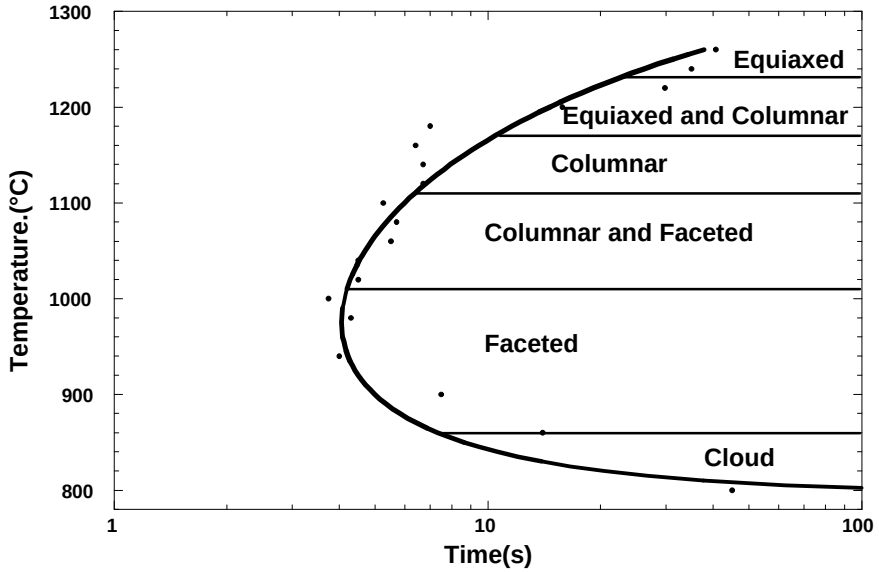

Figure 4. TTT diagram of the studied slag sample for the onset of crystallization.

The beginning of crystallization at different temperatures forms a classic single C-shaped curve as predicted by classical nucleation theory with a nose position at 1000°C. The time for the beginning of crystallization is generally short (4-7 s) between 1180-940°C. The obtained TTT diagram was compared with a TTT diagrams for a lower content of Na_2O and no CaF_2 obtained by Kashiwaya et al[5] and the comparison can be seen in figure 5. Increasing the content of Na_2O and adding CaF_2 increases the crystallization. The quantified comparison of TTT curves for different slag composition is a useful tool for design of mold slags with a predictable crystallization behavior.

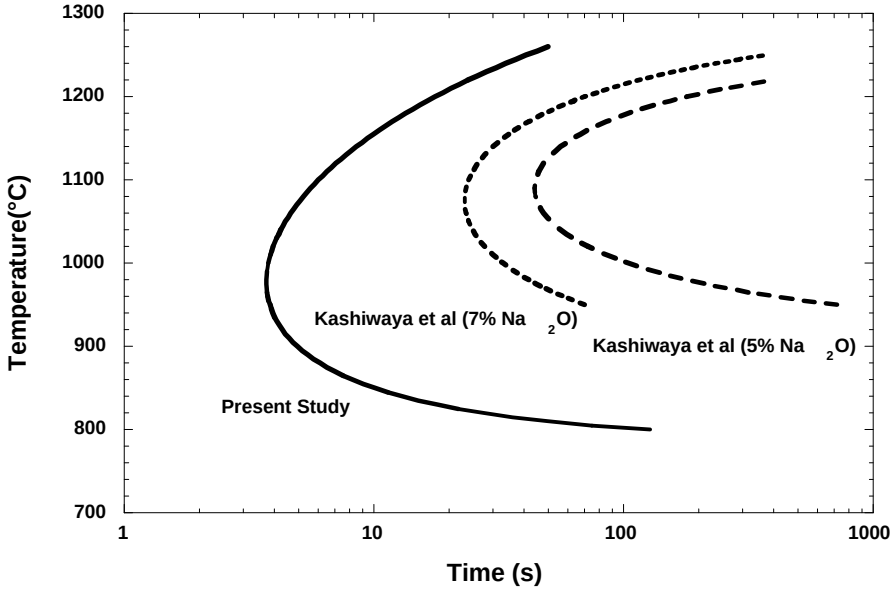

Figure 5. Comparison between TTT curves for different content of Na_2O and CaF_2 for the beginning of crystallization.

Depending upon the degree of undercooling at which the experiment was performed at, the precipitated crystals exhibit different morphologies. The crystal morphology follows the same pattern as in a previous study[5]. The morphologies has been classified into four different types:

1. Equiaxed crystals observed at higher temperature.

2. Columnar crystals that grow from each thermocouple towards the center of the sample.

3. Dendritic crystals with a macroscopically faceted shape precipitating across the whole sample

4. Extremely fine crystals appearing as cloud at high undercooling.

Details of the types of morphology and their occurrence on the TTT diagram is given in figure 4.

3.2 Continuous Cooling Experiments

A number of continuous cooling experiments were performed for various cooling rates in order to obtain a CCT diagram. The time and temperature for the beginning of

crystallization was determined when the first crystal could be observed and the result can be seen in figure 6.

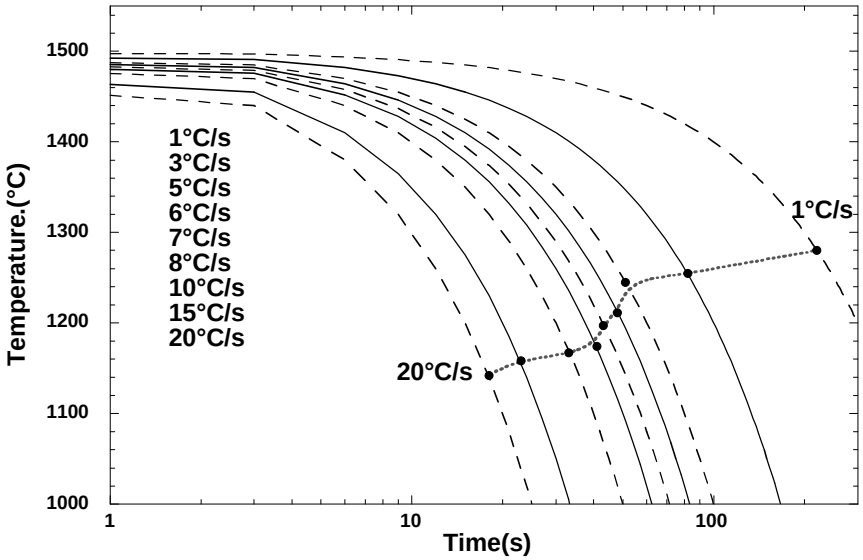

Figure 6. CCT diagram of the studied slag sample for beginning of crystallization.

With increasing cooling rate the time and temperature for the beginning of crystallization decreases. There is a drop of the curve between 5°C/s and 8°C/s. For cooling rates above 20°C/s no crystallization could be detected. A comparison between the TTT curve and the CCT curve is shown in figure 7. The onset of crystallization occurs at a longer time for the continuous cooling experiments than for the isothermal experiments. When the cooling curve reaches the TTT curve for beginning of crystallization the nucleation is low and further time (and therefore cooling) will be necessary before the first crystal can be observed. The morphology of the precipitated crystals follows the pattern developed from isothermal experiments. However as the temperature is transient, the predominant morphology is strongly dependent on the cooling rate. The first crystals to be observed for the 20°C/s experiment are columnar as predicted by the isothermal experiment but as the temperature decreases the predominate structure is of the cloud like type.

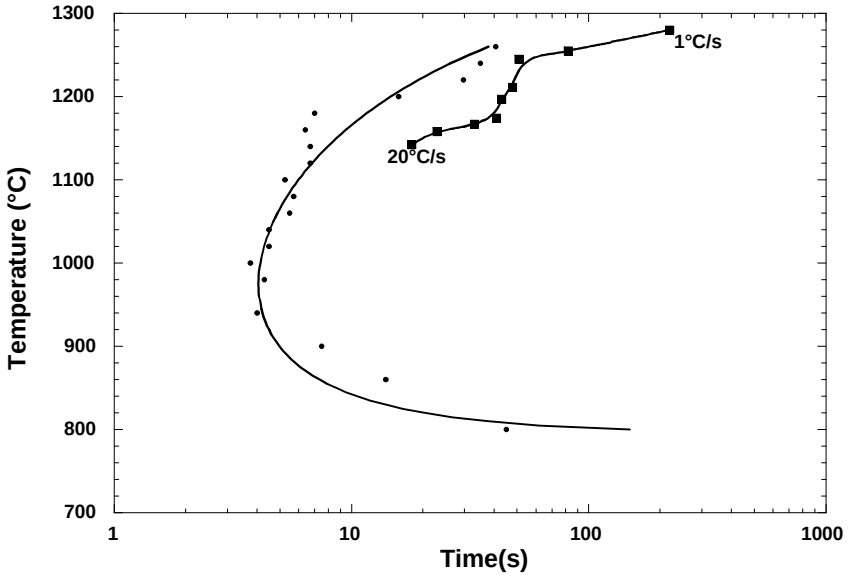

Figure 7. Comparison between TTT curve and CCT.

It is obvious that the temperature dependency of the precipitated morphology follows a certain pattern. If the crystal morphology of solid slag samples can be determined, it is therefore possible to predict the prevailing thermal field in the liquid slag during the crystallization.

3.3 Differential Continuous Cooling Experiments

The effect of cooling rate on the crystallization of a mold slag during continuous cooling with a thermal gradient has been studied. The time for the beginning of the crystallization was almost the same for all experiments, ~10 s. The first crystals to precipitate are very small (cloud), and as the cooling continues, faceted columnar and equiaxed crystals appears also in the sample. A schematic representation of the positions for different crystal morphologies can be seen in figure 8. The morphology of the crystals makes it possible to estimate the degree of undercooling for different regions in the sample. The amount and appearance of the crystalline fraction is very dependent on the cooling rate. Experimental images of samples with different cooling rates can be seen in figure 9. For a 1°C/s cooling rate the crystallization begins as very fine crystals after approximately 10 s for both samples and as the temperature of the hot side decreases both faceted, columnar and equiaxed crystals are formed. Some of the equiaxed crystals are transported to the hot side by fluid flow where they dissolve while the temperature of the hot side is above the melting point. The crystalline fraction forms a dense structure and grows towards the hot side as a front (fig.9). As the crystallization proceeds the composition of the remaining liquid changes due to rejection of solute. A liquid slag layer of at least 0.1 mm thickness

remains down to 1000°C. If the composition of the liquid layer would be the same as the original slag composition it would be fully solidified according to the TTT diagram in figure 4. To ensure lubrication through the full length of the mold, the understanding of segregation during the crystallization might indeed be a key issue when choosing mold slag composition. With increasing cooling rate (3°C/s) and 6°C/s) not all of the equiaxed crystals are dissolved at the hot side due to faster decrease in temperature of the hot side. The crystalline fraction appears more fragmented and liquid/glassy pockets can be formed in the crystalline structure (fig.9). With a high cooling rate (9°C/s) the crystal growth rate decreases fast and the crystals appears as a small fraction of fine and faceted crystals (fig.16).

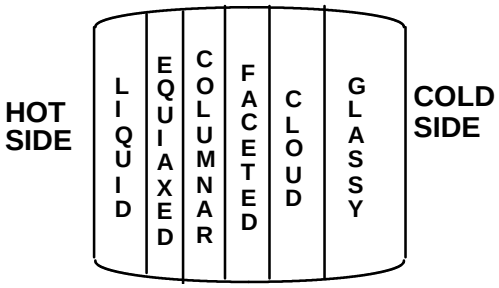

Figure 8. Schematic representation of the layers in the sample.

The amount of crystalline area fraction as function of time has been measured for different cooling rates of the hot side and the results are shown in figure 10. The maximum amount of crystalline fraction decreases with increasing cooling rate. In this case, when going from 1°C/s to 15°C/s cooling rate the maximum area fraction of crystals decreases from 70% to 10%.

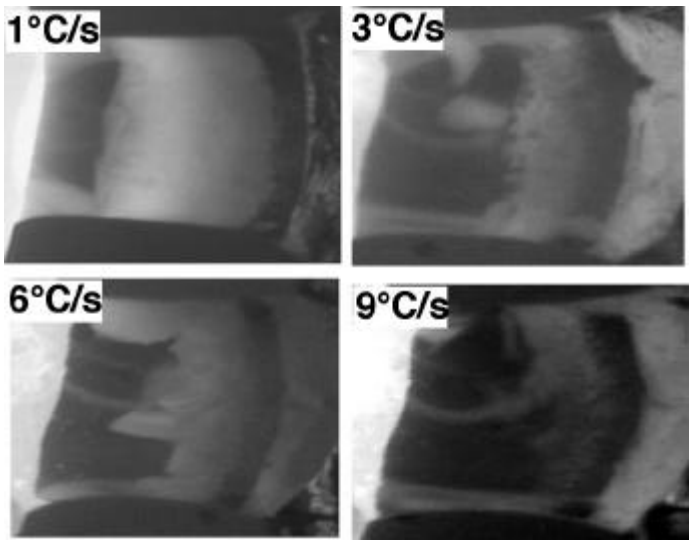

Figure 9. Experimental images for different cooling rates of the hot side (left hand side) taken at 60s after experiment start. The transparent phase close to the right hand side is glassy, the gray phase is crystalline and the to the left side remaining liquid.

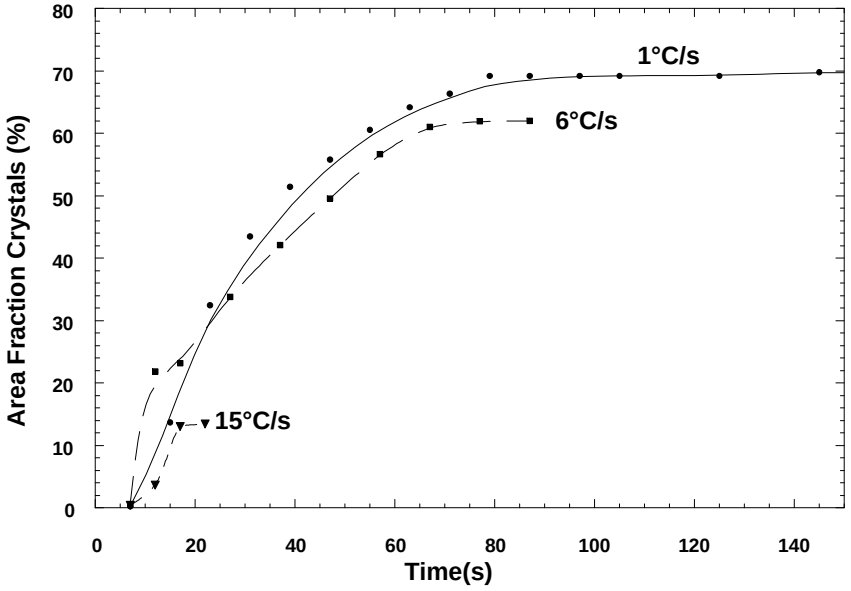

Figure 10. Crystalline fraction as a function of time for different cooling rates.

3.4 X-ray Diffraction

X-ray diffraction experiments have been performed on quenched samples from the isothermal experiments in order to determine the crystalline. The samples were quenched from a number of different temperatures. The dominant phase was found to be β-Ca_2SiO_4 (Larnite). The compositional difference between the precipitated crystalline phase and the liquid supports the theory that diffusion of the rejected solutes controls the crystal growth.

3.5 The effect of water vapor on mold slag crystallization

Previous studies[7-11] in glass forming systems indicates that there is an atmospheric effect on nucleation and growth phenomena within liquid silicates. As most industrial mold slags are based upon the calcium silicate system and are strong glass formers it was decided to test these slags to determine the effect of a humid environment on the crystallization behavior of these slags.

An attempt was made to determine the TTT curve in a humid atmosphere containing a partial pressure of water vapor of 0.054 atm. A partial pressure of 0.054 atm equals 100% humidity at 25°C. Isothermal experimentation was attempted over the same temperature range as in the dry atmosphere experiments; however, the onset of precipitation was observed within 1 second of the initiation of the experiment. Thus, the technique was only able to define crystallization start times at 1200,1180 and 1160°C. At lower

temperatures the onset of crystallization occurred during quenching even when the quench rate was increased to 350°C/s. The results for the humid atmosphere trials are shown in Figure 11 where it can be seen that the onset of precipitation in a humid atmosphere occurs in a significantly shorter time (1 second compared to 10 seconds) at 1200°C. Also the critical cooling rate for glass formation was 20°C/s in a dry atmosphere (fig. 6) and greater than 350°C/s in the humid atmosphere.

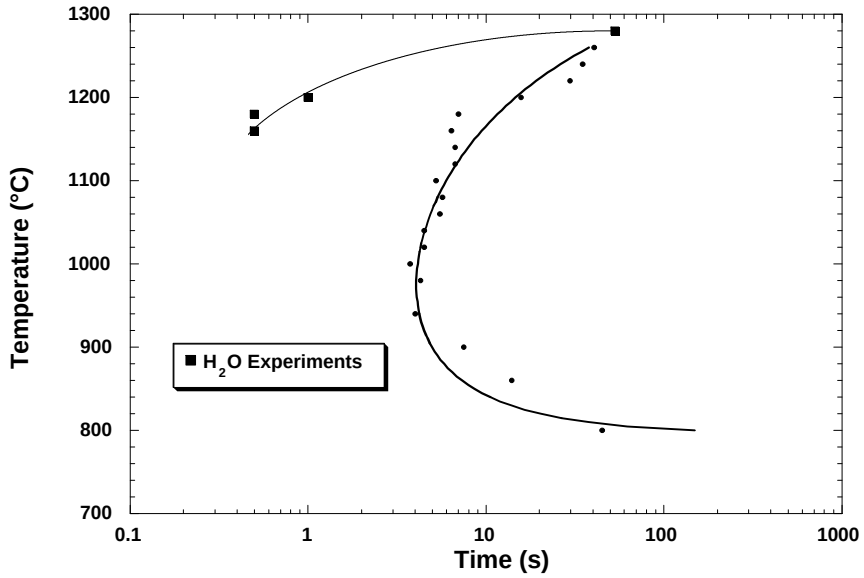

Figure 11. Comparison between isothermal experiments with and without water vapor

A second set of experiments was performed at 1280°C, which is 20°C above the measured liquidus temperature for the slag in a dry atmosphere. The water vapor was introduced 30 seconds before the beginning of the experiment and was also turned off and on during the experiments. After 53 seconds at 1280°C, crystallization occurred and the precipitated crystals covered the whole sample within a few seconds. The observed crystal growth rate was measured for both dry and humid atmospheres and results are given in figure 12. The crystal growth rate in a dry atmosphere at 1260°C was 3.5 μm/sec and 21.6 μm/sec at 1280°C in the humid atmosphere. In addition to a faster growth rate, the crystal density also significantly increased in the case of a humid atmosphere (figure 13). For example within 10 seconds there were 8000 observed precipitation sites per cm^3 in the humid atmosphere at 1280°C compared to 0 at the same time and temperature in the dry atmosphere experiments. At 1260°C in the dry atmosphere, where precipitation occurred, the crystal density after 10 seconds was only 500/cm^3 indicating that the evolution of sites for crystal growth is considerably slower in the case of the dry atmosphere. Thus, the presence of water vapor increases the crystal density and the crystal growth rate.

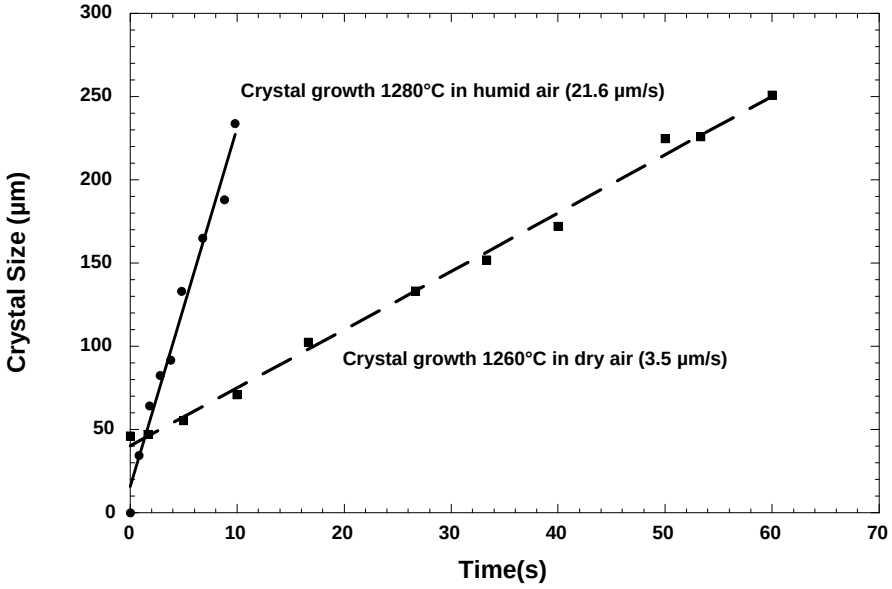

Figure 12. Comparison between crystal growth in humid and dry air.

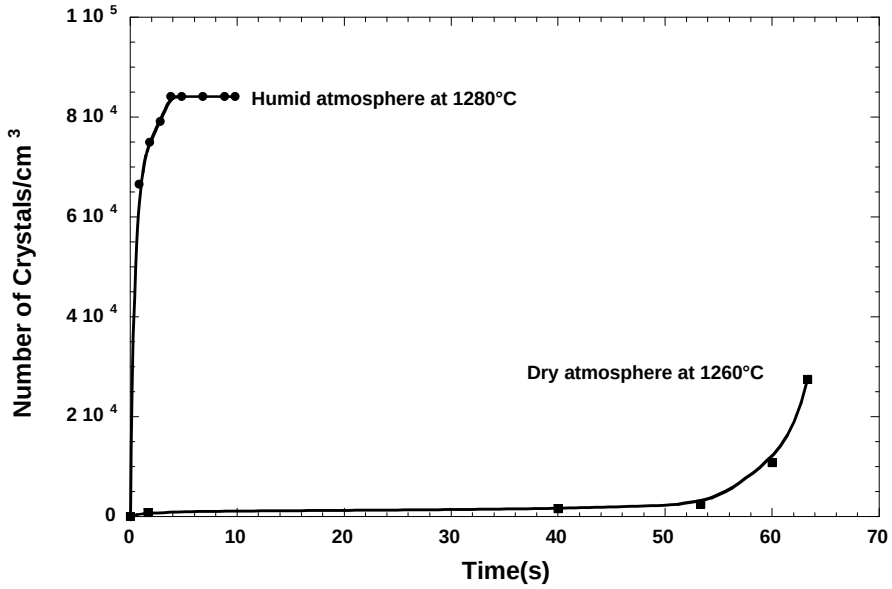

Figure 13: Evolution of crystal density with time.

Photographs of the second experiment are shown in Figure 14 where the onset of crystallization and subsequent crystal growth is shown. The water vapor was turned off after 150 s and the reaction tube was flushed with dry air. After the water vapor was

turned off the crystalline phase started to dissolve and the sample turned fully liquid again. This suggests that the crystalline phase was unstable without the presence of the water vapor in the atmosphere. The presence of water vapor caused not only an increase in the nucleation and crystal growth rate but also an expanded region of thermal stability of the crystal phase. After dissolution of the crystal, bubbles precipitated in the sample at the thermocouples and escaped from the sample (figure 14). After 650s the water vapor was turned on again; however, no further crystallization occurred. The water vapor was again turned off after 1050s and bubbles could again be seen forming in the sample. This result suggests that the slag chemistry is changed due to the interaction of the water vapor with slag. A probable cause is the loss of fluorine and sodium from the sample due to enhanced vaporization of NaF from the sample due to the presence of water vapor in the atmosphere[12].

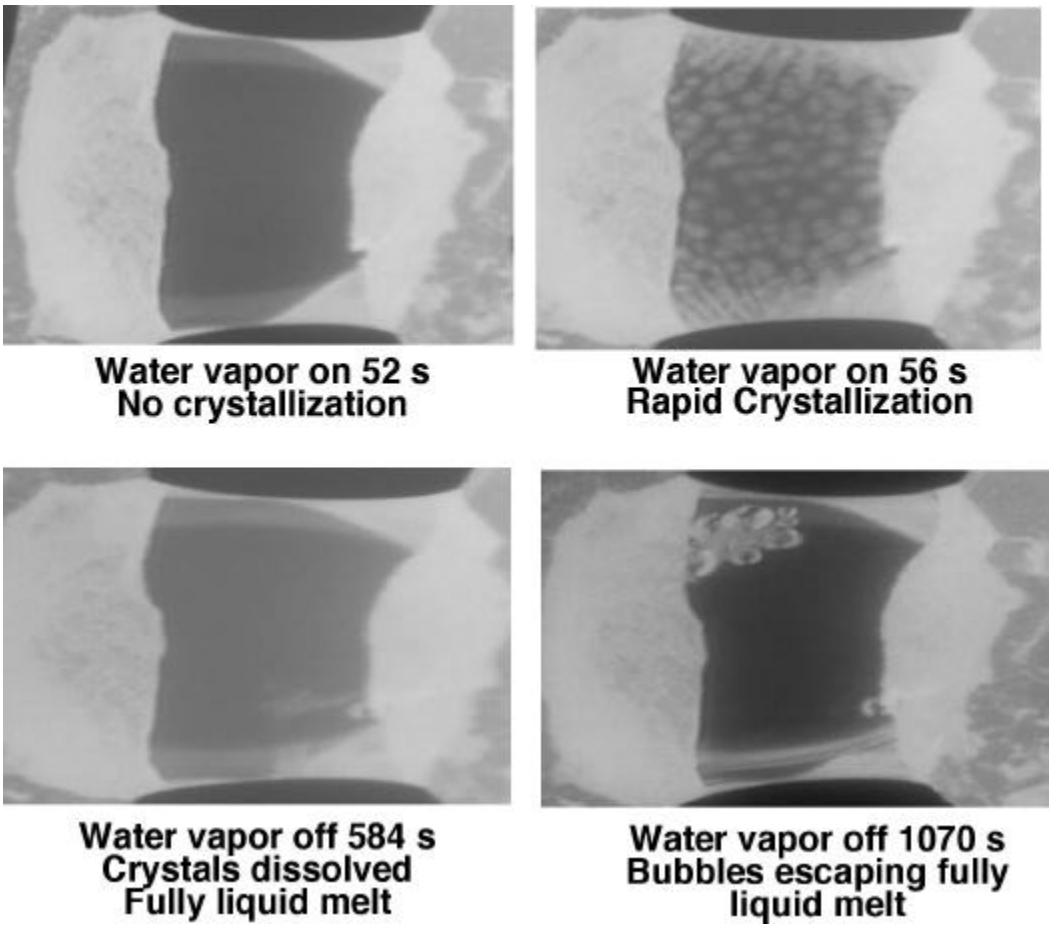

Figure 14. Experimental images from water vapor experiment at 1280°C. The time is from the beginning of the experiment.

The measurement of crystallization in humid atmospheres at temperatures above the liquidus temperature suggests that the liquidus temperature in this system is a function of humidity. The reversible nature of precipitation (the dissolution of the crystals when a dry atmosphere is reinstated) also suggests that the phase diagram for this system is a function of the water vapor partial pressure in the atmosphere. The fact that

crystallization and nucleation rate increased in the presence of water vapor also suggests that there is a structural modification to the melt in the presence of water vapor. Thus it is important to quantify the humidity of the atmosphere when measuring the crystallization behavior of liquid slags.

4. Conclusions

For a range of undercoolings between 0-460°C was the crystallization phenomena of a mold slag studied under a wide range of thermal conditions in both dry and humid atmosphere. TTT and CCT curves were obtained which proves that slag crystallization is a transient phenomenon. Depending on the degree of undercooling different crystal morphologies were precipitated. The amount of crystalline fraction depends greatly on the cooling rate. Increasing cooling rate drastically reduces the crystalline fraction. Nucleation rate and crystal growth rate increased significantly in the presence of water vapor. Crystallization occurred above the determined liquidus temperature for the system in a dry atmosphere, suggesting that the interaction of water vapor with the slag changed the position of the liquidus. The stability of the crystalline phase in humid atmospheres was directly related to the presence of water vapor in the atmosphere

4. Acknowledgment

The authors would like to thank the member companies of the Center of Iron and Steel Research for their support.

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