FLUORINE-FREE MOULD SLAGS FOR SLAB CASTING: EFFECT OF Na_2O ON THE CRYSTALLISATION BEHAVIOUR OF THE CaO-SiO_2-TiO_2 SLAG SYSTEM[1]

Jeferson Leandro Klug[2]
René Hagemann[3]
Nestor Cezar Heck[4]
Antônio Cezar Faria Vilela[5]
Piotr R. Scheller[6]

Abstract

The elimination of fluorine from slags is necessary because F-bearing materials pollute the environment and cause machinery corrosion at steelworks. Regarding the development of F-free mould slags for slab casting, the main problem is how to control the heat transfer between steel shell and mould. In commercial products the heat transfer control is obtained through the crystallisation of cuspidine ($3CaO.2SiO_2.CaF_2$) from mould slag. Thus, the fluorine-free slag which would be used as the substitute must show similar crystallisation behaviour. The present paper show results of a cooperation work between Technische Universität Bergakademie Freiberg and Universidade Federal do Rio Grande do Sul. Ti-bearing slags were studied through the Single Hot Thermocouple Technique, building time-temperature-transformation (TTT) diagrams. The results indicate that the system CaO-SiO_2-TiO_2-Na_2O can be used as substitute for F-bearing slags, regarding crystallisation behaviour, since the incubation times at TTT diagram can be similar to commercial products. This is possible because addition of Na_2O shorten intensely the crystals incubation times from the CaO-SiO_2-TiO_2 slag system.

Keywords: Fluorine free slags; Hot thermocouple technique; Mould slags; Slab casting.

PÓS FLUXANTES SEM FLÚOR PARA O LINGOTAMENTO DE PLACAS: EFEITO DE Na_2O NO COMPORTAMENTO DE CRISTALIZAÇÃO DO SISTEMA DE ESCÓRIAS CaO-SiO_2-TiO_2

Resumo

A eliminação de flúor de escórias de molde é necessária porque materiais que contêm flúor poluem o meio ambiente e causam corrosão na máquina de lingotamento contínuo. Considerando o desenvolvimento de pós fluxantes sem flúor para o lingotamento de placas, o principal problema é como controlar a transferência de calor entre a casca sólida em formação e o molde. Em produtos comerciais o controle da transferência de calor é obtido através da cristalização da fase cuspidina ($3CaO.2SiO_2.CaF_2$) da escória de molde. Assim, a escória de molde sem flúor que seria utilizada para substituir o produto comercial deve ter similar comportamento de cristalização. O presente artigo mostra resultados de um trabalho de cooperação entre a Technische Universität Bergakademie Freiberg e a Universidade Federal do Rio Grande do Sul. Escórias produzidas em laboratório contendo titânio foram estudadas através da técnica *Single Hot Thermocouple Technique*, construindo diagramas TTT. Os resultados indicam que o sistema CaO-SiO_2-TiO_2-Na_2O é um potencial substituto de escórias de molde que contêm flúor, considerando o comportamento de cristalização, pois os tempos de incubação nos diagramas TTT podem ser similares aos produtos comerciais. Isso é possível porque adicionar Na_2O ao sistema CaO-SiO_2-TiO_2 diminui drasticamente os tempos de incubação dos cristais.

Palavras-chave: Escórias sem flúor; Hot thermocouple technique; Pós fluxantes; Lingotamento de placas.

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[2] *Doctoral student, MSc., Met. Eng., PPGEM/UFRGS, klug@ufrgs.br (corresponding author)*

[3] *Doctoral student, Dipl.-Ing., Institut of Iron and Steel Technology / TU Bergakademie Freiberg*

[4] *Prof. Dr.-Ing., PPGEM/UFRGS, Núcleo de Termodinâmica Computacional para a Metalurgia*

[5] *Prof. Dr.-Ing., PPGEM/UFRGS, Laboratório de Siderurgia*

[6] *Univ. Prof. Dr.-Ing. habil. , Institut of Iron and Steel Technology / TU Bergakademie Freiberg*

1 INTRODUCTION

Mould powders or mould fluxes are synthetic slags which should fulfil different functions during continuous casting of steel,(1) as (i) protect the steel meniscus from oxidation, (ii) absorb inclusions floating up from the steel, (iii) provide thermal insulation to prevent the steel from freezing, (iv) provide the optimum level of horizontal heat transfer between shell and mould and (v) provide lubrication of the steel shell. The mould slag i.e. the mould powder which was melted in the mould during continuous casting is one of the most important slags in the melting shop.

The choice of the mould powder for slab casting is a difficult task because of the complicated nature of the powder composition, and because the mould powder has many important functions. Due to the complex requirements in the industrial process the choice is based on recommendations from manufacturers and trials in the caster, followed by investigations on the quality of the slabs. Normally in the melting shop different compositions – with reasonably small differences – are tested to get good results.(1,2)

The presence of crystals has a decisive effect on both the lubrication and the heat transfer between the mould and the steel strand. The crystallisation behaviour of the mould slag depends on the thermal conditions between mould wall and strand and the slag composition.(3) When a layer is formed directly on the mould surface either at the beginning of the casting or later on, it will form at first in a glassy state. If there is sufficient driving potential i.e. if there is enough time and the temperature is sufficiently high, devitrification of the layer will take place, resulting in a crystalline phase.(2) The presence of crystals in the liquid layer increases the friction between mould and strand, leading to high incidence of sticker breakouts. Mould slags with a high crystallisation tendency are deleterious to high-speed casting conditions. On the other hand, a high crystallisation tendency is beneficial in the casting of peritectic steel grades. Anyway, it is clear that in the continuous casting mould slags crystallisation control is a matter of utmost importance.

Commercial mould powders contain fluorine, usually as calcium fluoride (CaF_2). There is a clear trend in industry to eliminate fluorine from slags which are used during production of steel. Regarding continuous casting process fluorine in mould powders is undesirable from the environmental and health points of view due to the following reasons: (i) evolves easily from slags, producing health-injurious gaseous substances, such as hydrofluoric acid; (ii) creates problems for storage and utilisation of solid waste and (iii) causes machinery corrosion. Regarding machinery corrosion the hydrofluoric acid, which is generated during continuous casting process from mould powder, increases dramatically the corrosion rate especially below the mould where there is a high amount of water accelerating the corrosion process.(4)

The main problem related to the development of fluorine-free mould powders for slab casting is how to control the heat transfer between steel shell and mould. The crystallisation of cuspidine ($3CaO.2SiO_2.CaF_2$) from mould flux is thought to be the most effective way for the heat transfer control. Although the mechanism of the heat transfer control by the crystallisation of cuspidine has not been determined yet, two ideas have been proposed. One is that radiation heat flux is decreased by scattering at the boundary between the crystalline and the liquid layers and the other is that total heat flux is decreased by the large thermal resistance of the air gap formed as a result of the solidification shrinkage. Anyway, the crystallisation of cuspidine from mould flux has the great effect on heat transfer control.(5)

There are some papers indicating that TiO_2-bearing raw materials can be used to replace fluorine-bearing raw materials, regarding the heat transfer control function, by formation of TiO_2 crystals instead of cuspidine.(5-7)

Nakada and Nagata [5] analysed the basic system $CaO-SiO_2-TiO_2$ evaluating the possibility of having it as a candidate for fluorine-free mould flux through the crystallisation of $CaO.SiO_2.TiO_2$, determining the time-temperature-transformation (TTT) diagram of two slag compositions through differential thermal analysis (DTA). They concluded that it is possible to get the heat transfer control function, but the thickness of the crystalline layer was found to be smaller than that of the crystalline layer resulting from cuspidine precipitation. Then, they suggested that it is worth investigating the effect of Na_2O addition in the $CaO-SiO_2-TiO_2$ slags, since in this way it would be possible to decrease the incubation time of the crystals and consequently to increase the thickness of the crystalline layer.

Wen *et al.*(6) evaluated titanium-bearing blast furnace slags as a base material to develop F-free mould powders, evaluating their properties and their performance through laboratory experiments and plant trials. According to them the industrial trials indicated that F-free mould powders can effectively control mould heat transfer through perovskite ($CaO.TiO_2$) precipitated in the infiltrated slag layer instead of cuspidine in fluorine-bearing powder, with better slab surface quality than fluoride-bearing powders in terms of crack index.

Qi, Wen and Tang(7) studied mould slags using a device which simulates the heat flux through the mould slag film, based on the copper finger method, and reported that when increasing TiO_2 content in fluorine-free mould powders the activation energy for crystallisation from glassy solid mould fluxes and the activation energy for crystallisation from liquid mould fluxes are reduced. Thus, according to their report, from the perspective of the activation energy for crystallisation the fluorine-free mould fluxes containing TiO_2 have already reached the level of industrial mould slags containing fluorine, and can be used to replace them.

The crystallisation rate of crystals in titanium-bearing fluorine-free slags must be similar to the crystallisation rate of cuspidine in commercial mould fluxes. In the present work it is assumed that the crystallisation rate of crystals is linked with incubation times in time-temperature-transformation diagrams (TTT diagrams).

The Single Hot Thermocouple Technique (SHTT) can be used to build TTT diagrams. With this technique the sample is put on one thermocouple tip, heated and cooled at the desired rates. The advantage is to allow in situ observation of melting and solidification under various thermal conditions. Due to the low mass of the system (sample and thermocouple) high heating and cooling rates can be easily obtained (> 3.000 K/min). Besides SHTT, using the hot thermocouple technique another experimental mode is also possible: the Double Hot Thermocouple Technique (DHTT). With the DHTT the solidification behaviour can be observed in situ applying temperature gradients, simulating the conditions during continuous casting. In this mode the slag sample is placed between the tips of two thermocouples. Both sides can be controlled independently and mould-like temperature gradients or heat peaks can be applied.(8)

1.1 Objective

The objective of the present work is to evaluate the possibility of reproducing the crystallisation behaviour of cuspidine during continuous casting, building TTT diagrams through the Single Hot Thermocouple Technique in the $CaO-SiO_2-TiO_2-Na_2O$ slag system.

1.2 Experimental Set-up

The apparatus used in the present work was constructed in the Institute of Iron and Steel Technology of the Technische Universität Bergakademie Freiberg, Germany, and it was described in a previous work.(8) A schematic view is given in Figure 1. It consists basically of two systems: an observation system and a thermocouple system. In a vacuum chamber there are two water-cooled inserts left and right. Both of them hold a B-type thermocouple at tips. Each thermocouple is connected to a separate thermocouple controller. The material under study is melted directly on thermocouple in vaccum chamber. The thermocouple remains inside an additional heating, i.e. a kanthal coil which reduces heat losses from the sample to the surroundings.

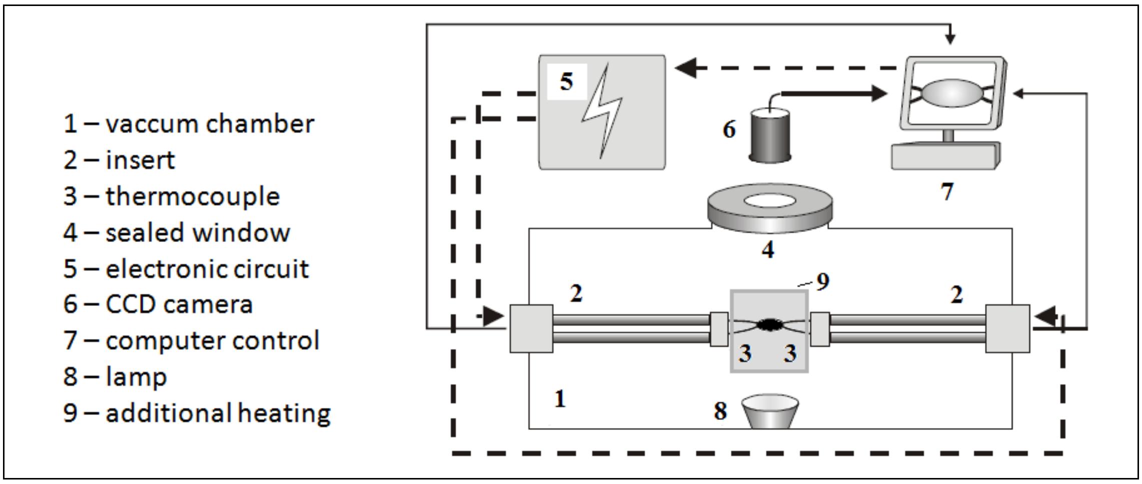


Figure 1. Schematic view of the experimental set-up used in the present work.

With this method it is possible to measure the temperature with a thermocouple while it is heated simultaneously. A computer manages the two thermocouple controllers, controlling individually heating and cooling conditions. A software superimposes information about time, temperature and sample image into videos files in a real-time system.

At Figure 2 it can be seen a picture of one typical thermocouple, which is produced welding two platinum wires (Pt30Rh and Pt6Rh) with a special technique. The welding must be nearly perfect to avoid measurement errors. For each material under study one particular thermocouple is used.

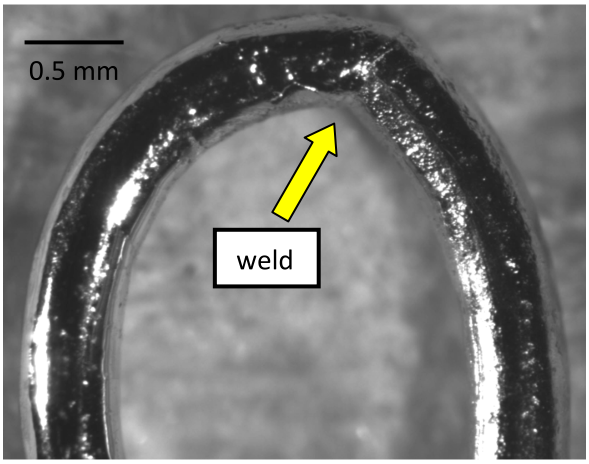


Figure 2. Typical thermocouple used in the experiments of the present work (tip), showing the region where slags are melted. Image obtained from a stereomicroscope.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of Slag Samples and Investigation Procedure

The composition of the slags which were investigated can be seen at Table 1. They were produced from $CaCO_3$, SiO_2 , TiO_2 , Na_2CO_3 and Al_2O_3 . They were pre-melted in carbon crucibles using an induction furnace. Then they were milled, decarburized at 700°C during 5 hours (except CST) in a muffle furnace and after analysed through X-ray Fluorescence (XRF). The carbon content was determined through LECO CS 244.

Table 1. Composition of the slags studied in the present work (%wt.) B means the ratio $\%CaO/\%SiO_2$

	%CaO	$\%SiO_2$	$\%TiO_2$	$\%Na_2O$	$\%Al_2O_3$	%C	B
CST	35.6	46.3	18.1			0.590	0.8
CSTNA_1	33.6	41.3	16.5	7.1	1.5	0.073	0.8
CSTNA_2	30.1	46.8	16.4	5.4	1.3	0.034	0.6
CSTNA_3	31.6	48.1	15.5	3.7	1.1	0.032	0.7
CSTNA_4	30.9	42.3	15.2	6.4	5.2	0.038	0.7

To execute the experiments small portions of premelted slags (5 - 10 mg) were pressed and put on the thermocouple tip. With the substances in the vacuum chamber it was applied 5 min of vacuum at 10 mbar. Then, the vessel was filled with Ar, maintaining a flux of 300 l/h during ten minutes and also during the measurements. The slag samples were heated and melted directly on the tip of the thermocouples, using one particular thermocouple per slag. After melting very high cooling rates (higher than 3000 K/min) were applied down to the desired temperature; from this point up to the beginning of the crystallisation the incubation time is measured by direct observation. With the incubation times for different temperatures time-temperature-transformation (TTT) diagrams were built.

For the Na_2O-bearing slags the samples were maintained at 1600 °C in short time (30s) after heating at 1000 K/min. At this high temperature the samples are completely melted in a few seconds. It was clearly observed that if the same sample is used to do many determinations at the same temperature the incubation times became longer. The reason for this effect is Na_2O loss at high temperatures, assuming that the higher the %Na_2O content the higher the crystallisation tendency. To avoid this problem the maximum amount of measurements per sample was ten. Each point in the TTT diagrams is the average of a minimum of three measurements.

From the video files recorded during the experiments observations related to the morphology of crystals were done at different temperatures.

2.2 Examination of the Accuracy of the Apparatus

Firstly the accuracy of the apparatus was checked measuring the crystallisation temperature of Na_2SO_4, CaF_2 and K_2SO_4. The crystallisation temperature ($T_{cryst.}$) is defined in the present work as the point where the first crystals can be detected visually through the recorded video files. The procedure before high temperature experiments (vacuum, Ar flow) is described above. Afterwards, the substances were melted 100°C above their literature melting points and cooled at 30°C/min. Their melting points (m.p.) from Patnaik(9) are: Na_2SO_4 - 884 °C , CaF_2 - 1418 °C , K_2SO_4 - 1069 °C .

3 RESULTS AND DISCUSSION

3.1 Examination of the Accuracy of the Apparatus

The differences between the literature melting points [9] which were estimated using DTA and the crystallisation temperatures for Na_2SO_4, CaF_2 and K_2SO_4 which were measured by SHTT are indicated at Figure 3. Twelve experiments were performed for each substance (experiments 1-6 were done to the left side and experiments 7-12 to the right side according to Figure 1).

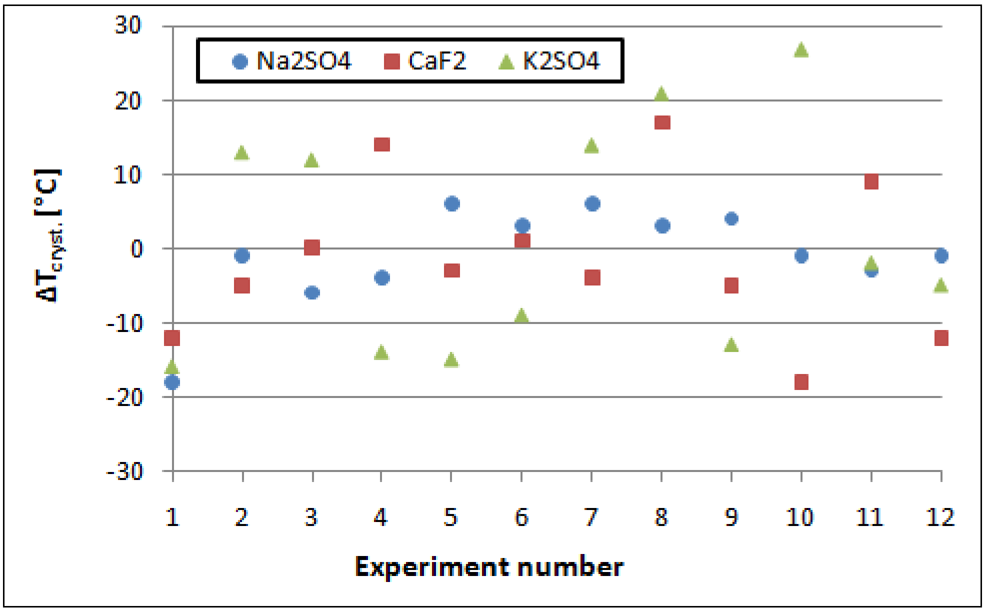


Figure 3. Comparison between literature and results from the present work. $\Delta T_{cryst.}$ is the difference between the literature melting point(9) and the crystallisation temperature which was measured by SHTT.

Assuming a normal distribution for $\Delta T_{cryst.}$ average values and standard deviations can be calculated, see Table 2. The average values are very near of the melting points from literature and the scattering is low. The small observed differences can be related to particular conditions for heterogeneous nucleation.

Regarding Na_2SO_4 and CaF_2 the crystallisation is intense and happens suddenly; in this situation it is easy to define accurately the beginning of the crystallisation. For K_2SO_4 , the substance which presents higher standard deviation, the crystallisation is not so intense and normally takes some seconds to be finished.

Table 2. Comparison between literature melting points and crystallisation temperatures measured by SHTT ($T_{cryst.}$). For each substance 12 measurements were performed

Substance	**m.p.**[(9)]	**average $T_{cryst.}$**	**standard deviation $T_{cryst.}$**
Na_2SO_4	884 °C	883 °C	6.6 °C
CaF_2	1418 °C	1417 °C	10.6 °C
K_2SO_4	1069 °C	1071 °C	15.4 °C

3.2 TTT Diagrams for Slags in the $CaO-SiO_2-TiO_2-Na_2O$ System

The slag CST studied in the present work has relatively low liquidus temperature (1366 °C, calculated from FactSage 6.0) and relatively low viscosity (ca. 10 P at 1400°C, from Schenck and Frohberg(10)). This slag system has been considered as a starting point to the development of fluorine-free mould powders. The slag CST has a composition similar to a slag studied in another work [5], whose TTT diagram was built from differential thermal analysis (DTA). Despite of using another technique the reported incubations times are similar to the results of the present work.

The slag CSTNA_1 was designed to have basicity and TiO_2 content similar to the slag CST, as it can be seen at Table 1. The TTT diagrams for the slags CST and CSTNA_1 are at Figure 4, in logarithmic scale. The Na_2O-bearing slag CSTNA_1 has higher crystallisation rate. Na_2O addition shortens intensely the incubation times from the $CaO-SiO_2-TiO_2$ slag system.

For doing a comparison with an industrial slag, at Figure 4 it can also be seen the TTT diagram of a commercial mould powder normally employed in the continuous casting of stainless steels, whose TTT diagram was also built using SHTT [11]. This commercial mould powder contains CaF_2 and Na_2O and does not contain TiO_2 .

With this new finding i.e. the fact that there is a great increase of the crystallisation rate when adding Na_2O from the $CaO-SiO_2-TiO_2$ system, other slags were produced with a lower Na_2O content to study the possibility of controlling the crystallisation. From CSTNA_1 were produced CSTNA_2 and CSTNA_3, maintaining basicity and TiO_2 content in similar levels. As expected it was observed shorter incubation times, especially to CSTNA_3 which has lower Na_2O content.

Industrial mould slags contain Al_2O_3 and because of this fact it was also produced CSTNA_4, which is a slag with composition similar to CSTNA_1 but containing more Al_2O_3. Despite of having a higher Al_2O_3 content the incubation times are similar, except at lower temperatures where there is some difference.

Industrial slags are more complex, since they have more components. Anyway, the present study can be used as a reference for future developments when designing fluorine-free mould powders for slab casting, where the control of crystallisation is imperative. In this way Na_2O-bearing and TiO_2-bearing raw materials could be used to mould powders industrial production; these raw materials can be less expensive than other possibilities such as B_2O_3 and Li_2O.

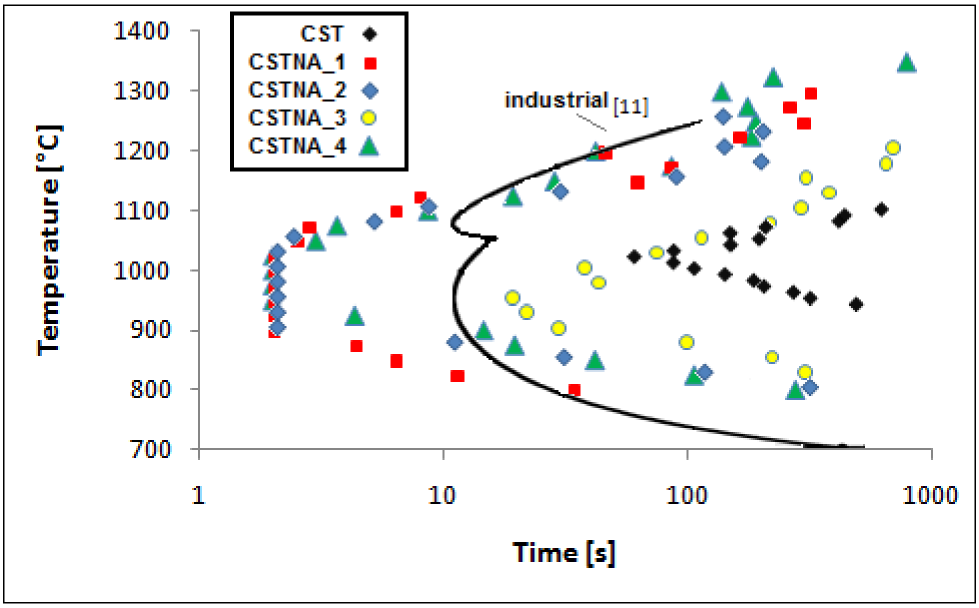


Figure 4. TTT diagrams for slags in the CaO-SiO_2-TiO_2-Na_2O system (composition in Table 1) and also for a F-bearing industrial slag.(11)

3.3 Morphology of the Crystals

It was observed for all the slags of the present work that the morphology of the crystals varies with temperature. The crystals have dendritic structure at higher temperatures and become small and dense at lower temperatures.

Below at Figure 5 there are some images got from the recorded video files for the slag CSTNA_1 and some observations related to the morphology of the crystals for this particular slag.

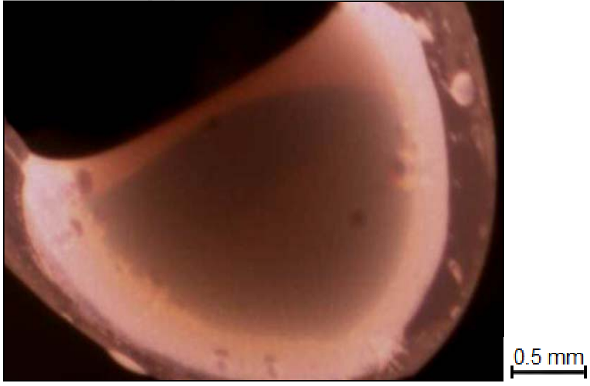
Firstly, at Figure 5 (a) it is showed an image of the slag completely liquid at 1600 °C, with the lamp below the sample off. It is normal to have some bubbles around the thermocouple borders, even using decarburized samples – the reason for the existence of these bubbles is not clear. For all the experiments the lamp below the sample was turned on; in this way the resolution image is higher.

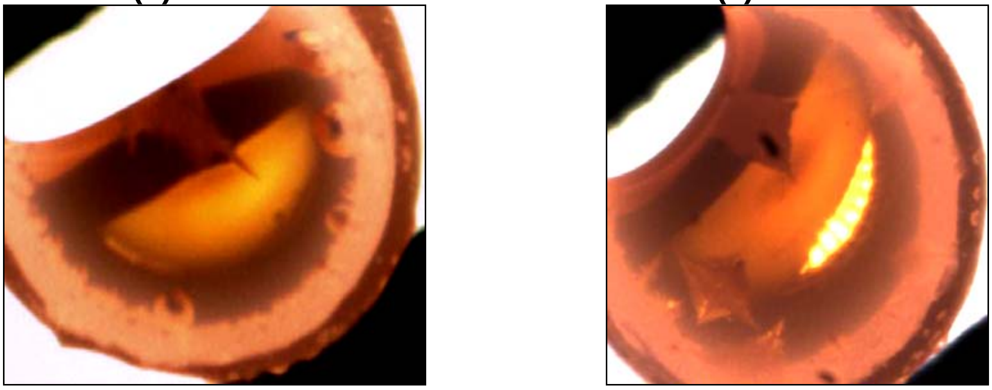
At higher temperatures dendritic structure can be observed, for example at 1325 °C and 1250 °C, see Figure 5 (b-c); it is common to observe dendrites nucleating from thermocouple borders. These temperatures correspond to long incubation times and consequently to lower crystallisation rates.

At lower temperatures dendritic structure is not observed. At 1150 °C, 1100 °C and 1050 °C for example – Figure 5 (d-f) – the crystals grow from different points in the sample, but none from the thermocouple borders. In a general way crystals can grow from the liquid slag or from solid glass (devitrification), depending on temperature. With SHTT it is difficult to determine if the sample is liquid slag or solid glass. Anyway, for transparent slags crystallisation can be observed in both situations, though at lower temperatures the conditions for visibility are not ideal.

At 900 °C the samples are translucent, see Figure 5 (g). Possibly at this low temperature the samples are solid glasses; the incubation time is 2 seconds and the samples are completely opaque in only 4 seconds.

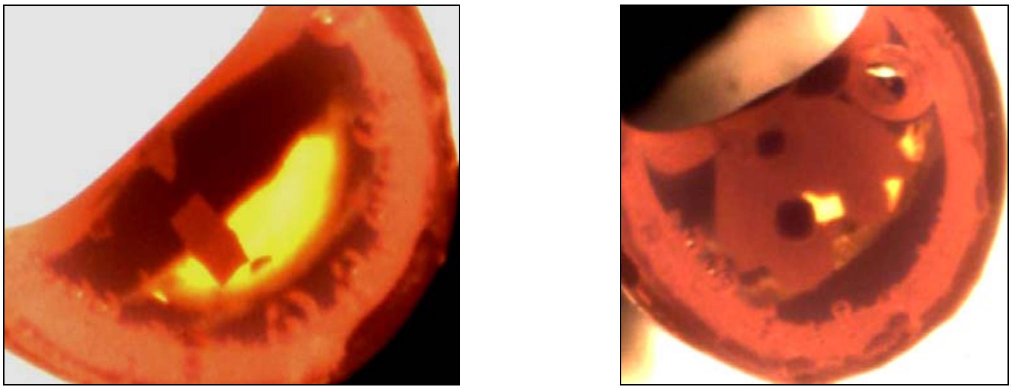
(a) 1600 °C , lamp off





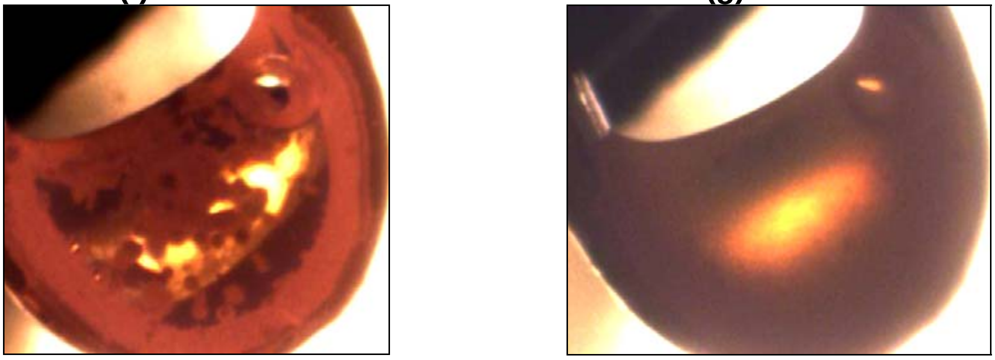
(b) 1325 °C

(c) 1250 °C



(d) 1150 °C

(e) 1100 °C



(f) 1050 °C

(g) 900 °C

Figure 5. Images got from the recorded video files for the experiments performed with the slag CSTNA_1 at different temperatures.

4 CONCLUSIONS

The results of the present work indicate that the system CaO-SiO_2-TiO_2-Na_2O can be used as substitute for F-bearing commercial mould powders, regarding crystallisation behaviour, since the incubation times at TTT diagrams and consequently the crystallisation rates can be similar to commercial products. This is possible because addition of Na_2O shorten intensely the incubation times from the CaO-SiO_2-TiO_2 slag system. In this way, Na_2O-bearing and TiO_2-bearing raw materials could be used to produce mould powders. Besides, the results also indicate that Al_2O_3 content up to 5.2 % do not change significantly the incubation times of CaO-SiO_2-TiO_2-Na_2O slags, considering the compositions of the present work.

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