EVALUATION OF SOLIDIFIED SLAG FILMS FROM MOULD POWDERS USED IN C.C., TAKEN FROM PLATE/MOLD INTERFACE

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SUMMARY

The literature quite clearly distinguishes nowadays the temperatures of crystallization and solidification in the characterization of mould powders. The need for painstaking study of this parameters has arisen from the quest for a full understanding of their influence on the obtaining of good surface quality of the plates produced, allied to high productivity levels, in terms of higher casting speeds and cutting down of the number of stops. This paper contains an analysis by means of optical microscopy of the layer of solidified slag from fluxes used in the continuous casting of low medium carbon steels. The prevailing crystaline phase, identified by DRX, consistis of cuspidine (3 CaO, 2 SiO_2, CaF_2). The positioning of the crystallized fraction of slag on the plate/mold interface within the thickness of the film is also discussed in displays variations. The research ascertains that there is a differentiation of micro-structure of the interface films, which is in accordance with the concept that for the steels more liable to longitudinal cracking the flow of removal of heat in the mold needs to be properly regulated. That role is lagerly performed by establishment of proper conditions for development of crystalline thickness at the interface. Hence we observe the fundamental principle that the flow of removal of heat in the continuous casting of low carbon steels is predominantly radiant, whereas in the solidification of medium carbon steels the contribution of a more conductive flow is greater. But the control of this flow of heat, as regards excessive reduction, needs to be studied on each machine so that the plate reaches the spray zone at suitable temperature.

Key words: Mould Powder, Continuous Casting, Crystallization.

INTRODUCTION

The quality, both superficial and internal, of steel plates produced in continuous casting (CC) is being more and more affected by increasing extent to which studies on characterization of micro-structures in the areas of engineering and materials science are being applied in the evaluation and formulation of fluxes. Materials Chemistry nowadays also reveals its effective potencial not only in the understanding of the various phenomena linked with the development of the phases responsible for ensuring lubrication at the plate/mold interface but also cooperates in the solution of a number of operational difficulties of CC having to do with the meeting of specific requirements of each operation.

Mould powders play a number of roles in CC operations. But to ensure the lubrication of the plate/mold interface and regulate the transfer of heat that will contribute to the sound condition of the plates there are two important tasks handled by these steel industry inputs with their multiple formulations, forms of presentation and production processes. Attention is drawn in the literature (1) to the importance of both the temperature of solidification of the fluxes and their greater or lesser tendency to crystallization, which factors are responsible for suitable lubrication of the plate in course of formation in the continuous casting process and for a heat transfer process adjusted inaccordance with the type of steel being solidified, respectively.

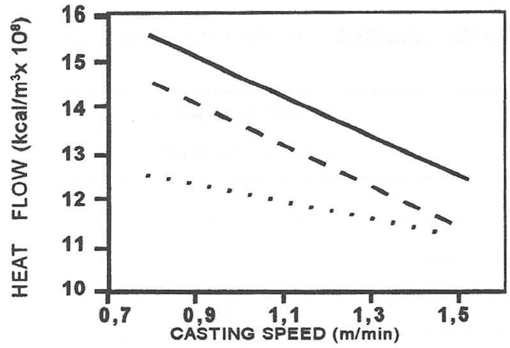


Figure I - Variation in heat transfer in CC mold, as related to the powder used and casting speed (1)

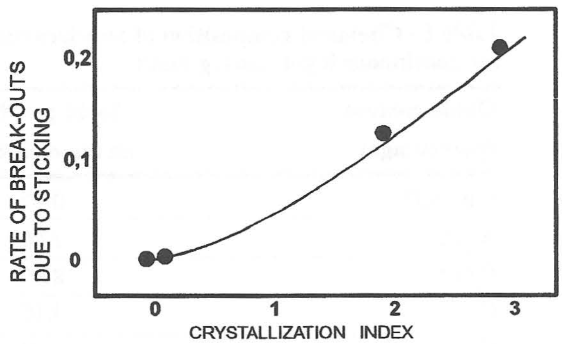


Figure II - Influence of crystallization on frequency of breakouts caused by sticking (1)

This study contains an evaluation of the texture of petrographic plates prepared from thin sections films of solidified slag withdrawn from the plate/mold interface after the CC of low and medium carbon steels, as a contribution to the understanding of the principles of formation of the film and its morphological characteristics.

Bommaraju, R., in a study dealing with optimization in the selection of fluxes in connection with the type of steel to be ingotted and the operational conditions present, indicates in clear terms the relationship between heat transfer, temperature of solidification, tendency to crystallization and occurrence of breakouts. (See Figures I and II).

Mills, K.C., in an extensive revision concerning the measurement and evaluation of the parameters of performance of mould powders (2), points out the importance of establishing conditions aimed at the development of crystallized thickness in the slag film on the plate/mold interface. Figure III emphasizes the crystalline phases normally developed on the interface films.

The flow of radiation heat (k_R) established through a film of vitreous slag present at the plate/mold interface may be twice the rate of flow established by conduction through a screen. But the spreading of radiant heat caused by the presence of crystalline spherulites in the slag film may reduce to 0.2 times the conductive flow established by the screen. Furthermore, at the moment when the crystallization of this film sets in, turning opaque a considerable portion of the thickness of the interface, heat transfer by conduction through the screen proceeds to make a far greater contribution to the speed of cooling, implying gentler cooling conditions as called for in the process of solidification of peritetic steel grades.

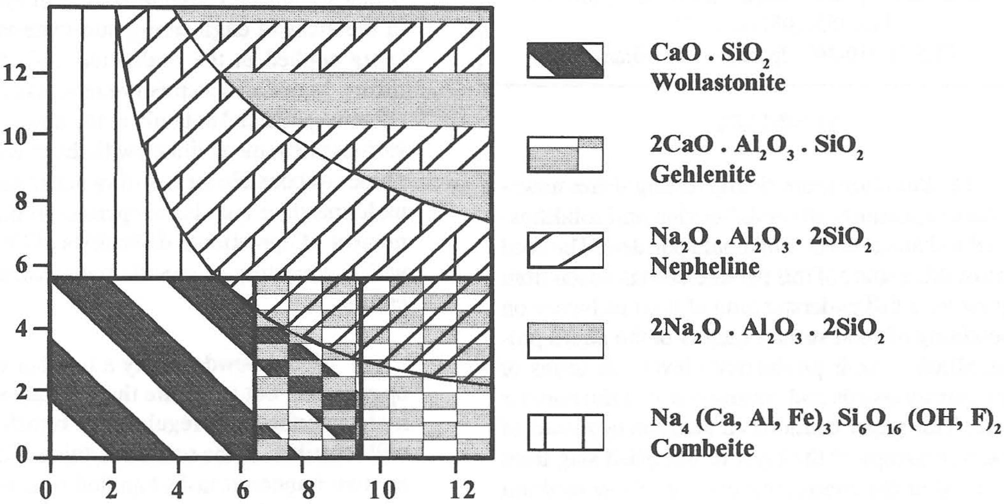


Figure III - Diagram showing the crystalline phases that may be developed from the chemical composition of commercially available powders (2). Cuspidine has been omitted in order to facilitate visualization

In that respect, the study of these films and the operating conditions that generated them is an important source of information when an endeavor is made, based on operational background data with a particular powder, to enrich its formulation so as to favor the development of a micro-structure made to measure for conditions to maximize yield from a CC operation.

MATERIALS AND METHODS

The chemical compositions of the fluxes used in the CC operations from which the samples were obtained are shown in Table I.

Table I - Chemical composition of powders that gave rise to the solidified slag films removed from the continuous ingot casting mold

Oxide content (percentage)	Mould powder for medium carbon steel	Mould powder for low carbon steel
CaO/SiO_2	0.97	0.92
Al_2O_3	7.00	6.00
R_2O *	8.90	11.50
C_t	4.10	6.00
F^-	6.00	7.50

* $Na_2O + K_2O$

The samples of the films of solidified slag from the plate/mold interface were obtained at time of placement of the mixture plate, on casting of different grades of steel within one and the same category. On account of the short time available for performing this operation, the total time period for withdrawal of the samples cannot be more than one minute, bearing in mind that the CC operation continues to proceed at a rate of 0.3 m/min. It is important to note that the ingot casting speeds traditionally used for low and medium carbon steels at USIMINAS (CC No. 3 caster) are 0.95 m/min and 0.65 m/min respectively. The samples were taken from the third top of the total height of the mold. It should be noted that the films of solidified slag would normally peel off from the wall of the mold at that time in any case, were the level of the steel to be maintained below the third top of the total length of the mold.

Optical transmission microscopy was used in evaluating the texture of the solidified material removed from the plate/mold interface. Based on the samples of the mould powder slags, and using petrographic techniques, the thin sections were prepared by the CPRM Mineral Analysis Laboratory. The ultimate thickness of the sheets was approximately 30 μm. The equipment used was an optical microscope equipped with transmitted and reflected light, coupled with an image analyzer. The micrographs were prepared with levels of magnification of x 25 and x 100. The use of crossed and semi-crossed nichols in the study of the sections was adopted having in view to obtain perfect definition as to the crystallinity or otherwise of the various regions observed in the thickness of the films of solidified slag.

X-ray diffractometry was the method employed to characterize the crystalline phases present in the solidified slag films from the plate/mold interface. The analyses were effected using Kα copper radiation and goniometer speeds of 2° (2θ) per minute, using a diffractometer at the National Research Council's Mineral Technology Center (CETEM) of CNPq.

RESULTS AND DISCUSSION

In a way to characterize the thin sections removed from the plate/mold interface, their thicknesses were measured. Figures IV and V present the values encountered for the films derived from the CC of both the low carbon and the medium carbon steels.

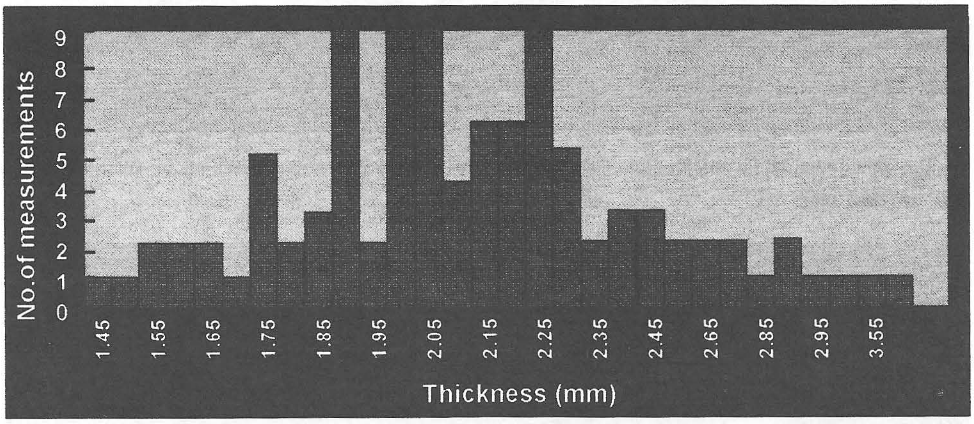


Figure IV - Range of variation in thickness recorded on samples of solidified slag removed from the plate/mold interface after CC of a low carbon steel (material from wide and narrow faces)

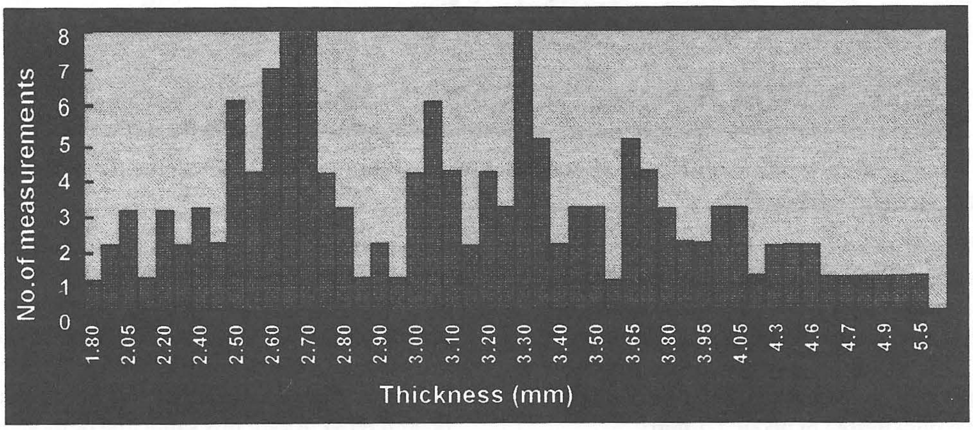


Figure V - Range of variation in thickness recorded on samples of solidified slag film removed from plate/mold interface after CC of a medium carbon steel (material obtained from broad and narrow faces)

The first observation arising from analysis of these graphs has to do with not only the range of variation recorded for the thicknesses of the films but also with the absolute values encountered. The literature (2), (3), (4), mentions that the values of the films vary within a range of 1.0 mm. Some studies have gone so far as to establish a range from 0.5 mm to 1.0 mm as that representing the thicknesses commonly encountered in CC operations, making no distinction as to type of steel involved. Even if it be considered that those authors were not referring to medium carbon steels, the thicknesses of the slag films present in the third top of the total length of the mold are at least two or three times greater.

On the other hand, as would be expected for the CC of low carbon steels, the films withdrawn from the CC for medium carbon steel are thicker, and it is not unusual to encounter values of 4.0 mm. As is known (5), (6), the peritetic grains of steel (0.08 to 0.14 of carbon) associate with the process of cooling and solidification in the mold a process of crsytalline transformation (ferrite [δ] to austenite [γ], characterized by additional linear contraction. As we shall see later in this study, this greater thickness in the case of the films derived from the CC of medium carbon steels is also connected with gentler cooling conditions induced by the actual profile of development of crystalline phases in a significant portion of the respective films.

To give a better idea involved the range of variation of thickness of the thin sections CC, Figures **VI** and **VII** show merely the measurements made on the materials removed from the plate/mold interfaces corresponding to the narrow faces.

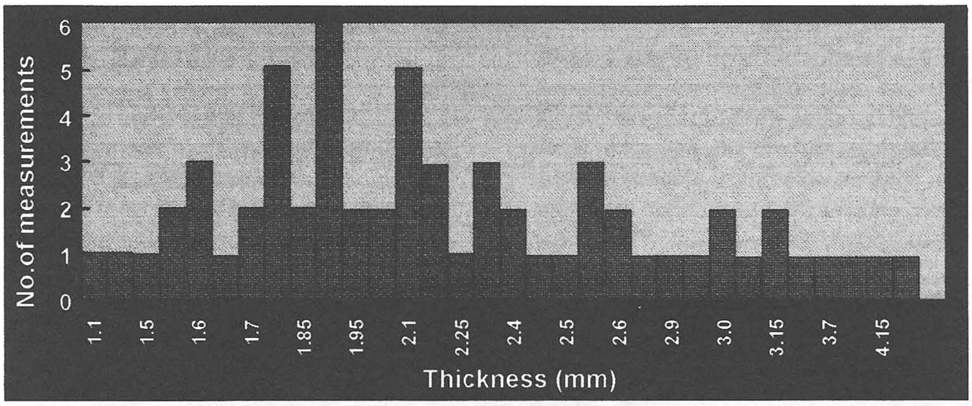


Figure VI - Range of variation in thickness of solidified films from plate/mold interface (from narrow face of mold) after low carbon steel CC

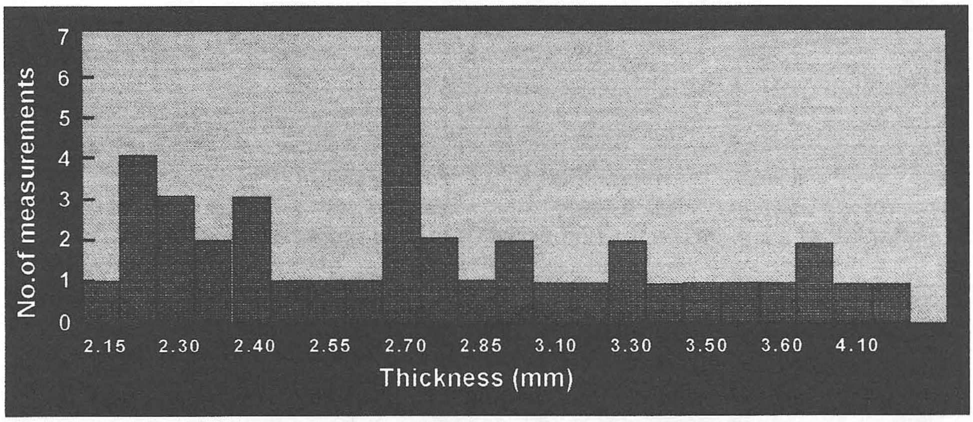


Figure VII - Range of variation in thickness of solidified films from plate/mold interface (from narrow face of mold) after medium carbon CC

Analysis of these figures by comparison with the previous ones (Figures IV and V) shows that the greatest contribution on the part of the films from the narrow faces occurs in the range from 1.8 mm to 2.0 mm, in the case of the low carbon steels. The films taken from this region after the CC of a medium carbon steel have thicknesses of about 2.7 mm.

From the literature (7) or from experience acquired in the Brazilian steel industry, it is known that the occurrence of breakouts may be associated with the absence or deficiency of lubrification at the plate/mold interface. Compliance with this requirement on the part of the powder, meaning assurance of adequate lubrification, depends considerably on both the level of Tc in this steel industry input and on its crystallization potential (8). Along this same line of thought but now considering the surface quality of the plates produced and the direct implications on the indices of scarfing for steels with more careful configuration, favoring of the synthesis of an adequate group of crystalline phases (2) that can regulate the speed of removal of heat suitable for each kind of steel can and should be sought.

Hence Figures **VIII, IX** and **X** display proposals for models of portions of CC molds in which we point out the plate/mold interface and the various layers comprising the flux slag film. Figure **VIII** proposes a condition which, in reality, is frequently encountered and that develops during continuous casting of low carbon steel. The crystallized fraction is present in such a proportion that, in terms of total film thickness, considering the vitreous fraction, that its interference in heat transfer by radiation is considerably reduced by comparison with the cooling resulting from the phenomenon of thermal conduction that is established in the film of flux at the interface.

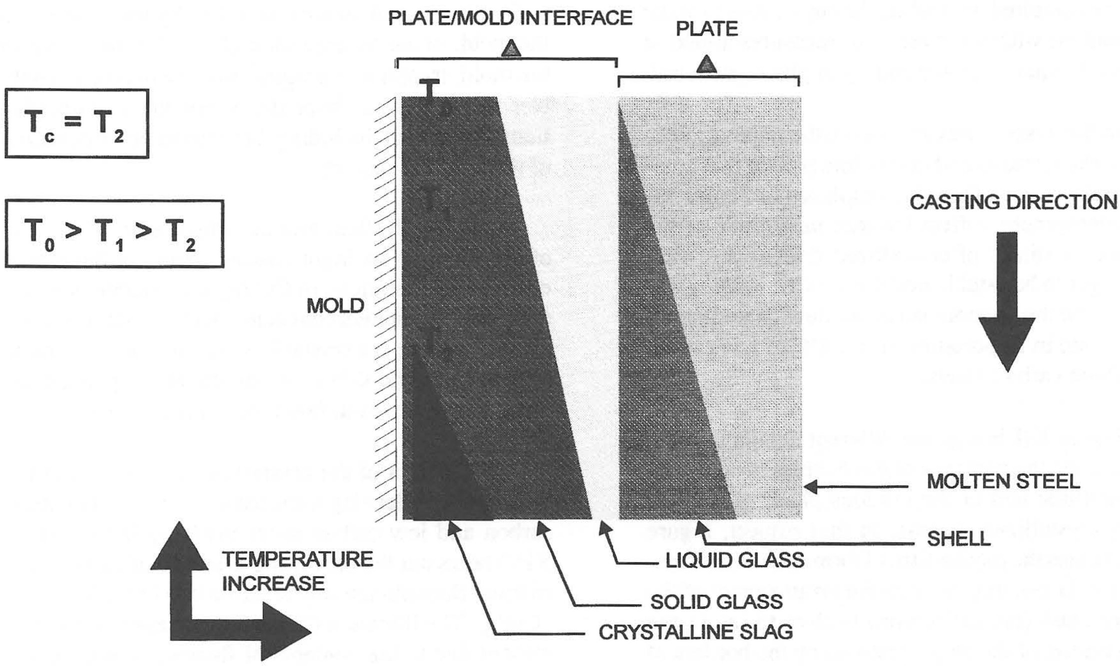


Figure VIII - Diagram representing the profile of the film on the plate/mold interface developed in CC for slags with low crystallization potential

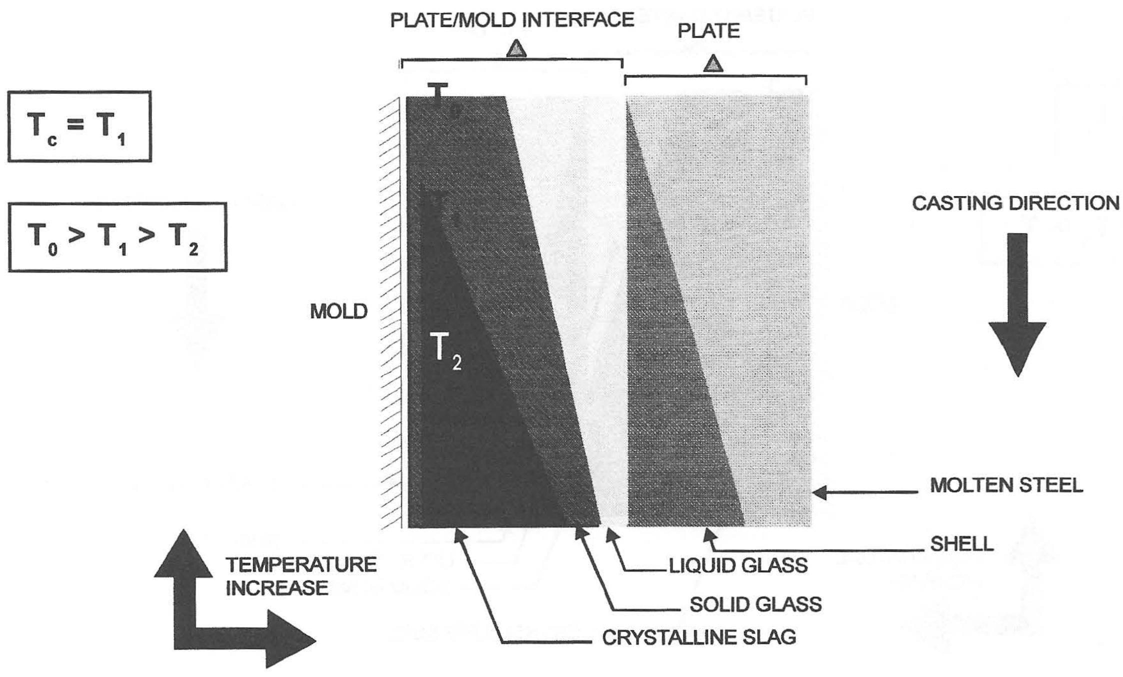


Figure IX - Diagram showing profile of plate/mold interface developed in CC for slags with crystallization potential adequate for steels, for example,with peritetic grade composition

The condition proposed as adequate for continous ingot casting of steels more susceptible to cracking involves emergence of a fraction of crystallized thickness in the film a good deal greater than that idealized for low carbon steels in general. The diagram in Figure **IX** is intended to show that the use of fluxes containing Tc at an adequate level, along with a chemical composition that favors the emergence of crystalline phases responsible for the significant reduction in quantity of heat transferred by radiation, is a basic condiion to be complied with when the objective is to make a contribution within the series of measures aimed at achieving adequate surface quality of plates produced.

In this respect we can observe the relative thicknesses of the vitreous and crystalline phases that comprise the slag films of the flux displayed in Figure **XI**. These micrographs reflect the true magnitude of the difference in values of crystallized thickness of film that may get to be established during CC, helping understand how the phenomena of conduction and radiation alternate in importance in the CC of low carbon and medium carbon steels.

Figure **XII** brings out different details of these films, such as: the presence of gas bubbles of considerable magnitude and of the vitreous phase of discrete perfectly crystallized regions. In that respect, Figure **XIII** illustrates the mechanism of formation of the crystallized thickness, inasmuch as the arrangement of the micro-structure (crystallization) is clear to see in the vitreous region of the slag contained by the borders of the crystallized surroundings already formed.

One additional observation that cannot be recorded in the black and white photo-micrographic record is that significant fractions of the vitreous layer that ensures lubrification of the surface of the plate in course of formation already displays a degree of micro-structural organization capable of crystallizing almost instantaneously. In view of this, and considering merely aspects connected with the powders, it would suffice for example variations to occur in the content and type of the inclusions absorbed by the powders in the mold, excessive corrosion of the SEN in the top of the mold, trapping of a significant fraction of gas bubbles in the film, to favor the emergence of imperfections capable of including heterogeneous nucleation of the vitreous slag, etc.

Figure **X** illustrates the situation in which loss of lubrification in ingot casting seems to have been entailed by alterations in CC regime capable of modifying the parameters connected with powder crystallization, causing the crystallized and hence solid thickness to reach the skin in solidification of plate, causing sticking and even break-out in many cases.

Analyses of the crystalline composition of the solidified powder slag films used in the CC of medium carbon and low carbon steels made by DRX (Figure **XIV**) bears out the prevailing presence of cuspidine, a calcium fluorsilicate whose formula is [$3\,CaO \cdot 2\,SiO_2 \cdot CaF_2$]. The literature (7) says this phase is frequently present due to the contents of fluorine present in the formulation of fluxes, generally in the 4.0% to 10.0%

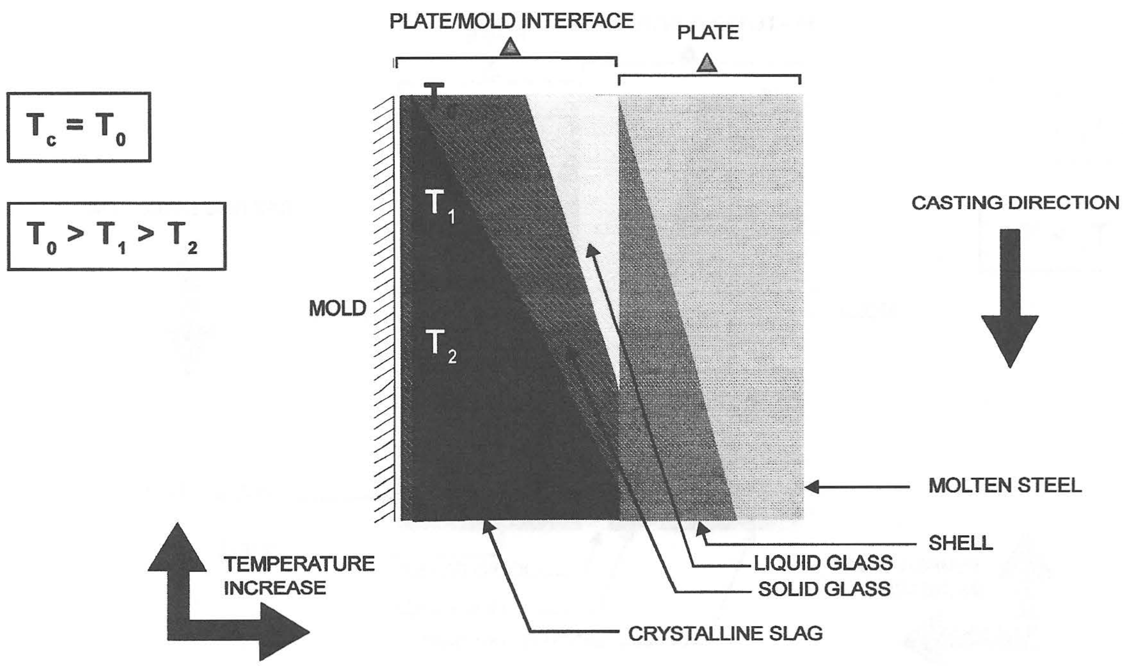
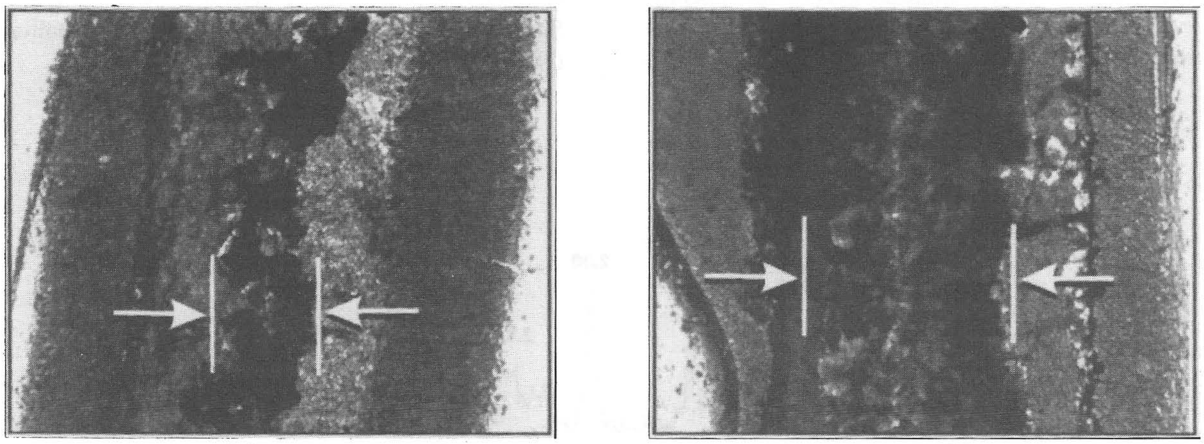
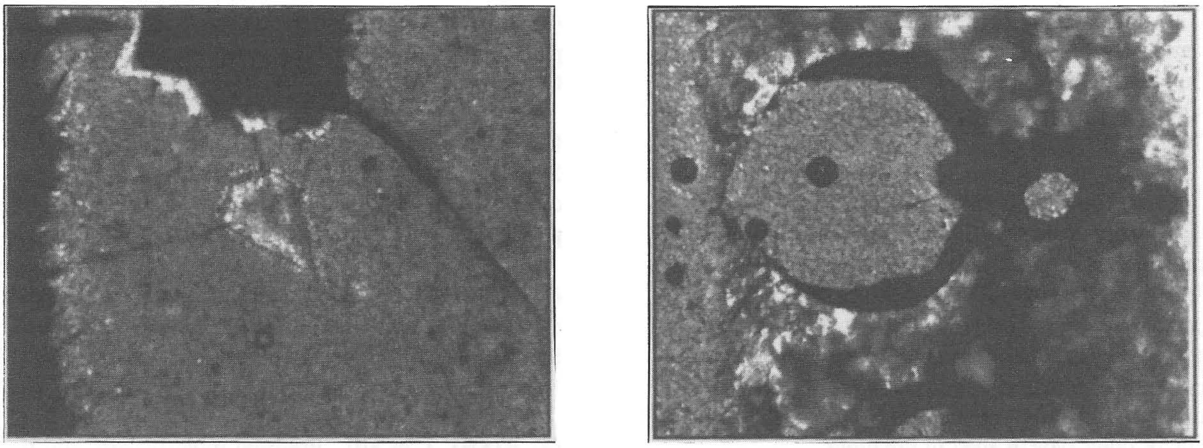


Figure X - Diagram representing profile of plate/mold inteerface developed in CC for conditions of excessive tendency to crystallization



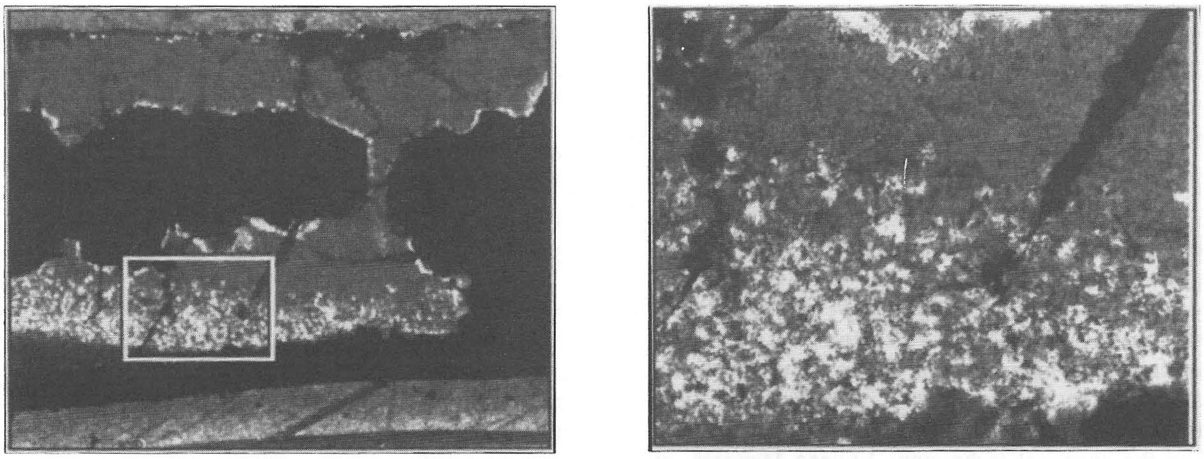
[a] [b]

Figure XI - Optical micro-graphs of solidified flux slag films removed from the plate/mold interface after casting of [a] a low carbon steel and [b] a medium carbon steel



[a] [b]

Figure XII - Optical micro-graphs of solidified powder slag films removed from the plate/mold interface after casting of [a] a low carbon steel and [b] a medium carbon steel. (100 x magnification)



[a] [b]

Figure XIII - Optical micrography of a solidified flux slag film removed from plate/mold interface after casting of a medium carbon steel (25 x magnification [a]; 100 x magnification [b])

range. Some other crystalline phases capable of being developed through thermal treatments of solid films of molten fluxes are: cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$), wollastonite ($CaO \cdot SiO_2$), gelenite ($2 CaO \cdot Al_2O_3 \cdot SiO_2$), nepheline ($Na_2O \cdot Al_2O_3 \cdot 2 SiO_2$), and pectolite ($Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$) amongst others.

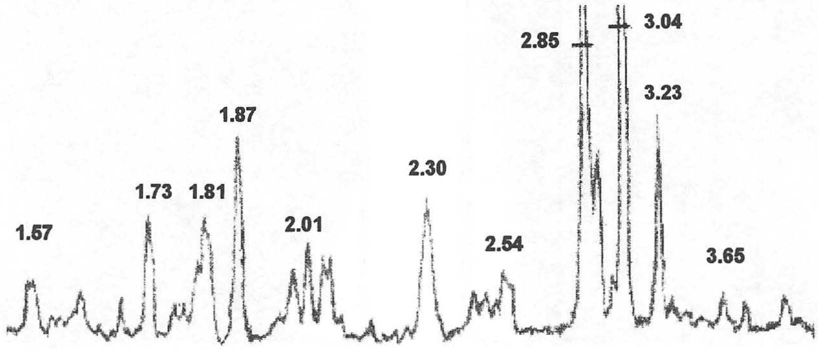


Figure XIV - X-ray diffractogram of solidified slag film removed from plate/mold interface, displaying some peaks characteristic of cuspidine - $Ca_4F_2 \cdot Si_2O_7$

CONCLUSIONS

This study proves that the thickness of the films removed from the plate/mold interface, of solidified flux slag used in continous ingot casting of steels is significantly higher than is frequently mentioned in the literature.

By applying optical microscopy by transmitted light, using polarized light, it was possible to reveal the thickest crystallized layer present in the films formed in the ingotting of medium carbon steels, by comparison with that of low carbon steels, which contributes to an understanding of the alternation in importance of the mechanisms of heat transfer by radiation or conduction, in relation to the solidification of one or other type of steel in the mold.

Observation of the tenuous stability of the vitreous fraction of the film that ensures conditions of adequate lubrication in low carbon steels clarifies the understanding that minor fluctuations in the operational conditions in the mold, or even factors linked with the stages of processing of the steel prior to the CC, may undoubtedly induce losses in productivity.

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