EVALUATION OF THE MOLD FLUXES CRYSTALLIZATION BY MICROSCOPY TECHNIQUES

L. Santini, E. Benavidez and E. Brandaleze*.

Departamento de Metalurgia, Facultad Regional San Nicolás, Universidad Tecnológica Nacional, Argentina.
* Corresponding autor: ebrandaleze@frsn.utn.edu.ar, phone: 54 3461 420830 ext. 217, 54 3461 420820

Recibido: Octubre 2009. Aceptado: Diciembre 2009.
Publicado: Enero 2010.

ABSTRACT

In continuous casting of steel, mold fluxes are used to prevent surface defect, such as longitudinal cracks. The crystallization of these materials promotes mild cooling of the steel shell. The mold powder selection to be applied in plant depends on operation parameters, physical properties and crystallization grade. To know the crystallization kinetics is necessary to prepare laboratory samples because it is very difficult to extract samples from the process. This study was carried out to analyze the crystallization behavior at different thermal conditions. A commercial mold powder was melted at 1300ºC and then quenched to obtain solid layers. These layers were heat-treated in an electric furnace between 400ºC and 1000ºC, maintaining the samples at different times. Then, specimens were prepared to microstructural study and a particular etching technique was developed to reveal the crystals present in the glassy matrix. Light microscopy and scanning electronic microscopy (SEM) were applied to evaluate the crystallization evolution. The columnar crystals grains developed at the surface of the samples transform from dendritic pattern to polygonal and acicular crystals. Besides, irregular crystals nucleated about 400ºC in the glassy matrix increased in size with time and temperature up to 700ºC. Then these crystals become to dissolve. In particular, at 700ºC was possible to evaluate the increase of the surface crystalline layer and the dissolution rate of the irregular crystals. All this information was useful to understand the crystallization behavior at the mentioned temperature range.

Keywords: crystallization, microscopy, mold fluxes, continuous casting, steel.

EVALUACIÓN DE LA CRISTALIZACIÓN DE POLVOS DE COLADA APLICANDO TÉCNICAS DE MICROSCOPÍA

RESUMEN

En la colada continua de aceros, los polvos de colada se utilizan con el objetivo de prevenir defectos superficiales. La cristalización de dichos polvos de colada permite controlar la velocidad de solidificación del acero en el molde. La selección de un polvo de colada depende no sólo de los parámetros de operación, sino también de las propiedades físicas a alta temperatura y de la tendencia a la cristalización de los mismos. Conocer la tendencia a la cristalización de estos materiales requiere de la realización de ensayos de laboratorio dada la complejidad que presenta el proceso de extracción de muestras en forma directa. Por tal razón se recurre a la preparación de capas de material fundido a 1300ºC y templado. Estas capas, en este estudio, se tratan térmicamente en el intervalo entre 400-1000ºC con diferentes tiempos de permanencia. Las muestras se observaron por microscopía óptica (M.O.) y electrónica de barrido (M.E.B.) para evaluar su comportamiento de cristalización. Se observó el desarrollo de cristales columnares en la superficie de las muestras cuya morfología cambió a cristales poligonales y aciculares. Los cristales irregulares que nuclean en la matriz vítrea alrededor de 400ºC aumentan en tamaño hasta que se alcanza la temperatura de 700ºC, y luego comienzan a disolverse. En particular, fue posible determinar el crecimiento de la capa cristalina superficial y la disolución de los cristales irregulares. Toda esta información resultó útil para conocer el comportamiento de cristalización en el intervalo de temperaturas estudiado.

Palabras clave: cristalización, microscopía, polvos coladores, colada continua, aceros.

INTRODUCTION

In continuous casting process of steel, mold fluxes (or mold powders) are used for several reasons. They are: 1) thermal insulation of the molten steel, 2) prevention of molten steel oxidation, 3) absorption of inclusions floating in the mold, 4) lubrication between the solidified shell and mold, and 5) control the heat transfer. In these days, it is desired to increase the casting velocity to raise the productivity of steel. But in the case of middle carbon steels or hipo-peritectic steels, having high sensitivity to longitudinal surface cracking, is difficult to increase the casting velocity. It is known, that longitudinal cracking is caused by uneven solidification of steel. In order to avoid this problem is important to decrease the heat flux in the mold.

Mold flux crystallization, during the steel continuous casting process, leads to mild cooling of the solidified shell. It is relevant to mention that the interfacial thermal resistance between the mold and the crystalline layer of mold flux controls the total heat transfer because radiation heat flux decreases in the crystalline phase [1]. Nevertheless, crystallization behavior has been still uncertain.

Some studies have shown the effect of the cooling rate on the crystallization temperature, providing the critical cooling rate through CCT and TTT diagrams [2]. Mills et al. [3] determined the crystalline fraction of slags films by use of thermal analysis and Khater et al. [4] studied the crystallizing phases and microstructure in aluminosilicate glass.

In order to understand the crystallization process of the mold flux, in this study, mold flux samples were melted, quenched and heat treated at different temperature conditions. The shape, type and proportion of crystals phases in all the samples were determined by light microscopy. The results allow to think that these microscopy techniques contribute to increase the knowledge about mold fluxes crystallization mechanisms.

MATERIALS AND METHODS

The chemical composition of the mold flux used in this study is presented in Table 1.

Table 1. Chemical composition of the mold flux.

Chemical composition (wt %)					
SiO_2	**CaO**	**MgO**	**Al_2O_3**	**MnO**	**TiO_2**
31,4	26,7	1,8	4,4	0,06	0,20
Na_2O	**K_2O**	**F**	**P_2O_5**	**C_{free}**	**Fe_2O_3**
11	0,62	9,05	0,1	4,41	1,40

Sample preparation.

Sample of 15 g, were melted in an electric furnace at 1300ºC using a graphite crucible and then poured on a polished stainless steel plate. A solid layer with a few millimeters of thickness was obtained. Then, parts of this layer were heat treated in the interval 400 - 1000ºC during different times of maintenance (15 min, 60 min and 180 min). A sample without treatment was preserved to realize a comparative study.

All samples were molded in a polyester resin, polished by water proof paper, diamond paste and finally alumina slurry. Then, they were etched with nital 2 % for a few seconds.

Microscopy method.

The polished and etched samples were observed by light microscopy using an Olympus GX51 microscope.

To evaluate the crystallization tendency, the columnar crystals developed on the surface of the samples and the irregular grains nucleated in the matrix, were separately measured using the image analysis system IA32. The crystal layer developed at the surface of the samples was determined using a lineal measurement method. The software brings the maximum and minimum values, the average and the standard deviation of the each set of measurements. The evolution of the irregular grains was determined using the elliptical method. The image analysis system in this case brings the individual values and the respective average of height and width of the ellipse applied on each measured grain.

Samples microstructures were also observed by scanning electronic microscopy (SEM) using a Philips 505 microscope.

RESULTS AND DISCUSSION

Thickness of the columnar crystal layer.

In figure 1 is possible to observe the crystalline layer developed at the surface of the following samples: (a) as quenched, (b) treated at 700ºC - 180 min., and (c) treated at 900ºC – 15 min.

In the same micrographs it can be seen the straight lines used to calculate the layer thickness parameters.

It may be noted that these micrographs were taken at different magnifications.

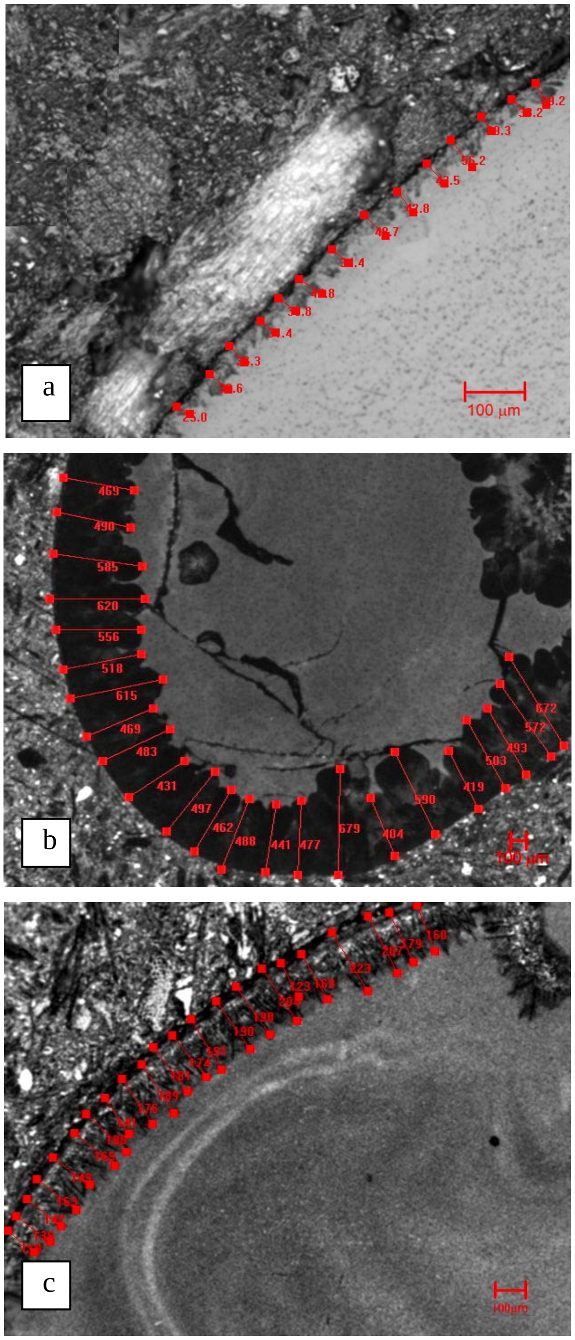

Fig. 1. Crystalline layer thickness measured by the lineal method on (a) as quenched, (b) 700ºC – 180 min and (c) 900º - 15 min samples.

The average thickness obtained for the samples: as quenched (without heat treatment) and heat treated at 400ºC, 700ºC, and 800ºC during 15, 60, and 180 minutes are present in Table 2.

Table 2. Thickness of the columnar crystal layer.
Note: (•) without heat treatment

Temperature (ºC)	**Maintenance Time (min)**	**Thickness (m)**
(•) 25	0	38,6
400	15	37,2
	60	
	180	
700	15	50,4
	60	138
	180	519
800	15	170
	60	394
	180	542

On basis of these results, it is possible to observe that the thicknesses of the crystalline surface layers change depending on the temperature and time conditions of the heat treatment.

It is important to consider that crystals in the surface layer are precipitated during quenching by a rapid crystallization from the supercooled melt. The main crystal stem grows quite rapidly during the early state of crystallization and at later stage primary branches grow at a slower rate out of stem, often at right angles to it. In this case the crystallization mechanisms involve previous nucleation in the melt and mass transfer through the liquid – solid interface [5].

Samples treated at 400ºC (15 min - 180 min) do not change the layer thickness of the columnar crystals respect of as quenched one, because at this temperature the diffusion process is not sufficient to promote these crystal growth.

Nevertheless, at 700ºC and 800ºC, an increase of crystalline layer thickness is observed and this phenomenon is enhanced with the increase of the heat treatment maintenance time. The crystal grows essentially by a diffusion process during which the deposition of solid in the face of the growing crystal is governed by the chemical composition gradient differences at the solid – solid interface [5].

Size of the irregular crystals.

In the sample treated at 400ºC - 180 min, small irregular crystal grains were identified in the glassy matrix. These irregular crystals grew under an equiaxed dendrite pattern. The growth process also was controlled by diffusion. Dubraswski and Camplin [6] report that for many fluorosilicate glasses a similar crystallization occur in the interval between 500 ºC and 690 ºC, after the glass transition temperatures (T_g).

In the present work, a size variation of the irregular crystals in the interval between 400ºC and 800ºC considering the different times of maintenance selected for this study was observed. Increases of the crystal size were detected in samples treated in the interval between 400ºC - 15 min and 600ºC - 60 min.

At 600ºC - 180 min the crystals not shown grain size changes, but at 700ºC between 15 min and 180 min, the irregular crystals in the matrix begins to dissolve.

In figure 2 (a), (b) and (c), the measurements realized on the samples treated at 700 ºC during 15 min, 60 min, and 180 min are observed.

Table 3. Values of height and width of the crystal.

Temperature (ºC)	**Time (min)**	**Height (m)**	**Width (m)**
600	15	18,2	18,9
	60	19,6	21,7
	180	18,8	18,8
700	15	170	174
	60	130	159
	180	61,2	69,8

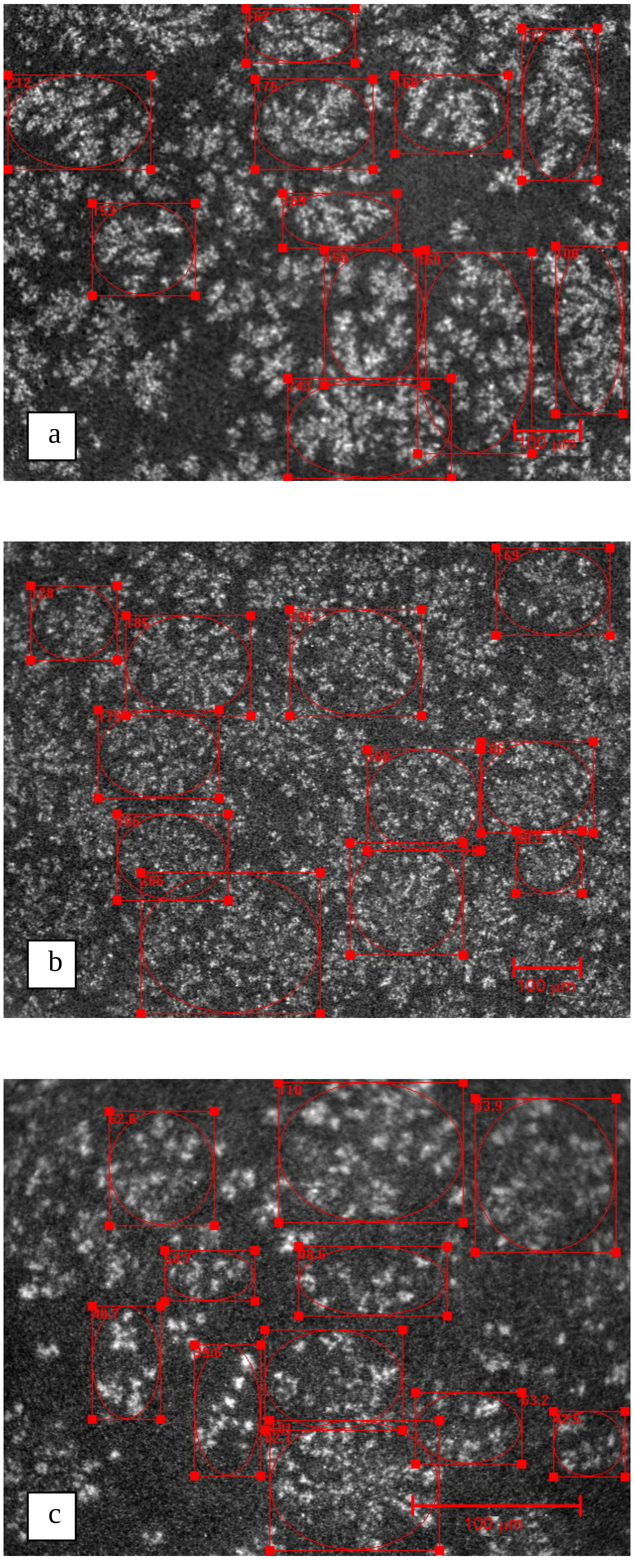

Fig. 2. Elliptical method applied to sample treated at 700ºC (a) 15 min, (b) 60 min, and (c) 180 min.

The values of height and width of the grains, measured in the samples treated at 600 ºC (15 - 180 min) and 700 ºC (15 - 180 min) are presented in Table 3.

These results are in agreement with a previous work [7] where mold fluxes containing F and Al_2O_3 developed a rapid formation and growth of crystals at low temperatures, even down 800 ºC.

At 800 ºC, a change in the morphology of crystals was observed. At this temperature, polygonal and acicular crystals were identified. It is important to mention that Lachnann and Scheller [7] also identify distinct crystals shapes at the same interval of temperatures applying double-hot-thermocouple-technique (D.H.T.T.) combined with X-ray diffraction analysis.

Crystallization percentage.

In order to determine the proportion of crystals formed in each sample at different heat treatment condition, the image analysis system was programmed to paint the matrix green and the crystals white. By this method it is possible to obtain a good contrast among the crystals and the amorphous matrix. An example of this method is shown in figure 3.

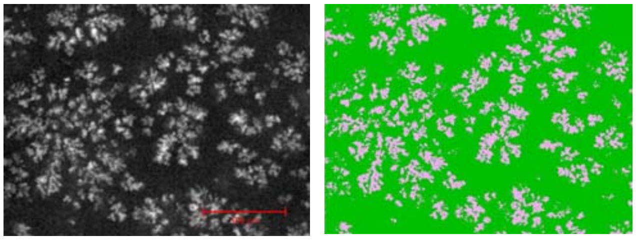

Fig. 3. Irregular crystals in the sample 700 ºC – 15 min, (a) original and (b) colored image.

The program quantifies the percentage of crystals in the selected area and also gives the standard deviation.

In Table 4, is possible to observe the values of crystallization percentage measured on the samples treated between 700ºC when the irregular crystals are dissolved and 1000ºC. At this last temperature, between 15 min and 180 min of maintenance time, an increase of crystal percentage is detected. These values confirm the polygonal and acicular crystals generation.

Table 4. Percentage of crystallization measured in the samples treated at 700ºC and 1000ºC.

Temperature (ºC)	**Time (min)**	**Crystallization (%)**
700	15	18,3
	60	12,2
	180	6,44
1000	15	8,04
	60	10,7
	180	18,4

Scanning electron microscopy.

The small crystals developed at higher temperatures than 800ºC were identified by light microscopy and the morphology verified by SEM.

In fig. 4, the polygonal and acicular grains present in the sample treated at 1000ºC during 60 min are observed.

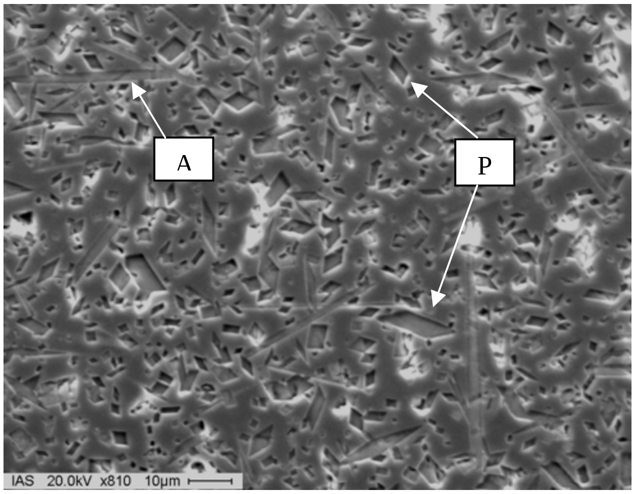

Fig. 4. Polygonal (P) and acicular (A) grains in the sample treated at 1000 ºC during 60 min.

Also, in the sample heated at 1000 ºC – 180 min, the morphology of the crystals located on the surface layer changed from columnar to different one, as it is shown in fig. 5.

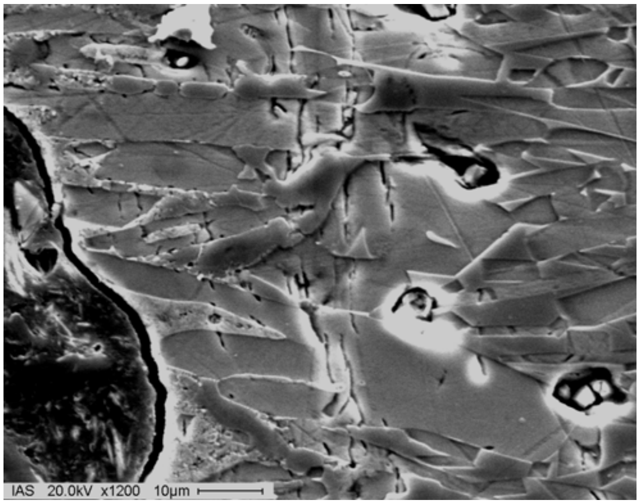

Fig. 5. Morphology of surface crystals in the sample treated at 1000 ºC during 180 min.

The morphology of the crystals at the center zone of the same sample, is shown in figure 6. In this case, crystals grains adopted round boundary morphology and the acicular grains began to loose their particular shape.

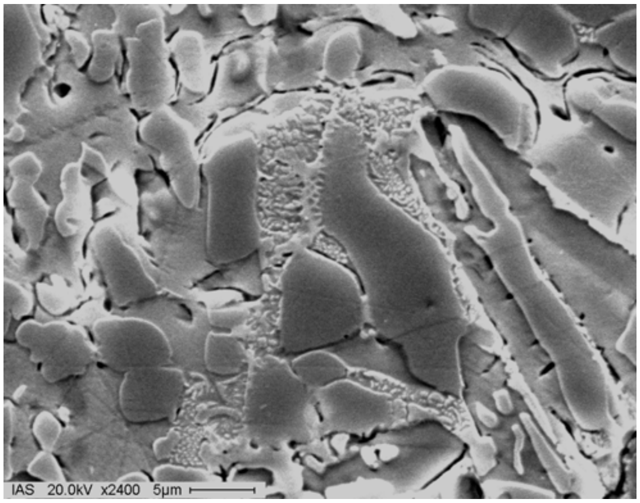

Fig. 6. Crystal morphology at the center of the sample treated at 1000 ºC during 180 min.

By this way, the light microscopy study clarifies the morphology evolution of crystals developed during each heat treatment selected for this study. Different crystal shapes are generated at different zones of the samples (surface and center), according to [1]. The columnar grains might grow from the surface of the specimen to the center. They constitute a crystalline surface layer and the thickness of it was determined by the lineal measurement. Fig. 7 shows the changes of this crystalline layer thickness at different time and temperature conditions.

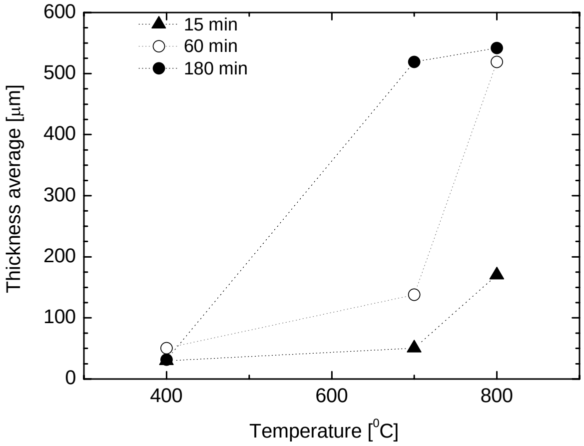

Fig. 7. Changes of the crystalline layer thickness with time and temperature.

At 400ºC the thickness of the columnar layer is approximately the same. But at 700ºC this thickness increase when the maintenance time increase. SEM observations show that the columnar grains have a dendritic growth.

Irregular grains are identified into the glassy matrix resulting of the crystallization process from the glassy state. These grains grew in a radial form and the temperature of nucleation is around 400 ºC.

In fig. 8 both phenomena the increase of the surface crystalline layer (see thickness) and the dissolution irregular crystals (see the percentage of crystallization) are presented.

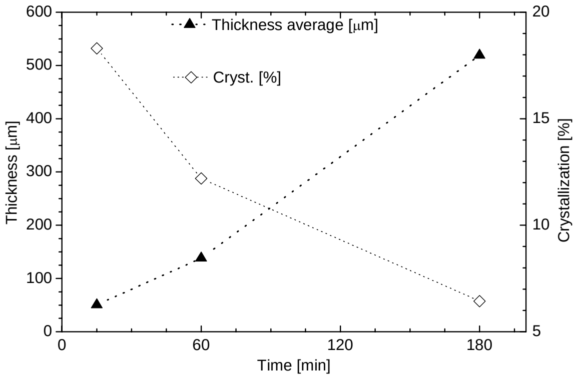

Fig. 8. Thickness increase of the surface crystal layer and dissolution of the irregular crystals at 700ºC.

At 800 ºC, the thickness of the surface columnar layer increase at 15 min and 60 min of treatment, but at 180 min, the crystals begin to dissolve. At higher temperatures (900ºC and 1000ºC) new crystal morphologies, acicular or polygonal shape, are identified in the central zone of the samples.

The morphological development of the crystals observed are related with a complex combination of different processes, including nucleation, growth, habit modification, phase transformation, ripening, agglomeration, and so on. The dominant system parameters are the supersaturation and the level of active cations or impurities.

Other researchers [8-10], describe that both mold flux chemical composition and temperature are the factors governing the type of crystals that can be formed. In Al_2O_3-CaO-SiO_2 systems, the driving force for precipitation is the volume-free energy change for crystallization of an infinitesimal amount of the phase at the expense of the metastable one. Crystal growth can be controlled by diffusion or interfacial reaction. For example, Na is not soluble in the crystalline phase and is rejected at the interface, so Na-concentration in the matrix is larger. On the contrary, Ca has a larger concentration in the crystals than in the matrix, so a depleted zone is formed in the matrix near the interfaces. In the case of Si, the concentration is similar in both phases (crystalline and glassy matrix). In this manner, the chemical composition gradient, the diffusion coefficients and thermal conditions determine the changes of the crystallization process in the samples. The crystal precipitation, transformation and dissolution of the phases in the matrix represent the future point of this study in order to complete the knowledge of mold fluxes crystallization process.

CONCLUSIONS

Columnar crystals grains with a dendritic pattern were develop at the surface of the samples. The thickness of this layer was measured by a lineal method applying an image analysis (light microscopy). This layer thickness increase at temperatures higher than 400ºC up to 800ºC.

Irregular crystals nucleated in the glassy matrix about 400ºC; increase in size with time and temperature up to 700ºC. Then these crystals become to dissolve. The elliptical measurement was useful to determine the evolution of the crystal size at different heat treatment.

At temperatures higher than 800ºC new morphology of the crystals were observed in the surface crystalline layer and in the center of the samples. The presences of polygonal and acicular crystals were confirmed by SEM.

The percentage of crystallization was determined bringing information of the crystals proportion at different temperatures and time. This information was consistent with the elliptical results on the crystal dissolution detected at 700 ºC.

From the present results, the light microscopy with basic tools of image analysis brings a new and simple form to evaluate the crystallization process of mold fluxes.

REFERENCES

[1] Mizuno H., Esaka H., Shinozuka K. and Tamura M. (2008), “Analysis of crystallization of mold flux for continuous casting of steel” *ISIJ International*, Vol.48, 3: 277-285.

[2] Wen G., Liu H. and Tang P., (2008), “CCT and TTT Diagrams to characterize crystallization behavior of mold fluxes”, *Journal of Iron and Steel Research*, 15: 32 – 37.

[3] Mills, K.C., Courtney L., Fox, A.B., Harris, B. Idoyaga, Z., Richardson, M.J. (2002) “The use of thermal analysis in the determination of crystalline fraction of slag films”, *Thermochimica Acta*, 391: 175-184.

[4] Khater G.A., Idris M.H., (2007), “Role of TiO_2 and ZrO_2 on crystallizing phases and microstructure in Li,

Ba aluminosilicate glass", *Ceramics International*, 33: 233-238.

[5] Mullin J. W. (2004), "Crystallization", *Elsevier Butterworth Heinemann*, 4th edition.

[6] Dubrawski J.V. and Camplin J.M., (1993) "Crystallization of mould powders used in the continuous casting of steel", *Journal of Thermal Analysis*, 40,329-334.

[7] Lachnann S., Scheller P. R., (2008) "Crystallization behavior of synthetic mould slags", *Proceeding of 6th European Conference on Continuous Casting 2008, Italy*.

[8] Rocabois P., Pontoire J. N., Lehmann J., Gaye H. (2001) "Crystallization kinetics of Al_2O_3-CaO-SiO_2 based oxide inclusions", *Journal of Non-Crystalline Solids*, 282, 98-109.

[9] Nakada H., Fukuyama H., Nagata K., (2006) "Effect of NaF addition to mold flux on Cuspidine primary field", *ISIJ International*,46, 11, 1660-1667.

[10] Vermeulen Y., Divry E., Rigaud M., (2004) "The influence of chemical composition on the crystallization and the heat transfer of synthetic mould fluxes", *Canadian Metallurgical Quarterly*, 43, 4, 527-534.