

Mold flux characterization for thin slab casting of steel^(*)

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Abstract

The mineralogical constitution and the melting-solidification behavior of two commercial fluxes for thin slab casting of steel were determined. The characterization of the commercial fluxes as received show the presence of wollastonite ($\text{CaO} \cdot \text{SiO}_2$), a sodium carbonate (Na_2CO_3), calcite (CaCO_3), fluorite (CaF_2) and carbon as the main components by X ray powder diffraction (XRD) and microscopic techniques. When fluxes were heated to 1573 K and further solidification, there was almost a whole transformation from the original compounds to cuspidine ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) and nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phases. The thermal gravimetric analysis showed an important weight reduction in both fluxes due to the thermal decompositions of calcite and sodium carbonate. The characterization reveals that fluxes are produced by an agglomeration process.

Keywords

Fluxes; Particle size; Cuspidine; Nepheline.

Caracterización de fundentes para molde de planchón delgado de acero

Resumen

Se determinó la composición mineralógica y el comportamiento de fusión-solidificación de dos fundentes comerciales para la colada de planchón delgado de acero. La caracterización de los fundentes comerciales por difracción de rayos X (XRD) y técnicas de microscopía muestra la presencia de wollastonita ($\text{CaO} \cdot \text{SiO}_2$), un carbonato de sodio (Na_2CO_3), calcita (CaCO_3), fluorita (CaF_2) y carbono como los principales componentes. Cuando los fundentes se calentaron a 1.573 K y después de la solidificación, hubo una transformación casi total de los compuestos originales a las fases cuspidina ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) y nefelina ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). El análisis termogravimétrico muestra una importante reducción de peso en los fundentes debido a la descomposición térmica de la calcita y el carbonato de sodio. La caracterización indica que los fundentes son producidos por un proceso de aglomeración.

Palabras clave

Fundentes; Tamaño de partícula; Cuspidina; Nefelina.

1. INTRODUCTION

Mold powders or mold fluxes are synthetic slags used to cover the liquid pool surface during the continuous casting of steel slabs^[1]. Mold powders for continuous casting molds are mechanical blends of several materials^[2 and 3], such as ashes, blast furnace slag, minerals, etc. Mold powders must fulfill several functions during the continuous casting of steel, like the protection of the metallic surface from oxidation, the thermal isolation of the surface, the absorption of non-metallic inclusions, the lubrication of the mold/metal contact area and the control of the heat transfer to the mold. They play an important role in the surface quality of the steel product and in the

overall efficiency of the continuous casting process control. More recently, high speed continuous casting was developed in order to improve productivity and conserve energy in the continuous casting of steel slabs^[4 and 5]. Improvement in mold lubrication is therefore crucial for efficient high-speed casting, and mold powder has been developed for this purpose. Thin slab casting powders are mixtures of oxides generally based on the SiO_2 - CaO - CaF_2 - Na_2O system. In some cases, they may contain Al_2O_3 , MgO , and K_2O as minority compounds. Graphite in 3 to 6 % is also commonly found in the fluxes to control the melting flux behavior, which depends on both their chemical composition and mineralogical constitution. Both the melting behavior and the melting rate of the powder

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control the depth of the molten slag pool and, consequently, the rate of infiltration of liquid slag into the mold/strand gap. The amount of liquid slag formed depends on several factors such as the thickness of the solid powder layer, the graphite content, the particle size and the apparent density of the powder. There are considerable variations in the constituents used by powder manufacturers, and when the casting powders are heated the constituents react to form different mineralogical phases^[6]. The structure of MO-SiO₂ (MO represents a basic oxide) systems has been extensively studied by metallurgist, glass scientists, and mineralogist; however, the CaF₂ addition to this system presents some contradictory results. Contrary to Na₂O, the addition of fluoride as CaF₂ to mold fluxes considerably reduced the viscosity, the melting point and the activation energy. However, the opposite behavior was observed when CaF₂ is present in higher quantities in mold fluxes, this is due to the fluoride capability of surpassing crystallization^[6 and 7]. The mineralogical constitution of the powder is of particular importance since it affects the melting rate of the powder, the lubrication characteristics and the heat transfer between the strand and the mold, thus impacting decisively the casting performance^[8 and 9]. One of the most effective means to decrease the heat flux is to use highly crystallizing mold fluxes. A crystalline layer in the slag film yields larger thermal resistance by producing air gap at the flux/mold interface. Cuspidine (3CaO·2SiO₂·CaF₂) is one of the most important crystallized compounds in mold flux film during thin slab casting process. Watanabe *et al.*^[10],

determined the primary crystallization field and the melting temperature of cuspidine. Differential thermal analysis have been carried out in order to determine the changes in thermal properties of mold flux^[11 and 12]. Romo *et al.*^[13], determined thermodynamically the stability phase diagrams of mineralogical species at different chemical compositions and temperatures. However, in spite of its importance, it does not exist any technical criterion or specification leading to the proper selection of flux powders for the continuous casting; instead, the selection of the powders is based on the casting expertise in each individual plant. Therefore, it becomes practically impossible to predict or control the surface quality of the slab. In this work, a study of the mineralogical and thermal behavior of two commercial fluxes for thin slab casting of steel was developed by microscopic techniques, X-ray diffraction and thermal gravimetric analysis.

2. EXPERIMENTAL

Two commercial mold fluxes (named A and B) used in an integrated steelmaking shop were studied; their chemical composition reported in their technical data sheet are shown in table I.

The samples were analyzed as received and after a heat treatment at 1573 K and cooled at two different rates. In one experiment, the fluxes were cooled slowly inside the furnace and in the other test they were rapidly cooled by pouring the molten flux on a copper

Table I. Chemical composition of commercial mold fluxes

Tabla I. Composición química de los fundentes para moldes comerciales

Chemical compounds	Mold fluxes (wt %)	
	A	B
SiO ₂	31.0-33.0	32.0-34.0
CaO+MgO	32.5-34.5	32.5-35.5
Al ₂ O ₃	2.5-4.0	2.0-3.0
Fe ₂ O ₃	< 1.5	< 1.5
MnO	2.0-3.5	< 0.1
Na ₂ O+ K ₂ O	7.0-9.5	11.0-12.5
F	4.5-6.0	6.0-7.0
C _{libre}	3.5-5.0	3.0-4.0
CO ₂	7.5-9.0	9.0-10.5
C _{total}	6.0-7.5	6.0-7.0
H ₂ O _{600°C}	< 1.0	< 1.0

plate. Both fluxes are used to produce medium carbon (0.07 - 0.1 % C) and peritectic (0.09 - 0.15 % C) steel.

2.1. Specimen preparation

The fluxes were compacted with a load of 1 ton within a stainless steel die to produce small cylinder flux samples of 6 mm diameter and 10 mm height. These samples were heated to their fluidity temperature, which was previously determined. The melting solidification test involves the comparison of the height of a cylindrical flux sample, (6 mm diameter and 10 mm height) with those of two different reference alumina tubes (8 and 5 mm height, respectively) as was reported by Cruz *et al.*^[6]. In order to know the degree of crystallinity, 30 g of each flux were contained in a platinum crucible and heated up to 1573 K in a Lindberg/Blue STF54434C tube furnace and then cooled slowly (~ 3 K/min) inside the furnace and rapidly (~ 250 K/min) by pouring the molten flux on a copper plate. The slag obtained was crushed to the size less than 100 µm and analyzed by X-ray powder diffraction.

2.2. Microscopic characterization

The size, morphology and a qualitative chemical analysis of the mold fluxes were determined with the SEM Jeol 6300 and with the energy dispersive spectra (EDS) analysis. An Au-Pd film was deposited on the surface of the powders to make them conductive. Images were obtained at 20 and 500 X with backscattering electrons with 15 Kv and 10 Amp. An

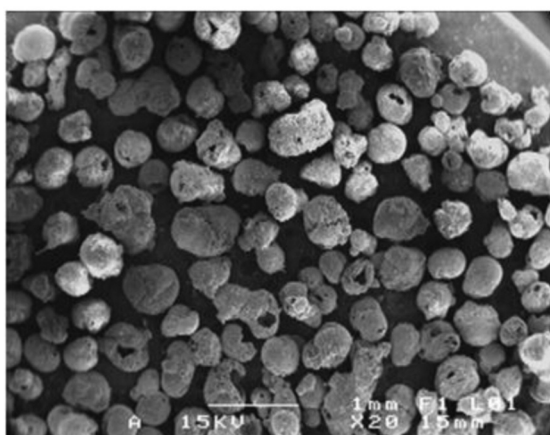


Figure 1. Microphotographs of commercial flux A to 20 X and its particle size distribution.

Figura 1. Fotomicrografías del fundente comercial A a 20 X y su distribución de tamaño de partícula.

image analysis was carried out at 10 X with the software image Pro Plus 4.0 to determine the particle size distribution. The mineralogical species were identified with a polarizing light microscope (Olympus BX41) at 20 X following a known technique^[14 and 15].

2.3. X Ray-Diffraction

The samples were analyzed in an X-Ray Bruker D8 Focus with monochromatic Cu K α radiation working in $\theta/2\theta$ configuration. Data were collected in an angular range from 20 to 100° with a step size of 0.02° and a counting time of 2° min⁻¹.

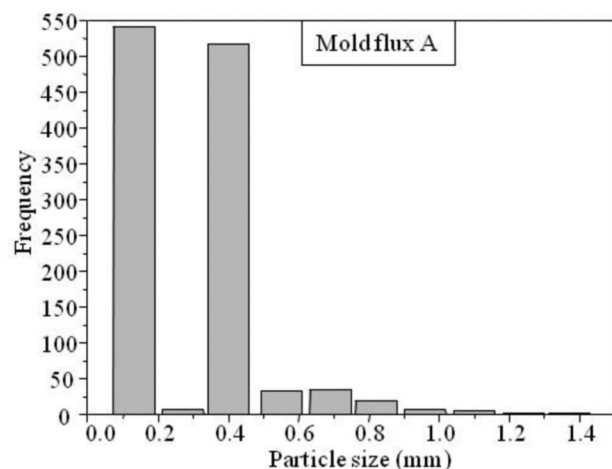
2.4. Thermal gravimetric analysis

A thermal gravimetric analyzer Mettler Toledo TGA/SDTA 851 was used to characterize the molten flux. A heating rate of 10 °C min⁻¹ was used with a nitrogen flow rate of 50 ml min⁻¹ in alumina crucibles. Data were collected in a temperature range from 250 to 1100 °C.

3. RESULTS AND DISCUSSION

3.1. Microscopic characterization

The results of the scanning electron microscope and the particle size distribution are shown in figures 1 and 2 for fluxes A and B, respectively for 20 X.



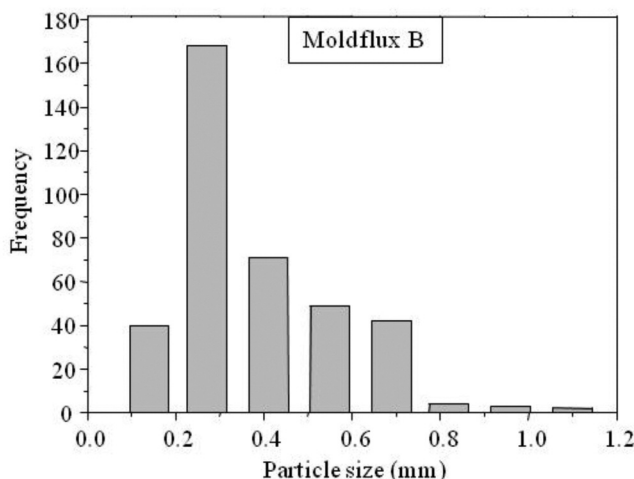
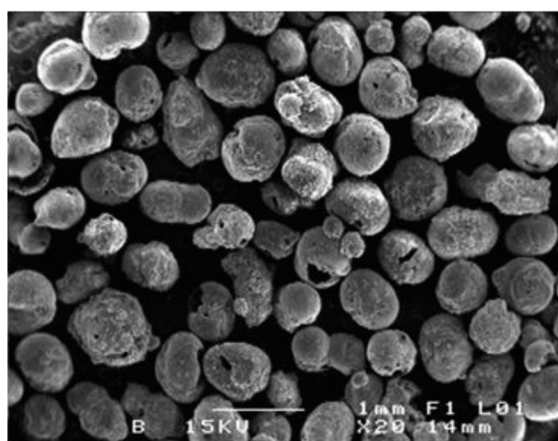


Figure 2. Microphotographs of commercial flux B to 20 X and its particle size distribution.

Figura 2. Fotomicrografías del fundente comercial B a 20 X y su distribución de tamaño de partícula.

It is observed that fluxes are hollow semi-spherical agglomerates in the range of 0.1 mm (100 μm) to 1.4 mm (1400 μm) in size. The higher quantity of material is in the range from 0.1 to 0.7 mm for the A flux, instead of 0.1 to 0.4 mm for the B flux. It must be noticed that, B flux contains the largest amount of fine particles; consequently it could be used at the beginning of the continuous casting process for the needed of a fast melt. However, the high content of particles sizing between 0.1 and 0.7 mm seems to be enough to meet the requirements of their specific melt process. The photomicrographs and the energy dispersive spectra obtained by scanning electron

microscope of the surface and the inner part of the A flux to 500 X are shown in figures 3 and 4, respectively.

As can be observed in figure 3, the powder surface is constituted mainly by sodium as Na_2CO_3 with small amounts of gold and palladium, which are due to the film deposited on the surface of the powders.

Silicon and calcium were also detected in minimum quantities. The inner part of the powder is constituted mainly by silicon and calcium, which can be attributed to the wollastonite ($\text{CaO} \cdot \text{SiO}_2$) and calcite (CaCO_3). Other elements were detected

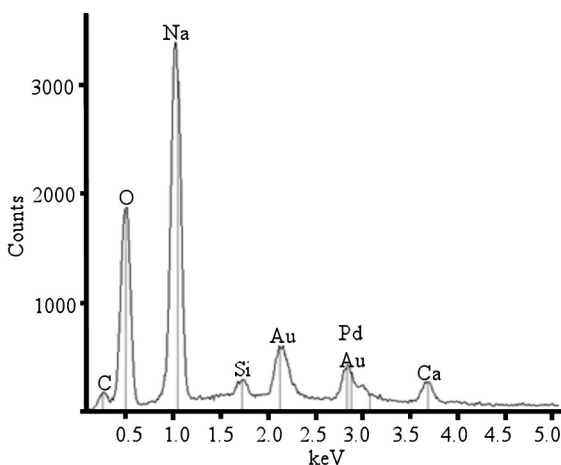
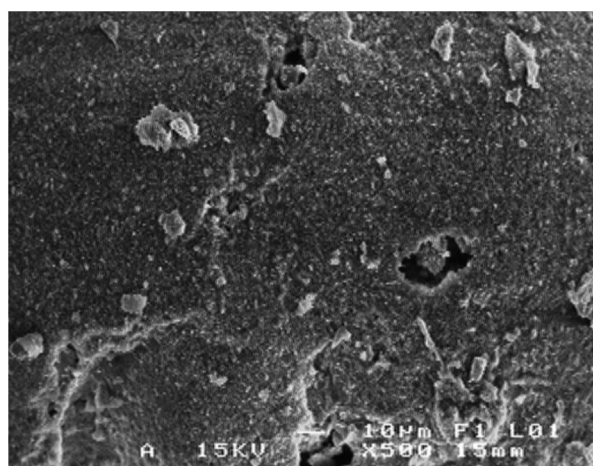


Figure 3. Microphotographs of the surface of commercial flux A to 500 X and its energy dispersive spectra.

Figura 3. Fotomicrografías de la superficie del fundente comercial A a 500 X y su espectro de energía dispersa.

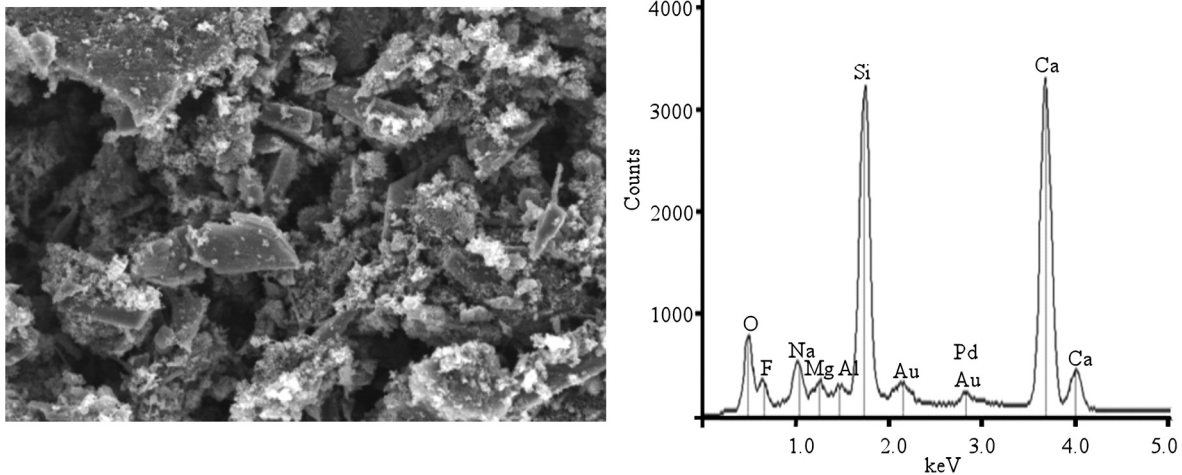


Figure 4. Microphotographs of the inner part of commercial flux A to 500 X and its energy dispersive spectra.

Figura 4. Fotomicrografías de la parte interna del fundente comercial A a 500 X y su espectro de energía dispersa.

in small amounts like aluminium, magnesium, sodium and fluorine. Fluxes according with their chemical composition contains higher amounts of fluor for fluorite (CaF_2), however the EDS technique is not appropriately to detect elements with low atomic number like fluor. Similar results were obtained for B flux. The micrographs of the commercial powders and the species identified in each of them are shown in figure 5 for both powders.

As can be seen, three kinds of mineral species, namely wollastonite, fluorite and opaque minerals, although in different proportions and with particular

morphologies, constitute the main components of the commercial fluxes. The general composition for the wollastonite in the figure 5 is $(\text{CaO} \cdot \text{SiO}_2)$ and occurs in tabular crystals for both fluxes. Fluorite (CaF_2), occurs in subhedral crystals in both fluxes, according with its cleavage properties, fluorite crystals are observed with a triangular pattern. Opaque minerals occur in anhedral crystals, and are considered to be hematite ($\alpha\text{Fe}_2\text{O}_3$) and graphite (C). Therefore, the commercial fluxes analyzed contain wollastonite a rich source of CaO and SiO_2 , the opaque minerals the source of FeO and carbon, and fluorspar the source

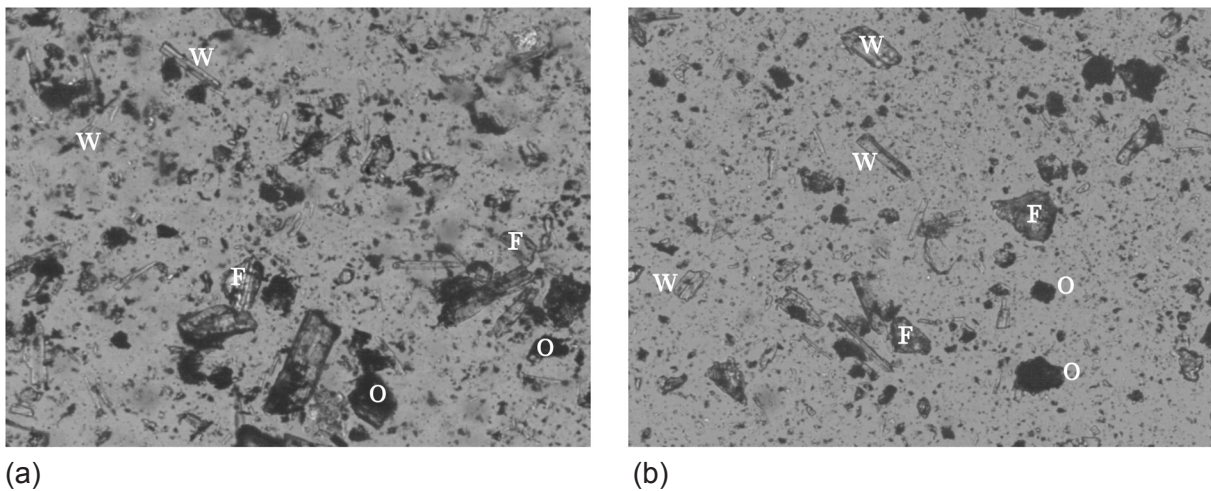


Figure 5. Microphotographs of commercial fluxes to 10 X for a) flux A and b) flux B: showing wollastonite W, Fluorite F and opaque minerals O.

Figura 5. Fotomicrografías de los fundentes comerciales a 10 X para a) fundente A y b) fundente B: se observa wollastonita W, Fluorita F y minerales opacos O.

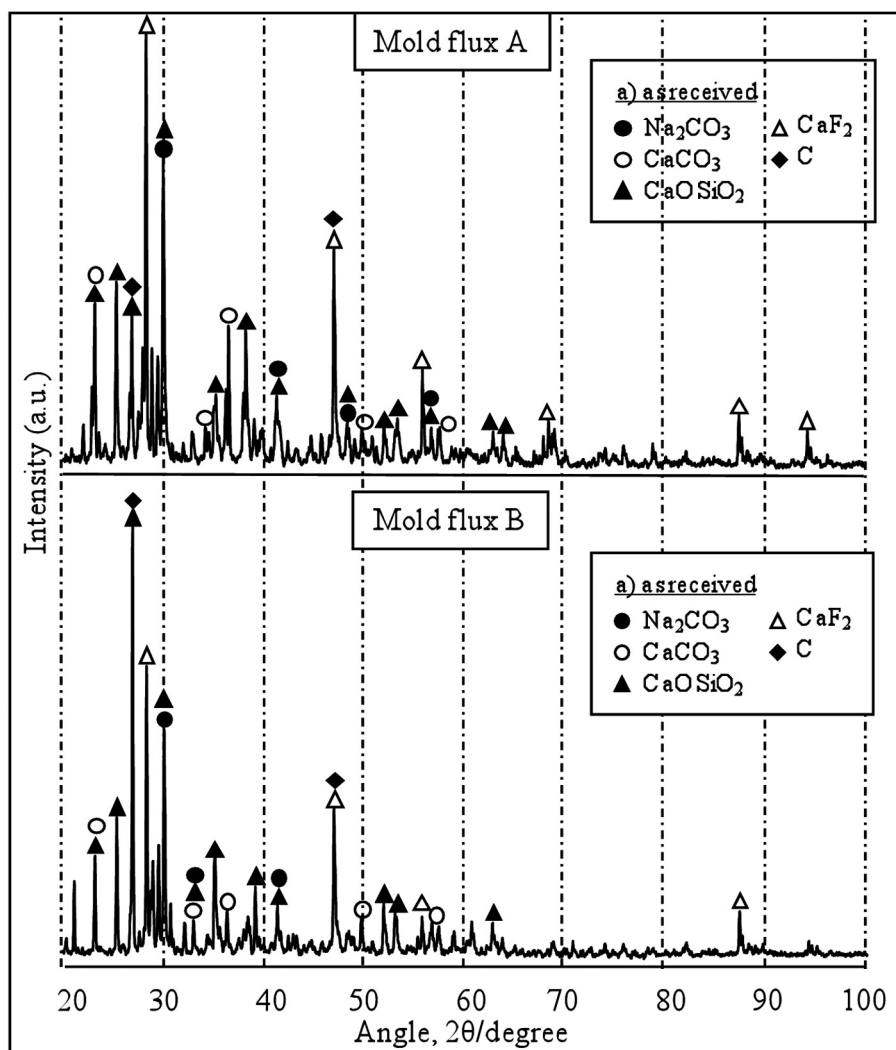


Figure 6. XRD patterns of the fluxes A and B, as received.

Figura 6. Patrón de difracción de rayos X de los fundentes A y B, como se recibieron.

of CaF_2 . The XRD patterns of the tested fluxes are shown in figure 6 for both fluxes.

The powders as received show simple chemical compounds such as CaCO_3 , C, CaF_2 , Na_2CO_3 . It is also observed the presence of wollastonite ($\text{CaO} \cdot \text{SiO}_2$), which appears in both fluxes as received.

3.2. Melting behavior

Table II shows the softening, melting and fluidity temperatures determined for each of the commercial fluxes studied.

As can be observed, the fluxes A and B, both possess high softening, melting and fluidity temperatures, as expected for powders used to produce

medium and peritectic carbon steels. When both fluxes were heated to 1573 K and cooled slowly, two mineralogical phases were formed: these are the cuspidine ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) and nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with small amounts of limestone (CaCO_3) and fluorite (CaF_2) as can be observed in figure 7.

The quantity of these phases was different in each flux, according to their original chemical composition. The slow cooling velocity allows almost a whole transformation from the original compounds to cuspidine and nepheline phases. An amorphous phase was observed in both fluxes for the fast cooling velocity.

The thermal gravimetric analysis reveals a similar behavior for both fluxes and figure 8 presents only the TGA results for the mold flux B.

Table II. Softening, melting and fluidity temperatures for the commercial fluxes

Tabla II. Temperaturas de ablandamiento, fusión y fluidez de los fundentes comerciales

Flux	Temperature (K)		
	Softening	Melting	Fluidity
A	1271	1321	1375
B	1238	1337	1371

The TGA curve shows a weight reduction of 12.5 % in the range of 450 to 900 °C, which is in good agreement with the amount of CO₂ released and reported in the chemical analysis for B flux. This weight reduction corresponds to thermal

decompositions of calcite (CaCO₃) and sodium carbonate (Na₂CO₃) releasing CO₂ gas. Also has been reported^[12] that exists a loss of silicon tetrafluoride in the temperature range studied. According with the mold flux characterization, the

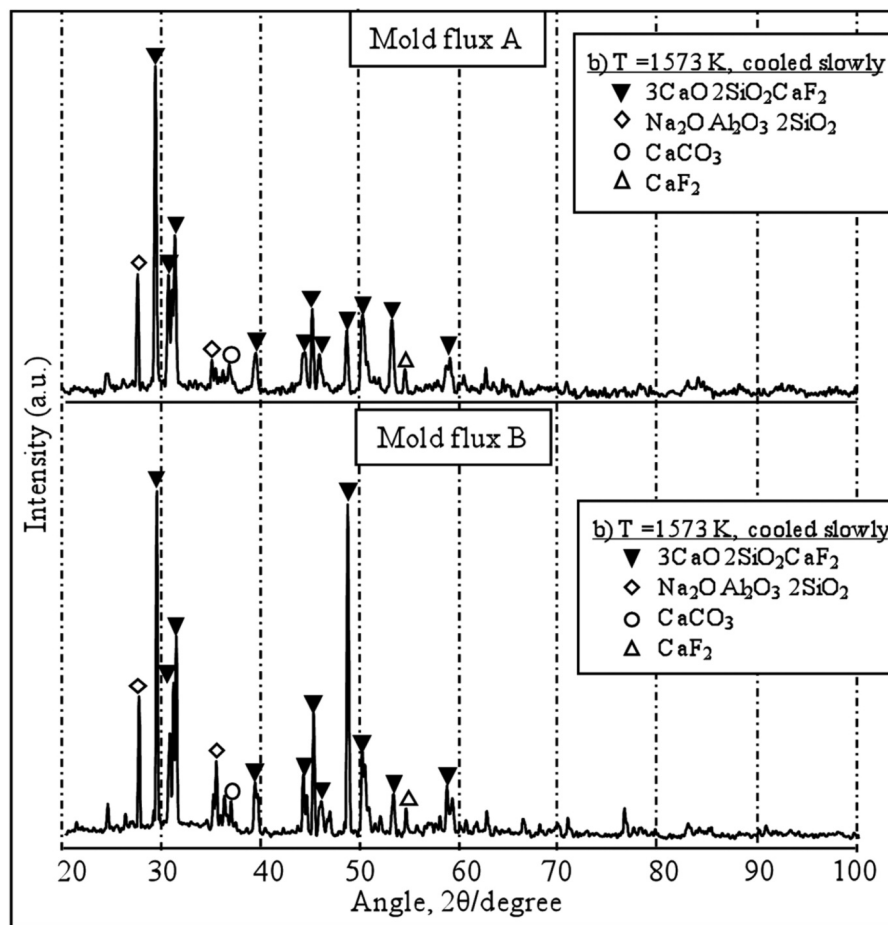


Figure 7. XRD patterns of the fluxes A and B, heat treated to 1573 K and cooled slowly.

Figura 7. Patrón de difracción de rayos X de los fundentes A y B, tratados térmicamente a 1.573 K y enfriados lentamente.

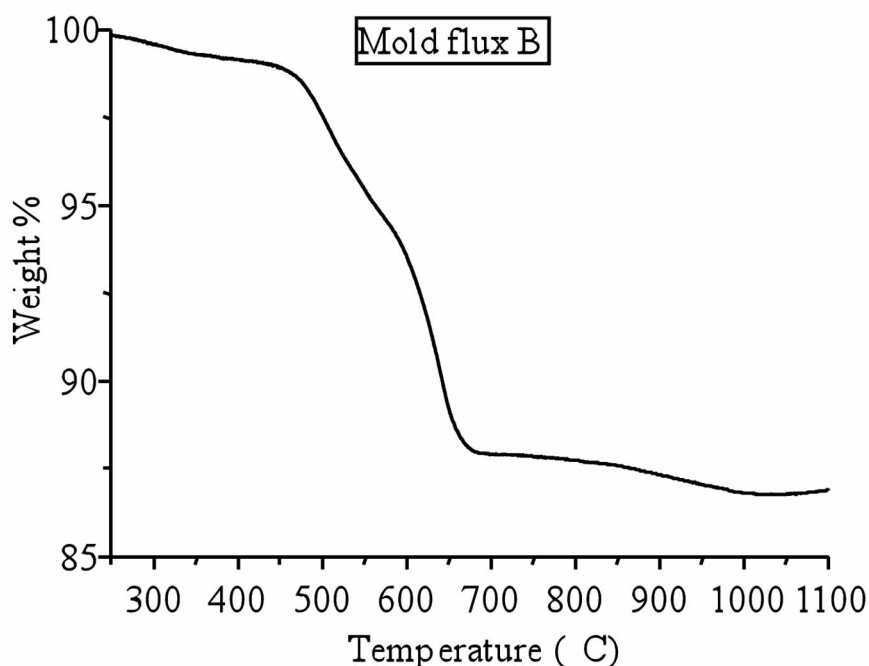


Figure 8. Thermal gravimetric curve of the flux B.

Figura 8. Curva termo-gravimétrica del fundente B.

spherical granular fluxes are manufactured by an agglomeration process like spray drying, where the sodium carbonate and carbon enclose the fluorite, wollastonite and calcite. The spherical shape allows a good flowability and minimal segregation or dust formation of raw materials, while the carbon on the outside of each granule allows a high melting speed which is desirable for the thin slab casting process. The melting solidification behavior results indicate that the casting process could be developed with the amorphous phase formation by the flux in the layer closer to the mold due to the fast cooled velocity, increasing the heat transfer from strand to mold. Closer to the amorphous phase a crystalline layer constituted mainly by cuspidine in the slag film yields larger thermal resistance by producing air gap at the flux-mold interface decreasing the effect of the strong shrinkage of peritectic steels.

4. CONCLUSIONS

— The mineralogical analysis revealed that commercial mold fluxes used in the thin slab casting of steel are produced by an agglomeration process. The spherical shape and size of granular fluxes allows a good flowability and melt requirements for the cast process. A layer of sodium carbonate and carbon enclose the fluorite,

wollastonite and calcite, which are the main components in the flux. XRD analysis confirm that the principal components of commercial fluxes are sodium carbonate fluorite and wollastonite and that the heat treatment at 1573 K induces the formation of cuspidine and nepheline phases for the slow cooling condition.

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