

MOULD POWDER SLAGS IN CONTINUOUS CASTING (CC):
CHARACTERIZATION AND EVALUATION OF CHANGES – A DRIVING FORCE
FOR THE DEVELOPMENT OF NEW PRODUCTS.

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ABSTRACT

The characterization and performance evaluation of mould flux powders at steel industries is very important nowadays. The materials science has been shown as an important tool for the comprehension of the processes that happen at the slab-mould interface and for the explanation and solution of problems occurring during the continuous casting (CC). The materials generated at this interface are the responsible for lubrication and heat transfer through the slag film. The performance change of the mould flux powder during the CC is a constant concern related to the productivity and slab surface quality. The most frequent contaminants on the mould slags are MgO, CaO, Al₂O₃, ZrO₂ e TiO₂. These arise from covering materials, slags, refractory materials and active additions, and may change the mould flux slags properties. The fluorine vaporization is also an important aspect to be considered, as it may change the viscosity, reducing the fluidity of the slag (the responsible for the slab-mould lubrication). The determination of T_{solidification}, T_{crystallization} (crystallization tendency of the mould flux powders and slags), T_{fluidity} (vaporization and contaminants influence) play a very important role in this study. The objective of this study was to characterize mould flux powders and slags and evaluate the changes of the performance parameters related to the slab-mould interface. The confirmation of the influence of chemical changes on the mould slags properties, are the driving power for the development of tailor-made products, able to minimize the modification of the properties of the mould slags. DTA, TGA, Heating Microscopy and XRD were used in this study.

INTRODUCTION

The increasing industrial development occurred along the twentieth century has demanded huge quantities of iron and steel. In order to reach the necessary productivity to supply the demand, many steel industries, at the first half of the twentieth century, changed the way the molten steel was converted to the solid state. They implanted a technique in which the steel was continuously cast. From then on, several tons of steel could be cast without exchanging the mould, as happened in the previous process (conventional casting).

The continuous casting (CC) (Figure 1) involves the transfer of the steel from ladles to the tundish. This one conveys the molten steel to one or more moulds through submerged entry nozzles (SEN). When inside the mould, the steel undergoes cooling and continuous oscillatory movement, allowing the extraction of the slab. This operation requires the use of a

material in order to decrease the friction at the slab/mould interface, allowing the sliding of the slab and the minimization of imperfections at its surface.

The materials called mould powders, besides lubricating the slab/mould interface, they promote the thermal and atmospheric insulation of the molten steel, avoiding premature cooling and re-oxidation, regulate and homogenize the heat transfer between the slab and the mould and absorb non-metallic impurities enclosed in the steel.

There are four main classes of mould powders ¹:

- Waste-based – mixture of powders in which ashes and blast furnace slag are the major constituents. As the properties of different shipments of wastes may not be constant, their properties as mould powders may change and prejudice its performance. They are commonly used in Europe.
- Synthetic – mixtures of common industrial powdered raw materials. Their properties are constant, but as they are finely divided, they commonly present some loss of very fine powder to the atmosphere, decreasing the quality of the air around the mould. Besides this, the raw materials undergo some chemical reactions inside the mould before the viscous liquid is formed, increasing the possibility of damage to the slab if the mixture enters in the slab-mould interface before the formation of the liquid. There is also some money waste related to the loss of powder to the environment and to the elimination of water of the raw materials used ^{2,3,4}.
- Pre-melted – the raw materials are melted and milled. This material is very homogeneous, has very good performance at the mould and does not present the disadvantages of the previous ones. However, it is much more expensive than them ^{2,3}.
- Granulated – spherical or extruded materials (agglomerated or aggregated). This material performance is almost as good as the pre-melted one, it does not generate air pollution and has an intermediate price between the synthetic and the pre-melted one ^{5,6}.

When added at the top of the mould, the mould powder melts generating a highly viscous liquid (mould slag). It penetrates the slab/mould interface and solidifies when in contact with the cooled walls of the mould, generating a glass in which, in some cases, crystalline phases grow. The occurrence of crystallization is related to the chemical composition of the mould powder, the changes in chemical composition related to absorption of impurities from the steel, and the temperature profile along the interface at the four walls of the mould (Figure 2).

When the mould slag incorporates the impurities coming from the steel, its chemical composition changes and its properties and performance may be affected. For example, if it causes an excessive increase in viscosity during the casting, the slab surface may be damaged or the operation may be interrupted if the skin (solidified steel) of the slab is tore, resulting in loss of profitability. The crystallization of the mould slag may also be altered by the incorporation of impurities from the steel. Mould slags that crystallize at higher temperatures have thicker crystalline layers and this may affect the good performance of the casting.

Magnesium, calcium, aluminum, zirconium and titanium oxides (MgO, CaO, Al₂O₃, ZrO₂ and TiO₂) are some of the most common contaminants the mould slags assimilate. Their origins

come from the addition of powder aluminum to the steel in order to deoxidize it, slags, and from erosion of refractories in contact with the steel. Aluminum and zirconium oxides have remarkable effects on the mould slag properties ⁷ (Figure 3), as soon as they increase not only viscosity, but also the crystallization temperature (Figure 4) ⁸.

The heat transfer from the slab to the walls of the mould is regulated by the structure present at the interface, being more intense when there is no crystallization. The crystalline layer present at the mould slag profile decreases the heat transfer by means of radiating energy. Therefore, mould slags that scarcely crystallize allow a faster heat withdrawal (conduction and radiation) than the ones who crystallize intensely. The necessity of a faster or lower heat transfer from the slab to the mould depends on the nature of the steel being cast (Figures 5 and 6) ⁹.

Another phenomenon responsible for changes in mould slag properties is the loss of fluoride compounds during the continuous casting (Figure 7). The fluorine role in the mould powders is to decrease the mould slag viscosity and allow its adequate performance. However, at the high temperatures reached at the mould and because of some large periods of casting at low speed for solving operational problems, some fluorine compounds become volatile and are evolved. Therefore, the decrease of the fluorine content of the mould slag implies in the increase of the mould slag viscosity and the modification of its crystallization temperature, rising the risk of damage at the slab surface or interruption of the process ¹⁰.

The aspects exposed above point out the important role of mould powders in CC, showing the necessity of studies on the nature changes undergone by the mould slags inside the mould, reflecting on changes of properties and performance. This work shows how some mould slags have their properties modified during the CC.

EXPERIMENTAL PROCEDURE

Three different mould powders were studied. Two of them (**MP1** and **MP2**) are applied in CC of low carbon steels (0.02 – 0.08 %) with speeds of 1.30 – 2.20 m/min (MP1) and 0.80 – 1.30 m/min (MP2). The third one (**MP3**) is used in CC of medium (0.09 – 0.14 %) and high (0.15 – 0.23 %) carbon steels with speeds of 1.25 – 1.40 m/min.

The characterization of mould powders was performed by means of:

- Chemical Analysis (CA)
- Emission Spectrometry (ES)
- Thermogravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)
- Heating Microscopy (HM)
- X-ray Diffraction (XRD)

The mould powders (MP1,MP2 and MP3) were melted in platinum cups and quenched in a steel plate in order to obtain mould slags free of contamination (MS1-0, MS2-0 and MS3-0).

Some mould slags of each mould powder were collected at the beginning and at the end of a single CC operation, representing the evolution of the mould slag (MS1-1 and MS1-2; MS2-1 and MS2-2; MS3-1 and MS3-2).

The characterization of mould slags was performed by means of: Emission Spectrometry (ES), Differential Thermal Analysis (DTA), and Heating Microscopy (HM).

Some samples of mould slags were heat treated in electric oven according to the exothermal peaks of the DTAs and submitted to XRD analysis, in order to study the profile of crystallization of these slags.

RESULTS AND DISCUSSION

The characterization of the mould powders are found at:

- Table 1 – Chemical Analysis (CA)
- Table 2 – Emission Spectrometry (ES)
- Table 3 and Figure 8 – Thermogravimetric Analysis (TGA)
- Table 4 and Figure 9 – Differential Thermal Analysis (DTA)
- Table 5 and Figure 10 – Heating Microscopy (HM)
- Table 6 and Figure 11 – X-ray Diffraction (XRD)

The exothermal peaks at the DTAs during the heating of the samples and the losses of mass pointed out by the TGAs are related to the burnout and/or decomposition of carbonaceous materials¹¹ that constitute the mould powders, which function is the regulation of the melting rate¹².

The exothermal peaks in the DTAs during the cooling show remarkable differences in the crystallization profile of the mould slags generated by these mould powders, indicating the different properties of these during CC.

The characteristic temperatures (HM) obtained for these mould powders point out their different viscous behavior during CC, becoming more viscous from MP1 to MP2 and to MP3.

The crystalline phases (XRD) present in the mould powders are very common raw materials for mould powder production.

The characterization of the mould slags are found at:

- Table 7 – Emission Spectrometry (ES)
- Figure 12 – Differential Thermal Analysis (DTA)
- Table 8 and Figure 10 – Heating Microscopy (HM)
- Figure 13 – X-ray Diffraction (XRD)

Table 7 shows remarkable increase in Mn and Zr contents between the non-contaminated slags and the ones collected from the mould for the three kind of mould powders studied. The Mn effect on the mould slag decreases of viscosity, and its film might not bear the ferrostatic pressure and cause the tore of the steel skin during casting. On the other hand, the Zr may increase viscosity and crystallization temperature, decreasing the lubrication and the heat transfer.

The mould slags 1 and 3 DTAs (Figure 12) show a slight decrease in crystallization temperature of the collected samples in relation to the non-contaminated one. This may not cause much harm, except for a little bit higher heat transfer. However, the mould slag 2 DTA (Figure 12) shows a splitting of the crystallization peak, pointing out a different crystallization behavior that may interfere in the lubricating properties of the mould slag.

According to the Table 8, the collected mould slags 1 and 3 show small increases in viscosity related to the non-contaminated sample, while the mould slag 2 shows a slight decrease. So, some attention may be paid about the maintenance of the lubricating properties at the interface, avoiding damage at the slab surface. Considering that the slab-mould interface stability in CC is a delicate equilibrium between lubrication (lower viscosity) and standing the ferrostatic pressure (higher viscosity), the adequate control of the products used is very important, in order to assure an adequate operation of the process.

The XRD analysis (Figure 13) of all the mould slags pointed out the same crystallization pattern, they were non-crystalline and when heat treated generated initially cuspidine and then nepheline. The heat treatment temperatures were chosen according to the DTA profile.

CONCLUSIONS

The techniques used in the characterization of the mould powders and mould slags are perfectly adequate to the screening and understanding of the changes in their properties.

The contamination levels observed and the oscillations of the crystallization profiles point out the necessity of using procedures able to minimize these changes, assuring the production of slabs with better surface quality and less frequent stops.

The incorporation of contaminants during CC changes mould slag properties and may effectively affect the surface quality of the slabs, because of the variation of heat transfer. This variation is often connected to changes in crystallization temperatures and viscosity.

The remarkable increase in zirconium content is related to erosion of the SEN. The operation improvement of the CC process may allow higher speeds and, therefore, less corrosion and less contamination.

The effective proof of the role of chemical species in the modification of the mould slag properties, indicate the importance of studies that intend to minimize the effects of such changes during CC.

Then, with the characterization of the mould slags and the comprehension of the interfering operational aspects, it becomes possible the development of new products with a larger performance flexibility, allowing its adequate functioning even at critical operational moments. This is our next work in this area: Micro-additions for quick slag optimization: activity and action.

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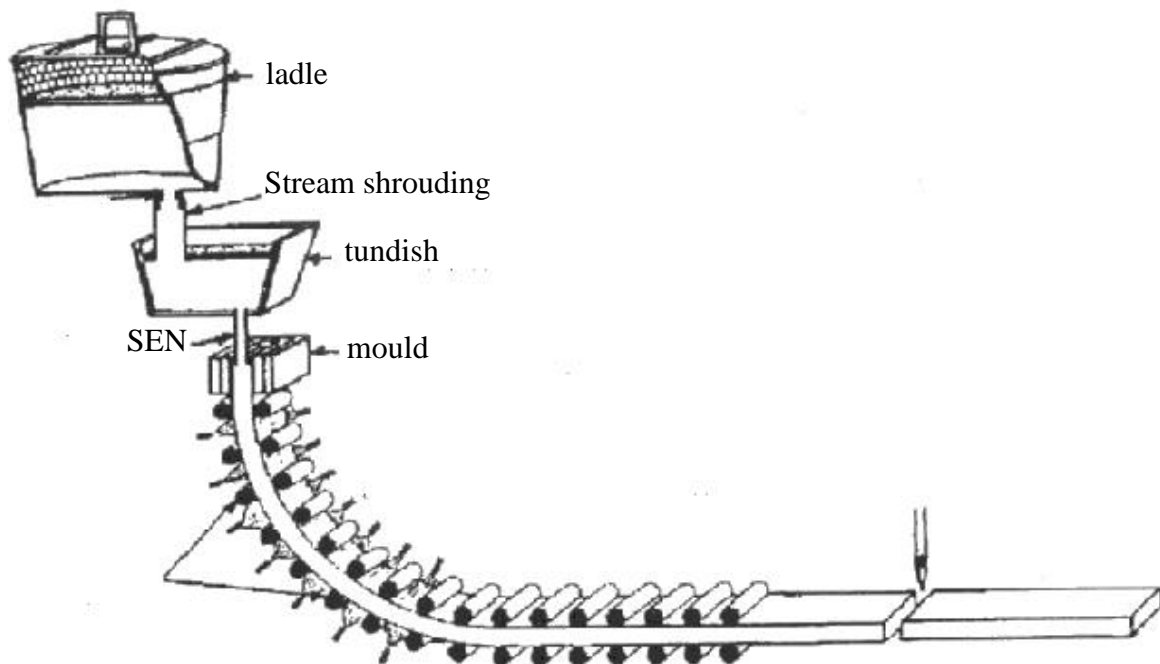


Figure 1 – Diagram of the Continuous Casting ¹.

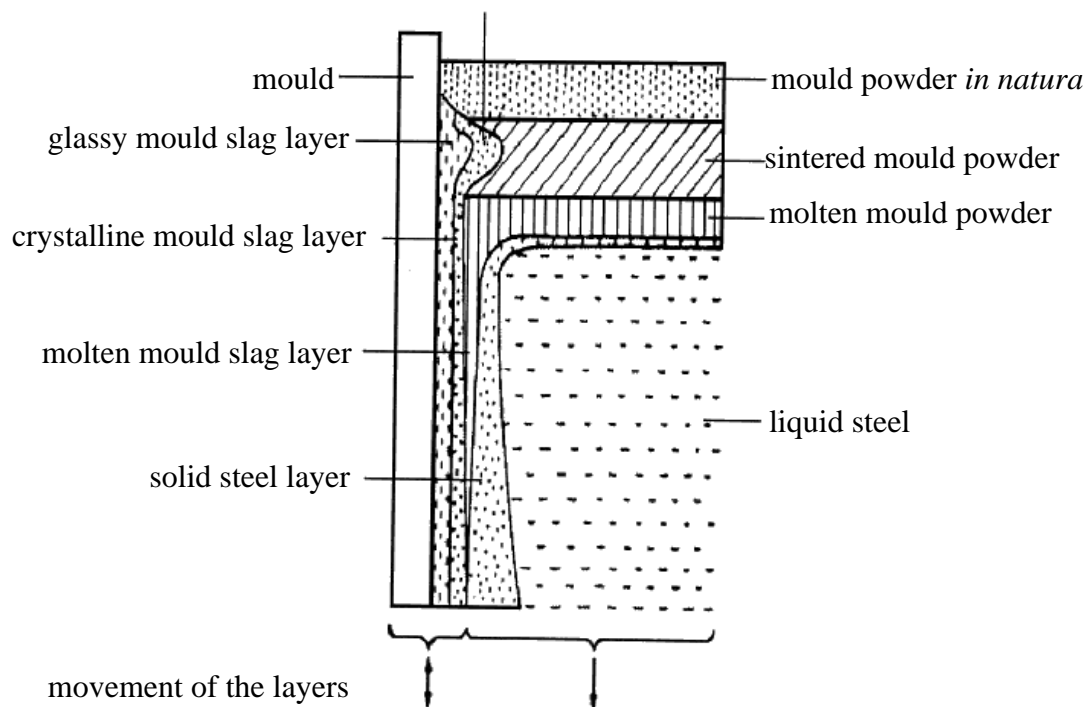


Figure 2 – Scheme of mould flux and mould slag location during operation ¹.

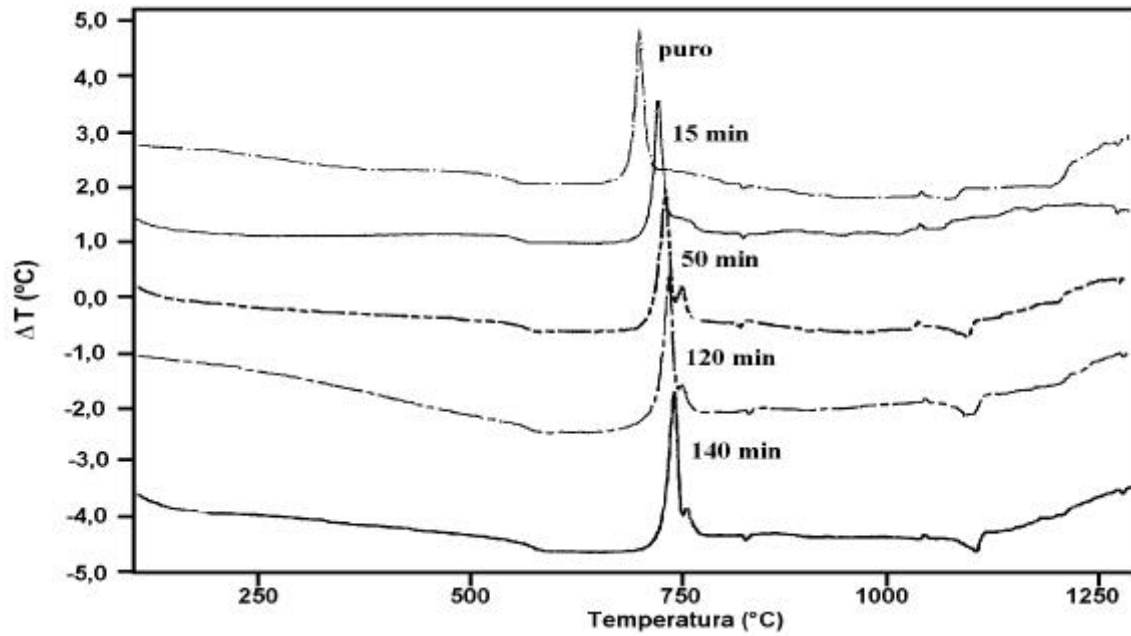


Figure 3 – DTA curves of mould slags collected along continuous casting. The peak temperatures range from 724°C to 759°C ⁷.

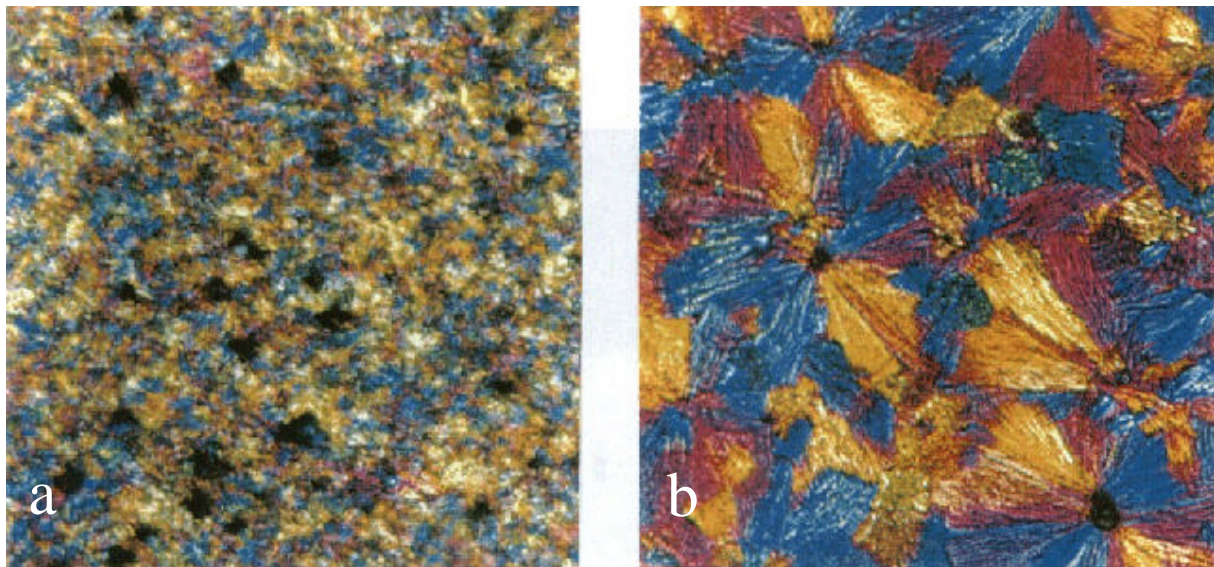


Figure 4 – Micrographies of mould slags contaminated with:
a) 0,7 % ZrO₂ and b) 1,5 % ZrO₂ ⁸.

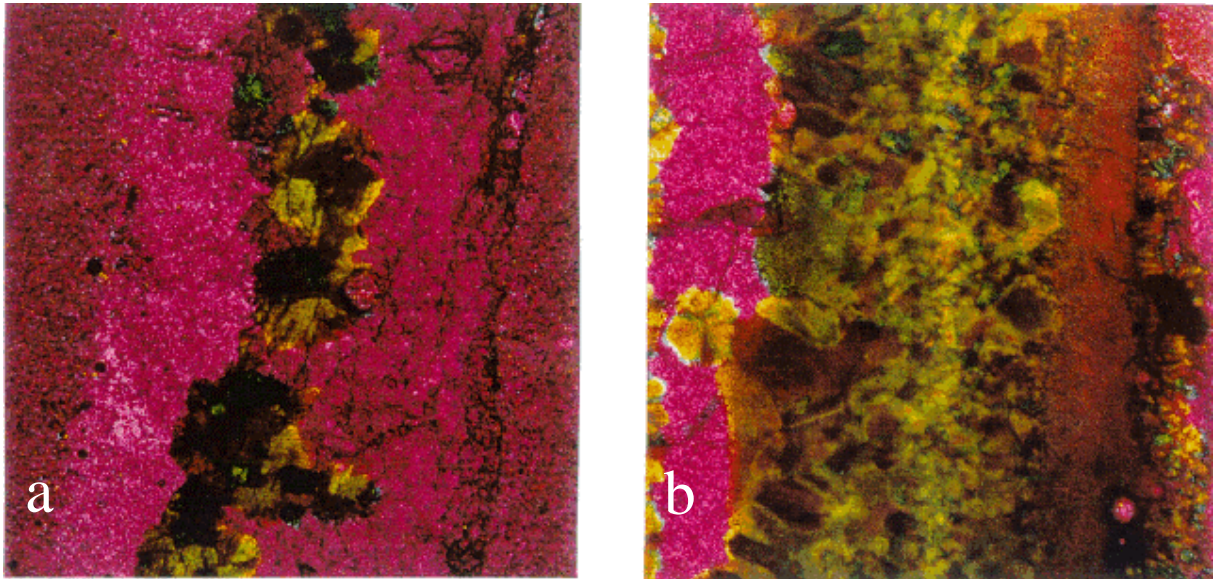


Figure 5 – Micrographies of solidified mould slags collected from the mould slab interface after the CC operation of a low carbon (a) and a medium carbon (b) steel (25X) ¹.

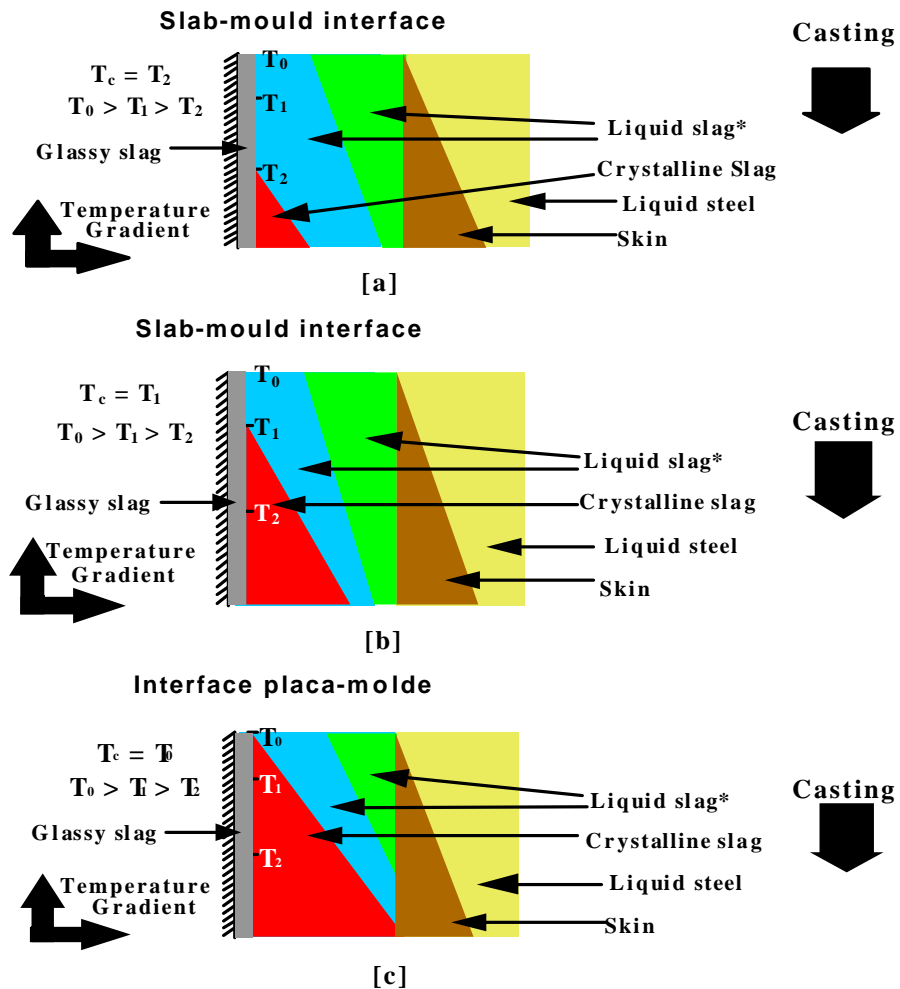


Figure 6 – Schematic model for the layers profile at the slab-mould interface of mould slags with: a) low, b) intermediate and c) high crystallization tendencies.

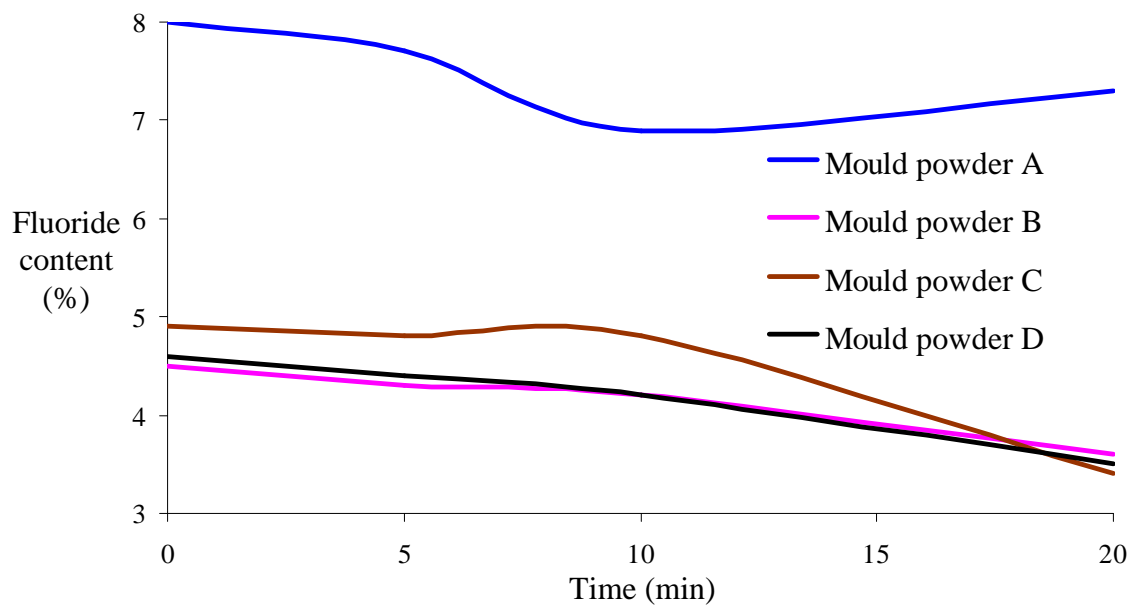


Figure 7 – Evolution of the fluoride content in mould slags at 1450 °C¹⁰.

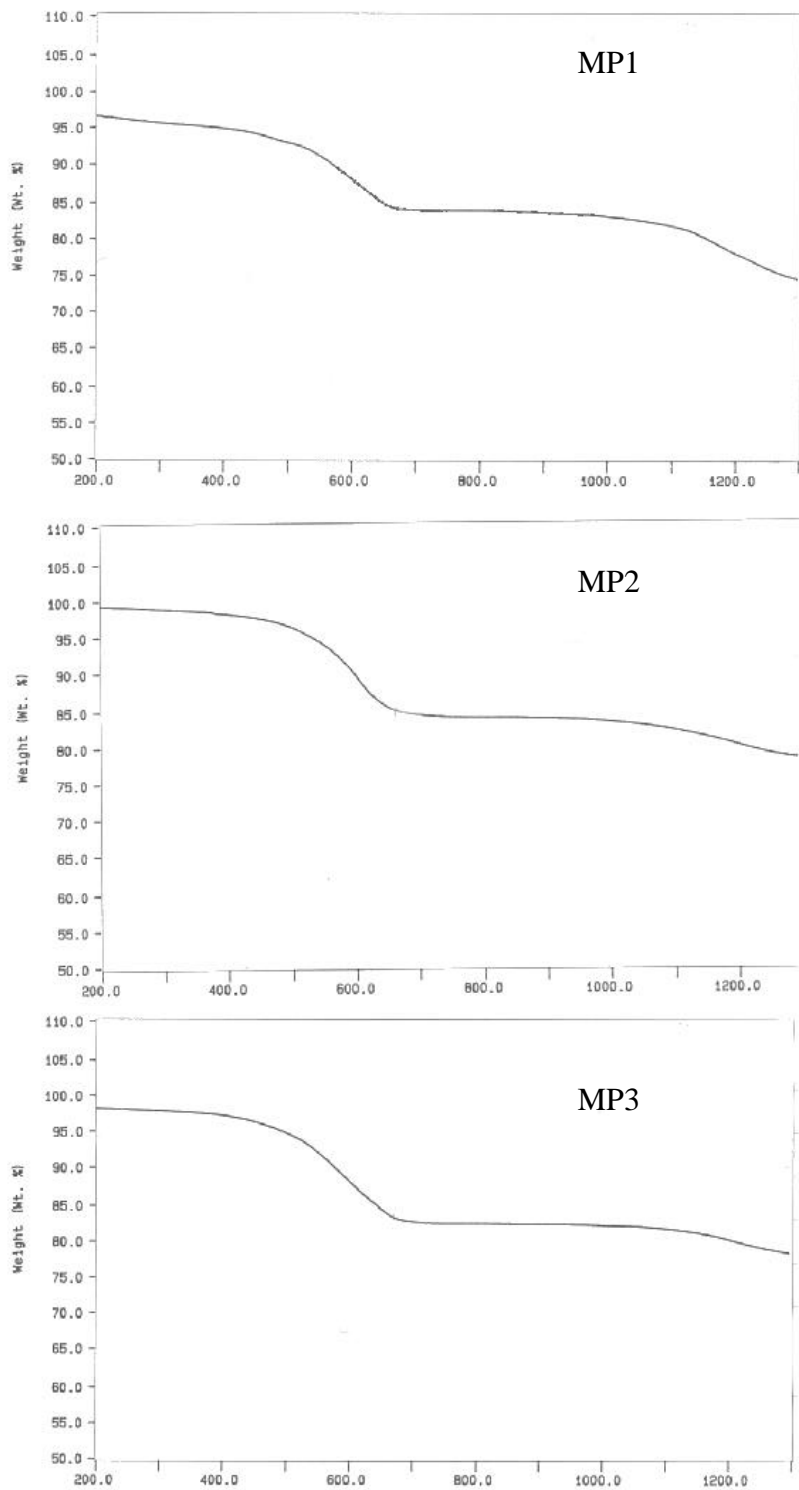


Figure 8 – TGAs of the mould powders.

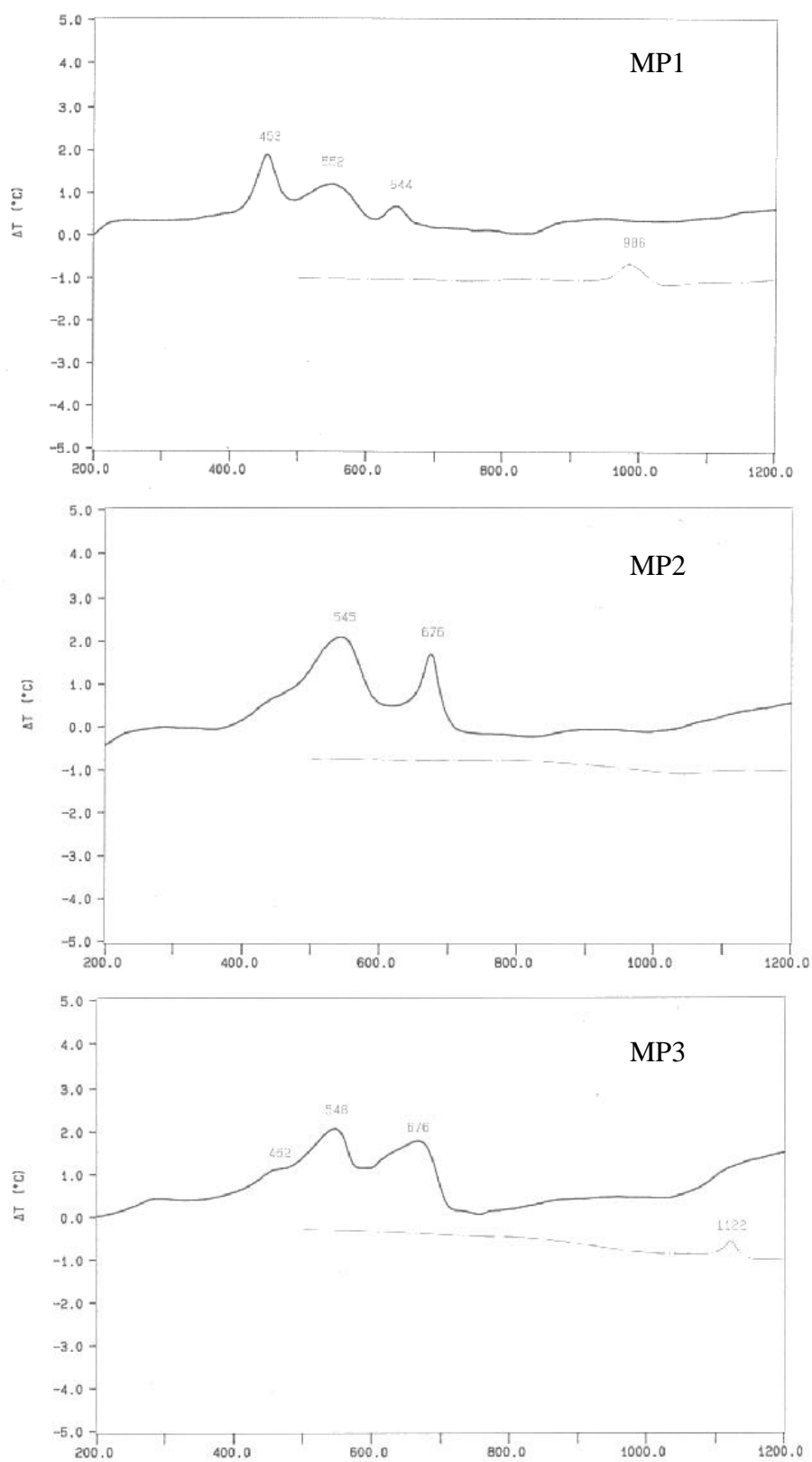
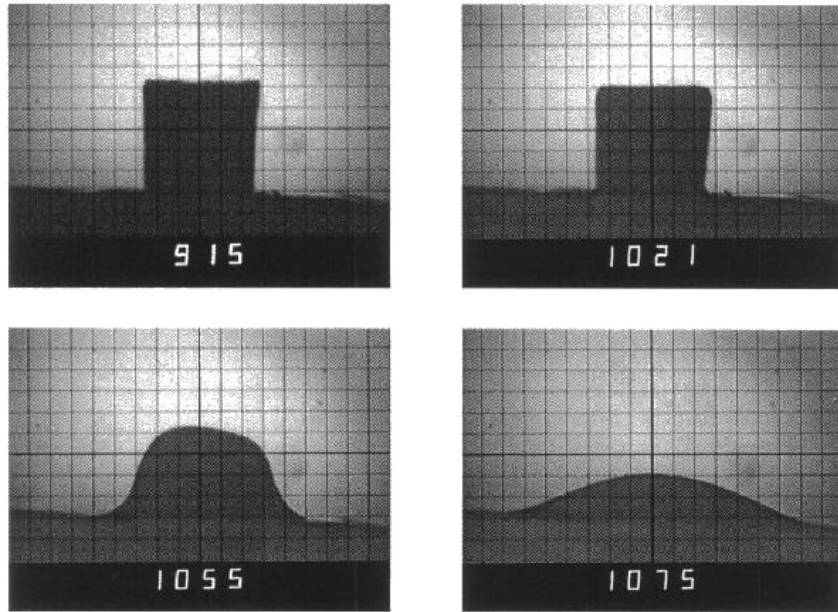


Figure 9 – DTAs of the mould powders.

MP1



MS1-0

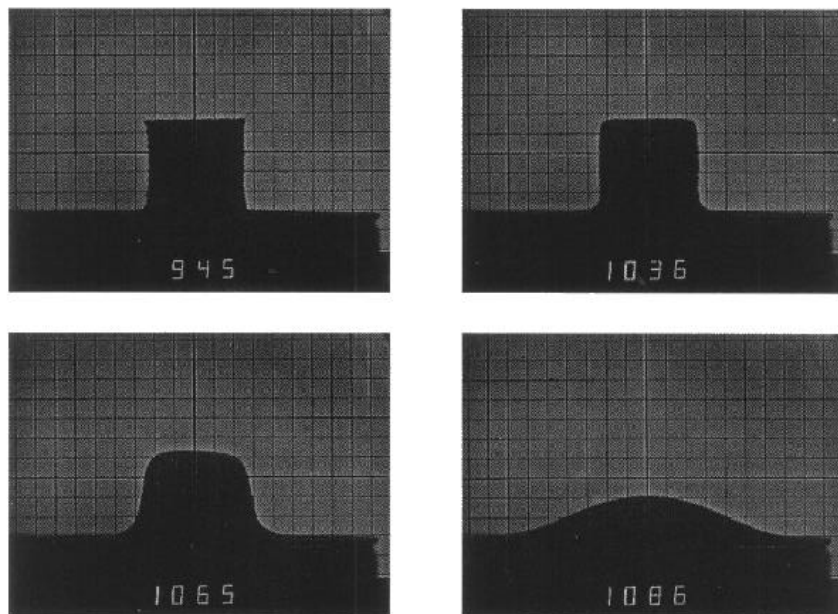


Figure 10 – Heating Microscopy of MP1 and MS1-0.

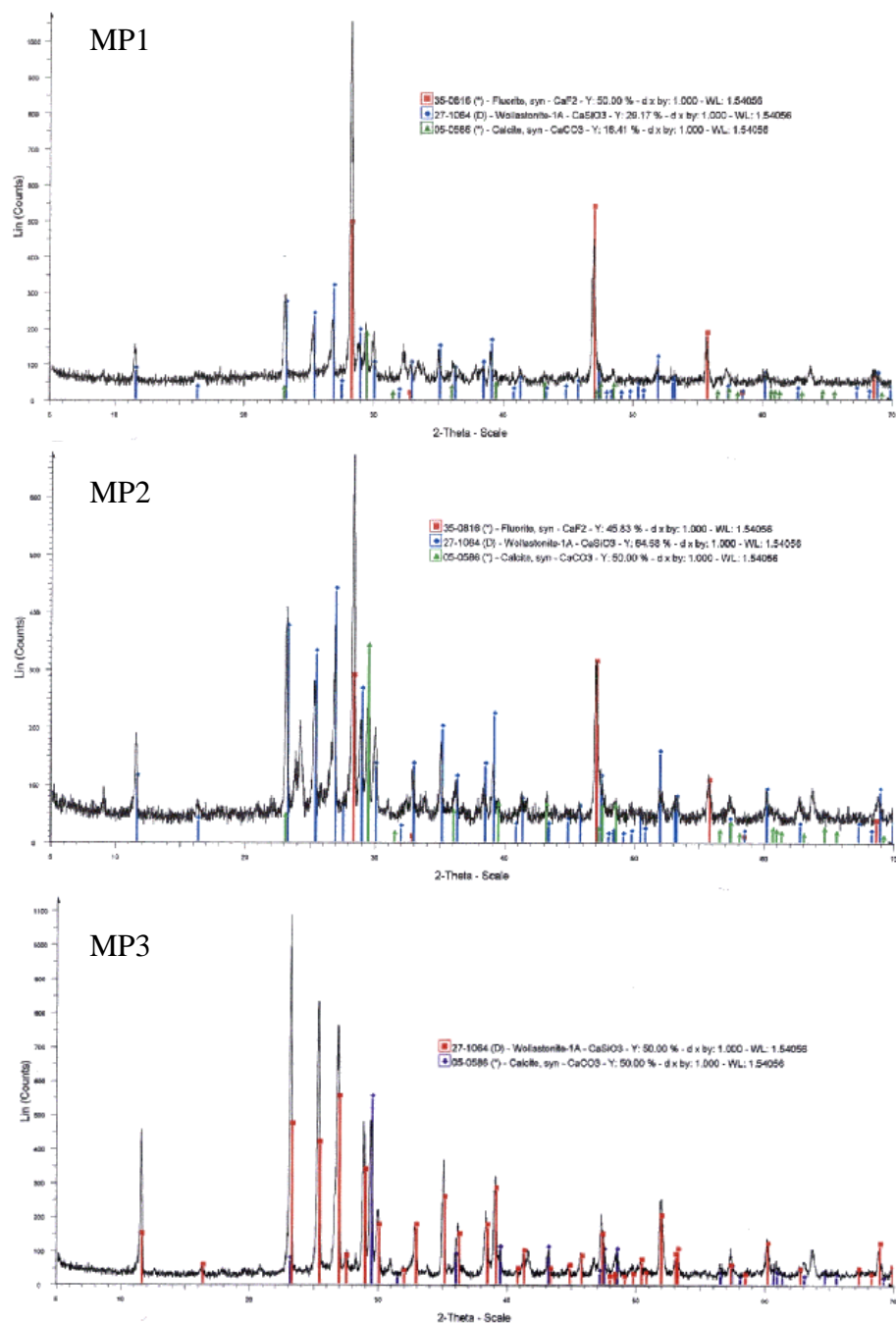


Figure 11 – XRDs of the mould powders.

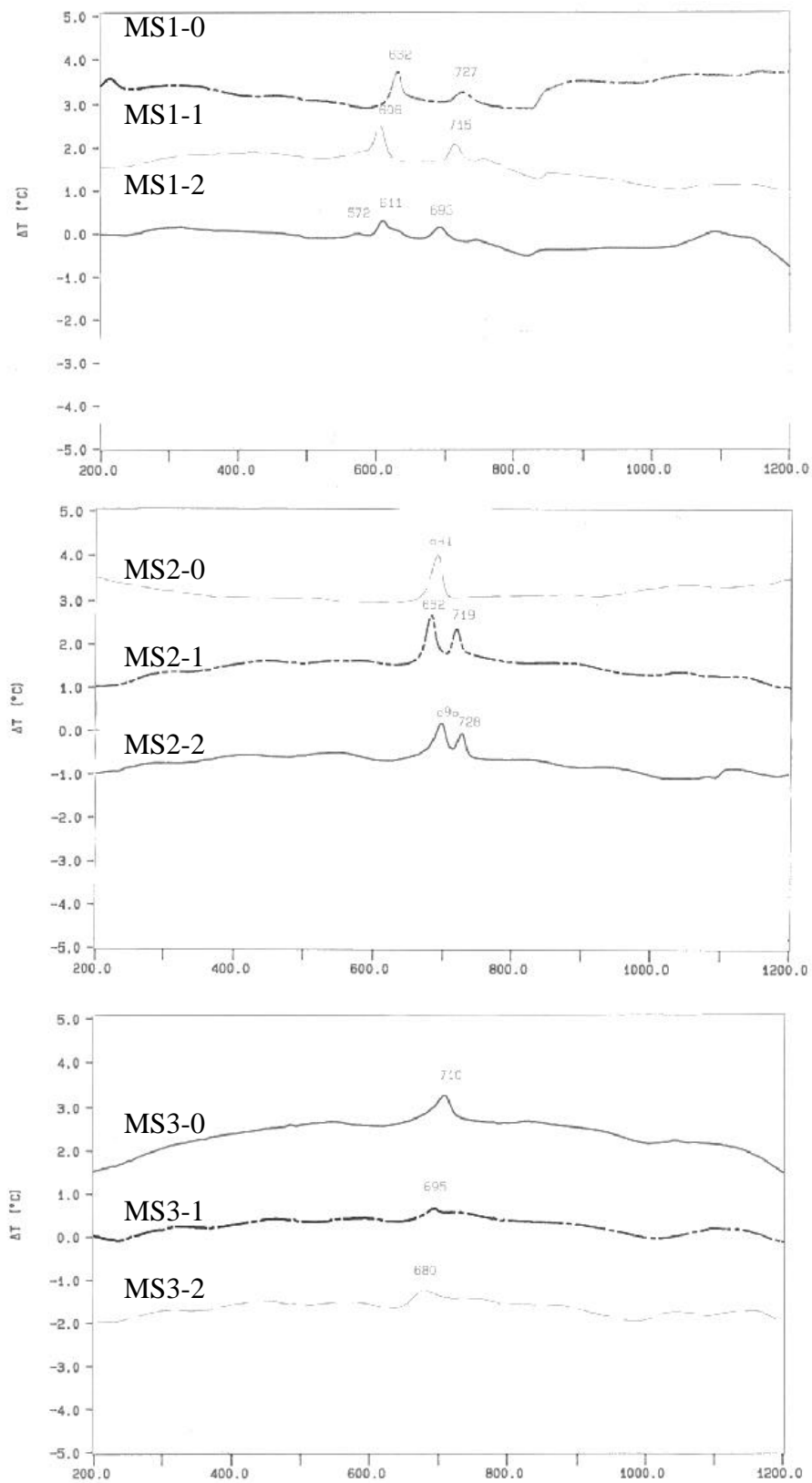


Figure 12 – DTAs of the mould slags.

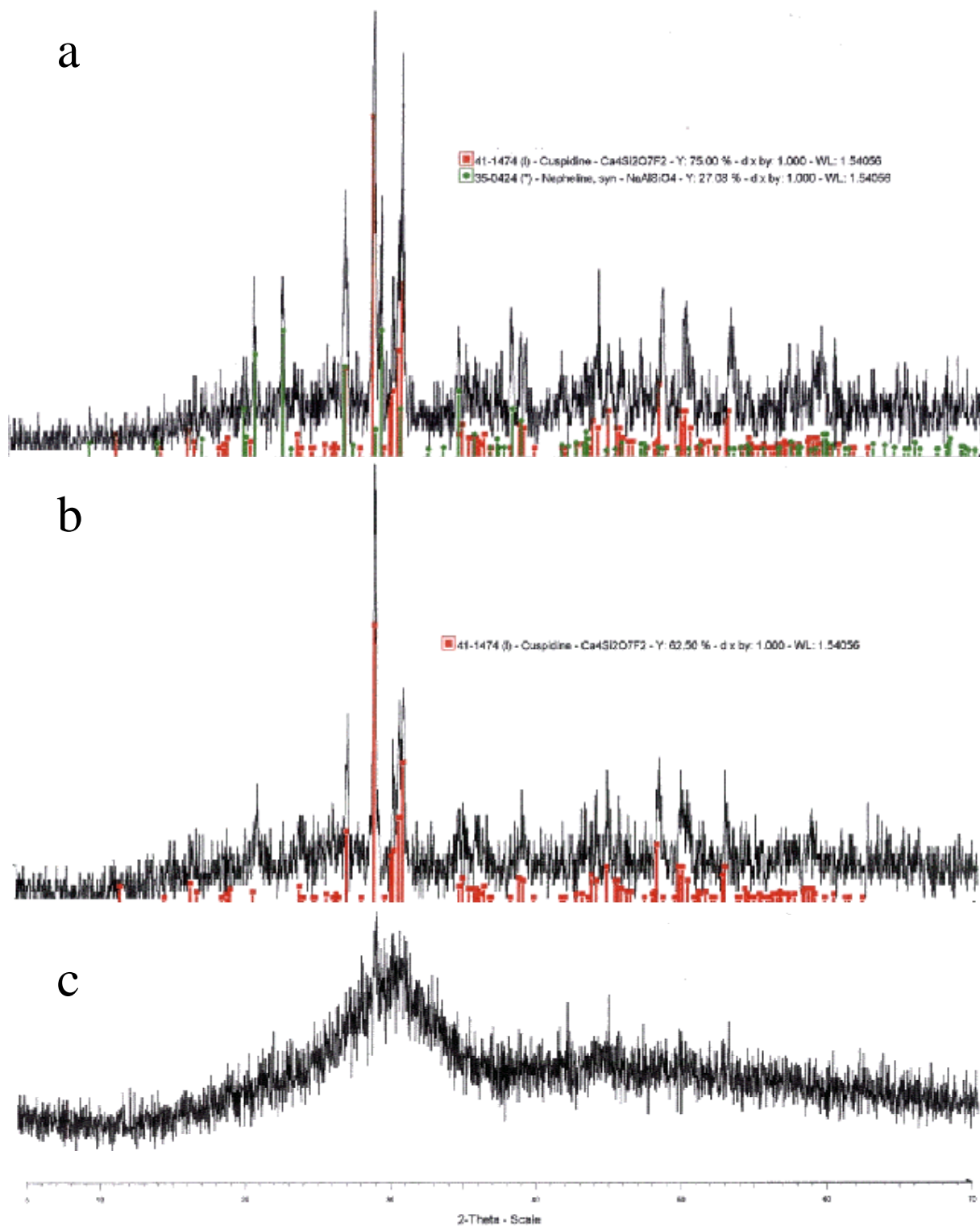


Figure 13 –XRDs of mould slag MS2-2 before (c) and after lower temperature (b) and higher temperature heat treatment (a).

Table 1 – Chemical composition of the mould powders studied.

Content (%)	MP1	MP2	MP3
SiO ₂	30.4	32.9	32.2
CaO	27.3	29.3	34.4
MgO	1.0	2.2	0.5
Al ₂ O ₃	3.9	4.4	3.9
Na ₂ O	11.3	6.5	7.4
K ₂ O	0.8	0.4	0.2
Fe ₂ O ₃	2.0	1.6	1.8
F	9.4	6.4	5.7
C _{total}	5.9	8.2	8.1
CaO/SiO ₂ ratio	0.90	0.89	1.07

Table 2 – Emission Spectrometry of the mould powders studied.

Content	MP1	MP2	MP3
Fe (%)	0.7	0.5	0.2
Mg (%)	0.5	0.3	0.3
Ca (%)	20	20	20
Ti (%)	0.1	0.1	0.02
Mn (ppm)	200	300	150
B (ppm)	2000	1500	1000
Ba (ppm)	200	150	20
Cr (ppm)	30	20	15
Cu (ppm)	20	30	10
Sr (ppm)	200	150	100
Zr (ppm)	70	20	20

Table 3 – Thermogravimetric Analyses of the mould powders studied.

	Temperature range (°C)	Loss of Mass (%)	Temperature range (°C)	Loss of Mass (%)
MP1	411-500	1.8	500-719	9.1
MP2	355-812	14.6		
MP3	328-763	15.3		

Table 4 – Differential Thermal Analysis of the mould powders studied.

	Peak temperature of the exothermal peaks during heating (°C)	Peak temperature of the exothermal peak during cooling (°C)
MP1	453, 547 e 644	986
MP2	539 e 675	—
MP3	549 e 677	1122

Table 5 – Heating Microscopy results of the mould powders studied (°C).

	MP1	MP2	MP3
Softening	1020	1070	1115
Melting	1055	1090	1125
Flowing	1075	1105	1135

Table 6 – X-ray diffraction analysis results of the mould powders studied.

Main crystalline phases	
MP1	Fluorite, wollastonite and calcite
MP2	Fluorite, wollastonite and calcite
MP3	Wollastonite and calcite

Table 7 – Emission Spectrometry of the mould slags

Content	MS1-0	MS1-1	MS1-2	MS2-0	MS2-1	MS2-2	MS3-0	MS3-1	MS3-2
Fe (%)	0.7	0.3	0.2	1	0.5	0.5	0.1	0.1	0.05
Mg (%)	0.7	0.5	0.7	0.3	0.3	0.3	0.3	0.3	0.3
Ca (%)	>20	>20	>20	>20	>20	>20	>20	>20	>20
Ti (%)	0.05	0.1	0.03	0.1	0.05	0.1	0.015	0.01	0.02
Mn (ppm)	500	5000	5000	300	>5000	>5000	150	>5000	>5000
B (ppm)	1500	1500	2000	2000	2000	1500	500	100	70
Ba (ppm)	150	200	150	150	150	150	20	500	500
Cr (ppm)	200	200	150	150	150	150	70	200	100
Cu (ppm)	50	30	70	50	20	30	30	30	30
Sr (ppm)	150	200	<100	150	100	150	150	150	100
Zr (ppm)	50	>1000	>1000	50	>1000	>1000	20	500	500

Table 8 – Heating Microscopy results of the mould slags (°C)

	MS1-0	MS1-1	MS1-2	MS2-0	MS2-1	MS2-2	MS3-0	MS3-1	MS3-2
Softening	1035	1050	1060	1100	1085	1090	1090	1100	1085
Melting	1065	1085	1080	1115	1095	1095	1105	1130	1120
Flowing	1085	1105	1100	1130	1120	1125	1135	1155	1150