DEVELOPMENT OF FLUORINE-FREE MOULD FLUXES [1]

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Abstract

Mould powders or mould fluxes are synthetic slags used to lubricate the mould during continuous casting of steel. Utilisation of fluorine-containing raw materials brings some advantages related to a stable continuous casting process and to production of clean steels. However, fluorine is undesirable from the environmental point of view due to the following reasons: (i) fluorides evolve easily from slags, producing health-injurious gaseous substances (such as fluoridric acid); (ii) corrosion of machinery; (iii) problems related to storage and utilisation of solid waste. In present work some preliminary results of a cooperation project of research and development between industry and university are showed. The project is aimed at the development of mould powders without fluorine and to apply them at steelworks plants. Regarding present work, important technological parameters of new recipes which do not contain fluorspar were determined, related to viscosity and melting behaviour. Moreover, computational thermodynamics was applied as a tool to develop mould powders.

Keywords: Continuous casting; Mould powders; Fluorine; Fluorspar.

DESENVOLVIMENTO DE PÓS FLUXANTES LIVRES DE FLÚOR

Resumo

Pós fluxantes são escórias sintéticas utilizadas para lubrificar o molde durante o lingotamento contínuo de aço. A utilização de matérias-primas contendo flúor traz diversas vantagens, relacionadas a um processo de lingotamento contínuo estável e à produção de aços limpos. No entanto, o elemento flúor é indesejável do ponto de vista ambiental devido às seguintes razões: (i) emissões de flúor acontecem facilmente a partir de escórias, produzindo substâncias gasosas prejudiciais à saúde (tais como ácido fluorídrico); (ii) corrosão da máquina de lingotamento contínuo; (iii) problemas de armazenamento de resíduos sólidos. No presente trabalho são mostrados alguns resultados preliminares de um projeto de pesquisa e desenvolvimento entre indústria e universidade. O objetivo desse projeto é desenvolver pós fluxantes sem flúor e aplicá-los em usinas siderúrgicas. Importantes parâmetros tecnológicos de novas receitas que não contêm fluorita foram determinados, relacionados a viscosidade e comportamento de fusão. Além disso, a termodinâmica computacional foi aplicada como uma ferramenta para o desenvolvimento de pós fluxantes.

Palavras-chave: Lingotamento contínuo; Pós fluxantes; Fluor; Fluorita.

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1 INTRODUCTION

Mould powders or mould fluxes are synthetic slags used to lubricate the mould during continuous casting of steel.(1) The chemical composition of industrial mould powders lies in the following ranges:(2) 35 – 45 % SiO_2; 25 – 35 % CaO; 5 – 15 % Al_2O_3; 2 – 7 % MgO; 15 – 25 % CaF_2; 5 – 15 % Na_2O; 5 – 15 % C.

At Figure 1(2) there is a schematic diagram of a copper mould containing mould powder and steel during solidification process. From this diagram the five basic functions of mould powders can be explained:

- lubrication at mould/strand interface, due to the fusion of mould powder;
- control of horizontal heat transfer, since a solid slag film is formed at mould/strand interface;
- thermal insulation, i.e. heat losses are avoided by mould powder layers above liquid steel;
- protection of liquid steel from atmosphere;
- inclusions absorption from liquid steel through liquid slag.

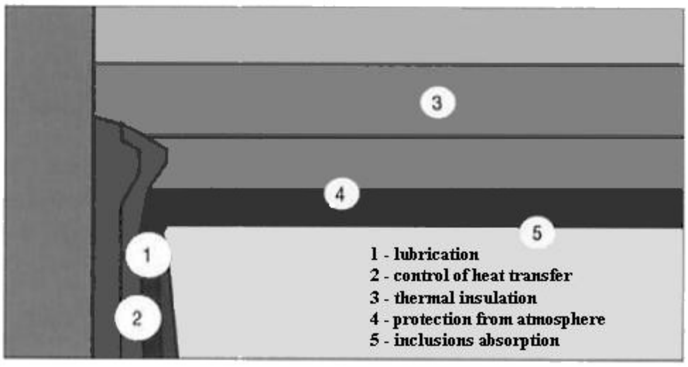


Figure 1 – Schematic drawing of the various layers formed in the mould.**(2)**

The main function of a mould powder is the creation of a lubricant film at interface mould/strand.(3) Lack of lubrication at this interface can cause sticker breakouts. Moreover, lubrication conditions explain the majority of ingots surface defects; mould powders must be selected considering this property.(4, 5)

Some of the raw materials used in industrial mould powders production are: wollastonite, bauxite, fly ash, *etc*. Moreover, fluorspar (CaF_2) and sodium carbonate (Na_2CO_3) are normally used to decrease viscosity and *liquidus* temperature.(2)

Utilisation of fluorine-containing raw materials brings some advantages related to a stable continuous casting process and to production of clean steels, such as:(2)

- the decrease (at *liquidus* temperature) of the slag viscosity (system $CaO\text{-}Al_2O_3\text{-}SiO_2$) – what promotes the necessary lubrication at mould/strand interface;
- the increase of the crystallization tendency (very important factor to peritectic steel slabs casting);
- the decrease of the driving force for redox reactions between liquid steel and liquid mould powder (slag).
- the positive behaviour regarding absorption of inclusions from steels, such as Al_2O_3(s).

However, fluorine is undesirable from the environmental and health points of view due to the following reasons:(6)

- it evolves easily from slags, producing health-injurious gaseous substances (such as fluoridric acid);
- it causes increased wear of refractories and corrosion of machinery;
- it creates problems for storage and utilisation of solid waste.

The high amount of fluorspar and sodium carbonate in industrial mould powders implies in an increase of fluoride content in water of the secondary cooling and at same time in the lowering of its pH value. Fluorides can be emitted into the gaseous phase above mould according to Equations 1 and 2.(2)

$Na_2O + CaF_2 \rightarrow CaO + 2\ NaF(g)$ (Equation 1)
$SiO_2 + 2\ CaF_2 \rightarrow 2\ CaO + SiF_4(g)$ (Equation 2)

The weak bounds of gaseous fluorides – NaF(g), SiF_4(g) – promote reactions with the residual moisture of mould powders, Equations 3 and 4. These reactions form HF(g).

$2\ NaF(g) + H_2O(g) \rightarrow Na_2O + 2\ HF(g)$ (Equation 3)
$SiF_4(g) + 2\ H_2O(g) \rightarrow SiO_2 + 4\ HF(g)$ (Equation 4)

Gaseous compounds which contain fluorine are formed when mould powder is heated by liquid steel. It is important to note the majority of gaseous compounds which contain fluorine are transported together with liquid slag at mould/strand gap. Then, at mould exit, these compounds react with the superheated steam of the secondary cooling; in this way, the formation of HF(g) according to Equations 3 and 4 is accelerated. NaF(g) formation starts at 456°C, and SiF_4(g) formation starts at 857°C.(2)

1.1 Possibilities to Replace Fluorine

It is clear there is steady interest in fluorine content reduction methods. Naturally the good properties of a fluorine-containing mould powder must be maintained by its substitute.

To diminish the amount of fluorspar in mould powders, a possibility is to increase Al_2O_3 content. At pseudo-ternary system $CaO\text{-}SiO_2\text{-}Al_2O_3$ it can be seen that, starting with wollastonite, Al_2O_3 addition (*e.g.* bauxite addition) decreases *liquidus* temperature.(7)

In a research project involving different European institutions(8) a good surface quality of as-cast strands (billet casting) with spring and bearing steels was accomplished during intensive experiments using mould powders or granules with a composition located closely to the eutectic of the pseudo-ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$, at 1266°C, combined with a more glassy solidification. When the composition of the powder is moved towards the wollastonite precipitation, the grinding index deteriorates due to a higher viscosity and a more crystalline solidification of the molten mould powder.

A core result of the aforementioned European project(8) is that Li_2O has a strong fluxing ability and can therefore be used as a fluorine substitute. However, the melting and solidification behaviour show differences with respect to the standard powders. This influences the performance of powders during continuous casting in terms of lubricating ability and steel solidification conditioning.

Schulz et al.(2) researched mixtures with lower fluorides emission potential, with the replacement of fluorine and/or sodium by lithium; the replacement of sodium is justified since in this case the formation of NaF(g) is avoided. Lithium utilisation in mould powders presents some advantages: (i) Li_2O causes significant decrease of *liquidus* temperatures and of viscosity; (ii) with Li_2O slags with better inclusions absorption potential can be produced; (iii) Li_2O is thermodynamically more stable than other options, such as Na_2O and B_2O_3.

When using boron as substitute of fluorine, according to Schulz *et al.* **(2)** there is a risk of redox reactions involving dissolved elements in liquid steel – such as aluminium and silicon –, what would cause boron pick-up. Furthermore, B_2O_3 could cause a viscosity increase in mould fluxes.

Regarding sodium-containing raw materials, it is an interesting material to substitute fluorspar, since Na_2O decreases viscosity, liquidus temperature and it also promotes inclusions absorption (though inclusions absorption when using Li_2O is better). It is important to observe that increasing Na_2O content to compensate for fluorine content diminution is possible up to 20% only, due to precipitation of the solid phase nefeline ($Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2$). Frequently Na_2O content in industrial mould powders is high (>10%).(2)

Wen et al.(9) developed fluorine-free mould powders for peritectic steel slab casting. Regarding conventional mould powders, horizontal heat transfer control is obtained by control of crystallization of the solid phase cuspidine. To produce fluorine-free mould powders, it is necessary to develop a composition which simultaneously diminishes viscosity and crystallizes in a way that control of heat transfer is obtained. The raw material used to substitute fluorine was ferrovanadium production slag, a material which presents a high content of TiO_2 and a high tendency to crystallize. Thus, the proposal of Wen *et al.* was to use slags of the system $CaO\text{-}SiO_2\text{-}TiO_2$, since in this way there is precipitation of solid phases containing titanium. It was showed titanium effect is similar to fluorine effect, to certain compositions ranges, since crystallization is also promoted at solid slag film.

1.2 Objectives

In the context of a cooperation project of research and development between industry and university, in the present work some preliminary results are showed. Main objective of this project is to develop mould powders without fluorine and to apply them at steelworks plants.

Regarding the present work, the objectives are the following:

- to determine technological parameters of new recipes which do not contain fluorspar, related to viscosity and melting behaviour;
- to apply computational thermodynamics as a tool for the development of mould powders.

2 METHODOLOGY

In the following paragraphs, the proposed methodology to evaluate mould powders melting behaviour and viscosity is described. The recipe (mixture of raw materials) named “Standard” is the mould powder Accutherm ST-SP/512SV-DS, produced by Stollberg do Brasil and used in steelworks plants. Derived from “Standard” three new recipes which do not contain fluorspar (R1, R2 and R3), using

Brazilian raw materials, were elaborated at Stollberg do Brasil. Carbon content and carbon type are the same to all recipes.

2.1 Characterisation of Brazilian Raw Materials

.Different Brazilian raw materials with fluxing ability, containing sodium and lithium, were selected to substitute fluorspar. Afterwards, elementary chemical composition of these materials was determined through x-ray fluorescence spectrometry.

2.2 Determination Of Mould Powders Viscosity Through Models

Viscosity is one of the most important properties of a mould powder. Several models have been reported to the estimation of viscosities from chemical composition. In the present work the following models were used: IRSID **(3)** and Iida.(10,11) Description of the models can be found in the respective references. Molar volumes at melting point, a needed property for the Iida model calculations, were taken from *FactSage* software (described below). Through IRSID model chemical compositions of recipes R1, R2 and R3 were determined. Afterwards, the melting behaviour of these recipes was evaluated.

2.3 Evaluation of Melting Behaviour

Evaluation of melting behaviour through computational thermodynamics: the computational thermodynamics software employed in the present work is the commercial package *FactSage* version 5.5. It contains the module Equilib, which is the Gibbs energy minimization workhorse of FactSage;(12) this module calculates the concentrations of chemical species at the state of thermodynamic equilibrium from elements or compounds selected as input. The following databases were used in the present work:(13) FToxid solution database (FToxid53Soln.sda), FSstel (FSstel53Base.cdb) and FACT53 (FS53Base.cdb).

Evaluation of melting behaviour through heating microscope: the specimen to be tested is put into a furnace of a heating microscope in an oxidizing atmosphere. A temperature regulator increases the temperature of the furnace with a linear heating rate of 10 °C/minute. After measurement, the characteristic temperatures of the sample material, such as deformation, hemisphere and flow points can be analysed. The working method refers to German standard DIN 51730.(14) Regarding repeatability limit (same operator, same apparatus) results shall be considered acceptable it they do not differ by more than 30°C (for all characteristic temperatures). Regarding reproducibility limit (different operators, different apparatus) the results shall be considered acceptable if they differ by no more than 50°C (also for all characteristic temperatures).

2.4 Evaluation of Viscosity Through Ramp Test

At Ramp Test 0.5 g of a mould powder sample is put in an Al_2O_3 vessel. Then, the vessel with the sample is heated in a furnace during certain period (*e. g.* 5 minutes) at 1280°C. The path formed by the slag (molten mould flux) on the vessel was measured through a freeware software (*PhotoFiltre 6.3.1*) from a photography. In this way, the path formed by different slags can be compared.

2.5 Determination of Viscosity by Viscometer

Viscosity measurements of slags were carried through by a high-temperature equipment and a rotation viscometer, at Stollberg Germany. After preparation of the specimen (decarburisation, fusion at 1350°C and crushing to obtain grains of 2-5 mm diameter) and preparation of the measuring device, the measuring procedure is executed; it is computerized and runs automatically. A computer calculates and prints the graph "viscosity (Pa·s) *versus* temperature (°C)".

3 RESULTS AND DISCUSSION

From mould powder Accutherm ST-SP/512SV-DS ("Standard" in the present work) were elaborated at Stollberg do Brasil three new recipes which do not contain fluorspar – R1, R2 and R3 –, using the aforementioned Brazilian raw materials, see Table 1. Residual fluorine content of R1, R2 and R3 is explained by the utilisation of others raw materials.

Table 1 – Chemical compositions of the recipes analysed in the present work

Mixture	SiO_2	CaO	MgO	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O	F	Li2O
Standard	35.43	25.30	2.95	12.27	0.51	2.57	3.84	1.55	3.87	-
R1	33.80	22.78	4.75	10.79	0.35	1.91	7.99	1.59	0.48	-
R2	35.61	24.03	4.42	9.48	0.32	1.54	6.91	1.13	0.51	0.33
R3	38.39	25.44	4.46	7.85	0.23	0.96	6.38	0.73	0.62	0.36

3.1 Determination of Viscosity

A Ramp Test result can be seen at Figure 2. This result is related to the period of 5 minutes in a furnace at 1280°C. Through image analysis of a digital photo the paths formed by slags were measured; the differences in relation to Standard are: R1 = 16,2%; R2 = 10,8%; R3 = 47,1%. Thus, mixture R3 probably has a viscosity value lower than Standard, R1 and R2.

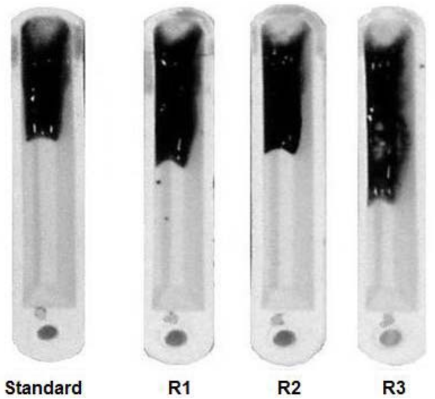
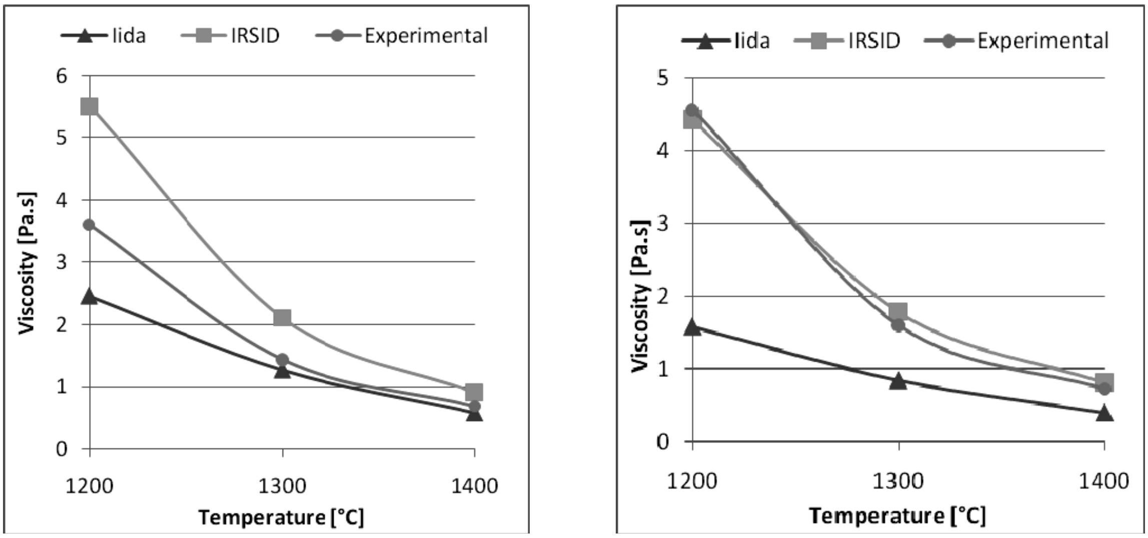


Figure 2 – Ramp Test result: recipes Standard, R1, R2 and R3 (5 min in a furnace at 1280°C).

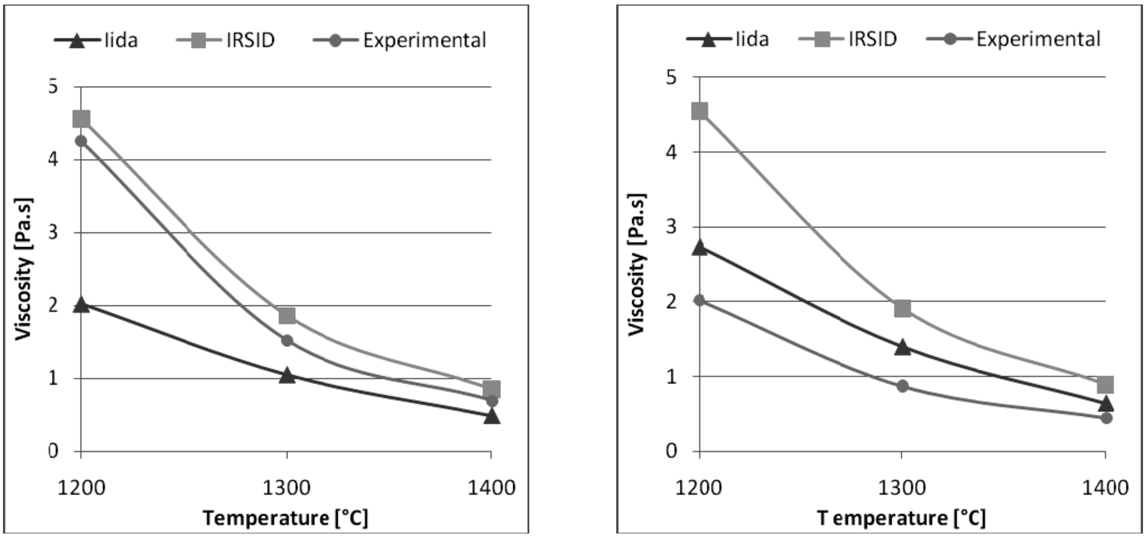
At Figure 3 calculated viscosity values (Iida and IRSID models) can be seen in comparison with viscosity values determined through the viscometer. Standard and R3 experimental values have a better agreement with the results from the Iida model than those from the IRSID model. R1 and R2 do get better agreement with IRSID model.

It is interesting to note R3 experimental values are very different when compared with the other recipes. R2 experimental values are more similar to Standard than values of the other recipes. Viscosity differences between R2 and Standard at 1200°C, 1300°C e 1400°C are respectively 18%, 6% and 0%.



Standard

R1



R2

R3

Figure 3 – Calculated viscosity values (Iida and IRSID models) compared with experimental values determined through the viscometer. Recipes Standard, R1, R2 and R3.

3.2 Determination of Melting Behaviour

Regarding melting behaviour of mould powders, it has a major impact on the casting conditions stability and strand surface quality.(15)

The melting behaviour of a synthetic slag, such as a mould powder, can be evaluated through a heating microscope and also by computational thermodynamics. In a recent work(16) experimental data from a heating microscope were correlated with results obtained by the commercial package *FactSage 5.5*.; work main objective was to evaluate the behaviour of ashes generated after the injection of pulverized coal (PCI technique) inside a blast furnace.

Computational thermodynamics was applied in the present work to evaluate melting behaviour of the recipes without fluorspar (R1, R2 and R3). The chemical equilibrium was calculated by *FactSage 5.5* at several temperatures (and $pO_2 = 0.21$ atm). In this way, the phases and their proportions at each temperature were determined. At Figure 4 recipes R1, R2 and R3 liquid slag fractions, as function of temperature, are showed.

As it can be seen in Figure 4, R3 has a higher amount of liquid slag at lower temperatures (T < 850°C). On the other hand, R1 gets a significant amount of liquid slag only when temperature is above 850°C. R2 presents an intermediate behaviour.

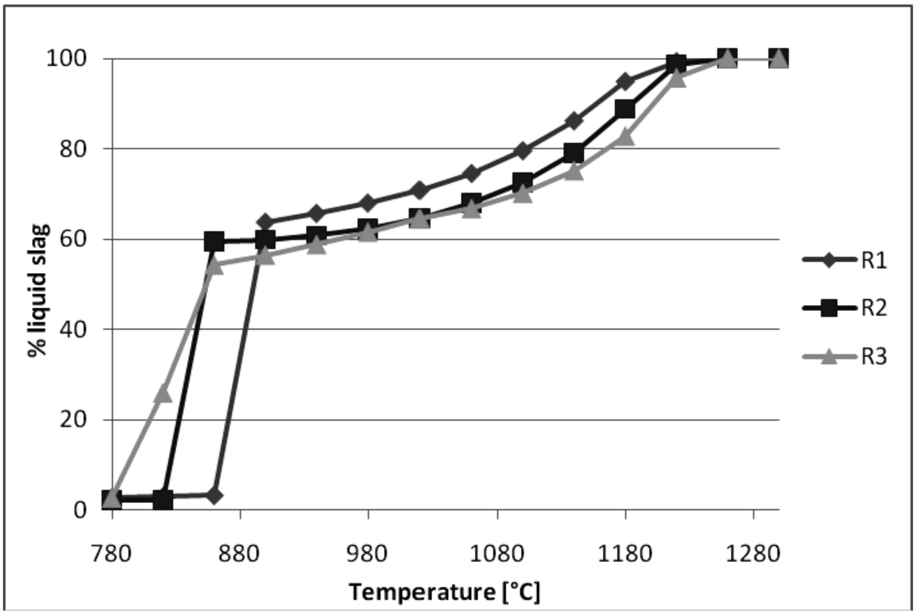


Figure 4 – Liquid slag percentage as function of temperature. Recipes R1, R2 and R3 (computational thermodynamics results).

At Figure 5 it can be seen heating microscope results. Mixture R3 characteristic temperatures are very different from Standard. R2 is the mixture with less dissimilar values.

R2 is the mixture which is closer to Standard, regarding melting behaviour. Characteristic temperatures differences between Standard and R2 are, considering deformation, hemisphere and flow temperatures, respectively +19°C, -32°C and -11°C (repeatability limit is 30°C(14)).

Despite timeless nature of a thermodynamic analysis, some correlations can be established between *FactSage* results and heating microscope characteristic temperatures.

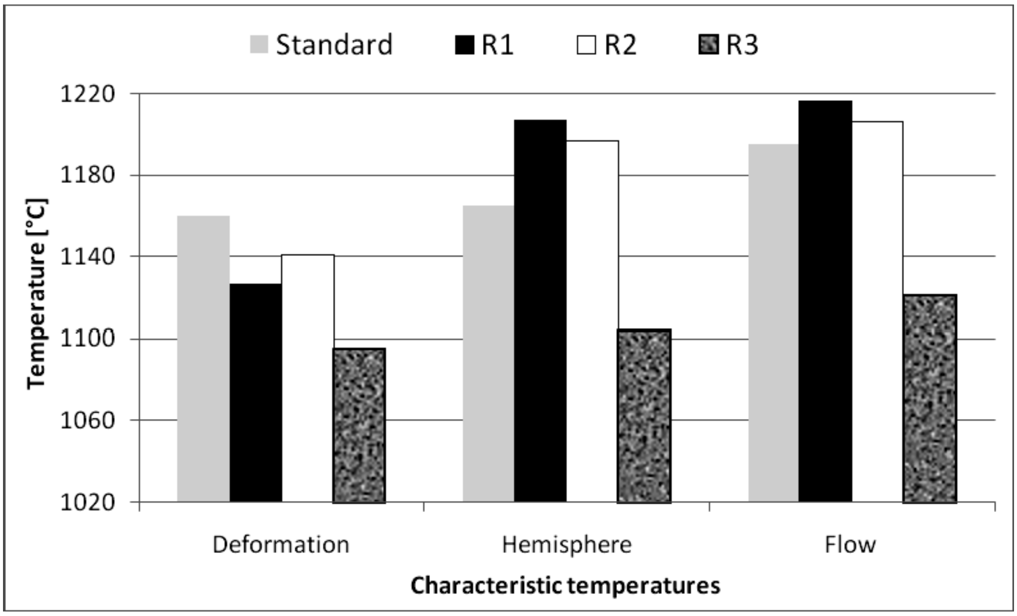


Figure 5 – Characteristic temperatures. Recipes Standard, R1, R2 and R3 (heating microscope results).

Eccentric behaviour of the mixture R3 can be explained by the existence of different solid phases (which in turn present different refractorinesses). Depending on the chemical composition, there are different phases and proportions of phases. For example, R3 has higher SiO_2 content and lower Al_2O_3 content than Standard, R1 and R2. This fact could explain the easier fusion of the mixture R3.

For example, considering 100 g of mould powder at 780°C (~ 100% solid, see Figure 4) the three main solid phases according to *FactSage* are (there are others in lower amounts):

- R1: $Na_2Ca_2Si_3O_9$ (45.43 g), $Ca_2MgSi_2O_7$ (10.81 g), $CaMg_2Al_{16}O_{27}$ (10.6 g);
- R2: $Na_2Ca_2Si_3O_9$ (39.49 g), $Ca_2MgSi_2O_7$ (17.66 g), $Mg_4Al_{10}Si_2O_{23}$ (7.65 g);
- R3: $Na_2Ca_2Si_3O_9$ (36.47 g), $Ca_3Al_2Si_3O_{12}$ (15.63 g), $CaMgSi_2O_6$ (10.7 g).

At 780°C it can be seen the main phase is $Na_2Ca_2Si_3O_9$ (NC_2S_3) for all the analysed mixtures. The high quantity of NC_2S_3 can be explained by the relatively high sodium content of the studied mould powders.

It is interesting to note the second main phase of R3 at 780°C is the solid phase grossularite ($Ca_3Al_2Si_3O_{12}$). In a pseudo-ternary CaO-SiO_2-Al_2O_3 phase diagram,(7) grossularite has a lower melting point (1265°C). However, a computational thermodynamics analysis is more appropriate than an analysis which uses only a pseudo-ternary phase diagram, since a mould powder has several components (CaO, SiO_2, Al_2O_3, MgO, Na_2O, K_2O, Fe_2O_3, *etc.*). In this way, the interactions of all components of the mixture can be simultaneously determined.

Starting from ambient temperature, when the temperature is raised several chemical transformations take place, since the phases originally present at mould powders raw materials suffer transformations depending on temperature.

According to Marschall, Kölbl and Harmuth(15) sodium calcium silicates such as $Na_2Ca_2Si_3O_9$ (NC_2S_3) are formed during the heating process of mould powders. These crystals are developed by reactions of sodium and calcium containing phases. The conclusions of these researches were based on a series of experimental investigations, such as DTA including thermogravimetry, x-ray diffraction of annealed samples, reflected light microscopy, scanned electron microscopy, and hot stage microscope.

When the temperature is further raised to 980°C the liquid slag fraction is higher than 60% (see Figure 4) and there is no more NC_2S_3. At this temperature the three main solid phases are:

- R1: $Ca_2MgSi_2O_7$ (21.36 g), $Ca_3MgSi_2O_8$ (2.51 g), Fe_2O_3 (1.9 g);
- R2: $Ca_2MgSi_2O_7$ (27.61 g), $Ca_3Fe_2Si_3O_{12}$ (2.66 g), Fe_2O_3 (0.69 g);
- R3: $Ca_2MgSi_2O_7$ (28.61 g), $Ca_3Fe_2Si_3O_{12}$ (3.03 g), $CaSiO_3$ (1.47 g).

According to literature several minerals can be formed during heating of mould powders:(16) cuspidine $Ca_4Si_2O_7F_2$, wollastonite $CaSiO_3$, anorthite $CaAl_2Si_2O_8$, gehlenite $CaAl_2SiO_7$, carnegieite $NaAlSiO_4$, pectolite $NaCa_2Si_3O_8(OH)$, $Na_2Ca_2Si_3O_9$ (NC_2S_3), akermanite $Ca_2MgSi_2O_7$ and villiaumite NaF. Cuspidine is the most important phase (in the case of mould powders which contain usual fluorine contents).

Besides melting behaviour, computational thermodynamics can also be applied to determine chemical interactions between liquid slag and liquid steel. In a recent work(17) commercial package *FactSage* was applied to determine the chemical interactions between a proprietary mould flux (Stollberg Germany) in contact with a TRIP steel. Results suggest that computational thermodynamics can be used to predict the complex chemical interactions between liquid steel and mould fluxes.

4 CONCLUSIONS

Regarding viscosity calculations from elemental chemical composition, Iida model can be used to foresee viscosity values.

Computational thermodynamics can be used as a tool to the development of fluorine-free mould powders. The phases of the recipes which do not contain fluorspar (R1, R2 and R3 in the present work) and their proportions at different temperatures were determined through *FactSage* commercial package. Results obtained from thermodynamics were correlated with heating microscope results and others experimental results from literature.

Regarding viscosity and melting characteristics, one recipe which does not contain fluorspar (R2 in the present work) reproduces approximately the properties of the mould powder Accutherm ST-SP/512SV-DS, produced by Stollberg do Brasil.

5 FURTHER WORK

Melting rate must also be evaluated and compared with conventional mould powders. Chemical interactions between liquid slag and liquid steel will be evaluated thermodynamically and through high-temperature laboratory furnace.

After all tests at laboratory scale, a fluorine-free mould powder will be selected to be tested at a steelworks plant (billet casting).

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