The Impact of MnO, Li$_2$O, ZnO and TiO$_2$ on Mold Powders Viscosity Using Hot Stage Microscope Analysis

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Abstract

The aim of conducting this research was to evaluate the viscosity change in the continuous casting of steel mold powders by altering their chemical compositions, using hot stage microscope analysis. 4 low-fluorine samples containing such compositions as MnO, Fe$_2$O$_3$, Li$_2$O, TiO$_2$ and ZnO, as well as another fluorine-free sample containing a combination of Fe$_2$O$_3$ and TiO$_2$, were prepared in this research. The viscosity of the reference powder (the mold powder applied in high-speed continuous casting in steel industry), as well as the viscosity of the above-mentioned samples, was evaluated using hot stage microscope analysis. The results of hot stage microscope analysis revealed that the viscosity of the reference powder was similar to that of low-fluorine and fluorine-free samples. Finally, a fluorine-free sample containing a combination of Fe$_2$O$_3$ and TiO$_2$ was introduced as an optimized composition which could be a substitute for the currently-used mold powder applied in the continuous casting of steel with high speed, considering its similar viscosity to be that of the reference powder.

Keywords: Mold Powder, Viscosity, Hot Stage Microscope.

1. Introduction

Mold powders, generally composed of SiO$_2$, CaO, Al$_2$O$_3$, Na$_2$O and fluorine (CaF$_2$), are used as raw materials in steel industry [1-3]. These powders are significantly used in continuous casting of steel slabs as they play a crucial role in making the process of continuous casting smooth, and improving the final quality of the product [4]. Among the most important functions of these powders, one can mention protecting the molten steel surface from oxidation, preventing from thermal loss, lubricating, absorbing impurities, and controlling heat transfer between the steel shell and mold through the solidified steel shell [5-8]. F$^-$, among all materials composing mold powders, performs the most important task. F$^-$ is added to the chemical composition of the mold powder through such compositions as CaF$_2$, resulting in controlling the viscosity of the mold powder and ensuring the desired lubrication between mold walls and the solidified steel shell; this leads to the improvement of the final quality of the product [9-11]. However, the emission of poisonous substances

from powders containing F$^-$ in cooling waters and its destructive effects on the environment have encouraged researchers to replace F$^-$ with other more environmentally–friendly substances. The emission of such poisonous substances containing F$^-$ as HF, SiF$_4$, etc. has been one of the most challenging issues for both researchers and environmentalists since these compositions cause the decay of the equipment used in continuous casting industry and the contamination of water, thereby endangering security and safety in the environment by being solved in cooling water and acidifying it [12-14]. Due to some technical reasons such as reducing the melting temperature and viscosity and creating crystalline particles in the flux film, F$^-$ is of great use in the chemical composition of mold powders in steel continuous casting industry. Hence, considering a replacement for it must be accompanied with considering these features [15]. The aim of this research was to estimate the viscosity of laboratory–prepared samples of mold powders by changing their chemical compositions. It should be considered, however, that it was necessary to estimate the viscosity of the industrial mold powder used as a reference powder in this research and so, it was used with high speed in steel continuous casting industry in order to reach this goal.

2. Experiments
2.1. Sample Preparation

The mold powder applied in high speed steel

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continuous casting industry was used as a reference powder in this research with the basicity of 0.94 (CaO/SiO_2=0.94). The chemical composition is indicated in Table 1.

Portland cement clinker was used as the main composition in laboratory-prepared samples in this research. A type of Portland cement clinker with the lowest harmful impurities of sulfate was used since these laboratory–prepared samples needed to be sulfate free. The chemical composition of the above -mentioned Portland cement clinker is given in Table 2. Other compositions such as silica (SiO_2), sodium carbonate (Na_2CO_3), fluorine (CaF_2), manganese oxide (MnO), magnesium oxide (MgO), hematite (Fe_2O_3), titanium oxide (TiO_2), zinc oxide (ZnO) and lithium carbonate (Li_2CO_3) were also used in this research.

Five powder samples each weighing 50 g were prepared by applying the aforementioned compositions. Table 3 shows the chemical compositions of these samples based on wt. % regardless of thermal loss.

Table. 1. Chemical composition of the reference powder in terms of weight percentage.

Chemical composition	Weight percentage
LOI	15- 18
C(total)	7- 9
C(free)	$4.5 - 6.5$
SiO_2	$28 - 29.5$
Fe_2O_3	$1 - 2.5$
Al_2O_3	$3 - 5$
CaO	$26 - 28$
MgO	$5 - 6$
$Na_2O + K_2O$	$6 - 8$
MnO	$4 - 6$
F^-	$3 - 4$
S	< 0.3
H_2O (120 ºC)	< 0.8

Table. 2. Chemical analysis of Portland cement clinker in terms of weight percentage.

Chemical composition	Weight percentage
SiO_2	21.78
Al_2O_3	5.41
Fe_2O_3	3.14
CaO	64.32
MgO	1.89
K_2O	0.73
Na_2O	0.28
SO_3	0.01

In order to mix and homogenize these laboratory–prepared samples with each other, ethanol and ball mill grinding was used. In other words, ethanol with 96% purity and the same weight as each sample was poured into ball mill grinding cups along with each sample. The sample and the added ethanol in the cup were mixed for five minutes with 600 rpm. Considering the fact that the samples contained ethanol, they were put into a drier with the temperature of 110 ºC for 3 hours to dry up in order for the ethanol to evaporate and the samples to dry. To study the effect of sample powders' viscosity and compare them with the viscosity of the reference powder, hot stage microscope analysis was conducted.

Table. 3. Chemical analysis of the prepared samples in terms of weight percentage.

Sample name	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	Na$_2$O	K$_2$O	F$^-$	TiO$_2$	ZnO	Li$_2$O	C	S
1	33.8	32.7	2.6	1.5	10.41	5.84	9.03	0.34	2.09				1.72	0.004
2	33.8	32.7	2.6	5.7	6.23	5.84	9.03	0.34	2.09				1.72	0.004
3	35.2	34	2.7	1.56	6.5	6.07	9.4	0.36	2.2			0.22	1.87	0.004
4	32.08	32.5	2.57	1.49	6.19	5.81	8.98	0.34	1.04	5.2	2.08		1.71	0.004
5	31.7	33.7	2.67	4.78	6.42	6.02	9.32	0.36		3.24			1.77	0.004

2.2. Studying the Effect of Viscosity by Conducting Hot Stage Microscope Analysis
2.2.1. Sample Preparation using Hot Stage Microscope

Each sample was first ground to turn into a soft powder. Then, the powder was changed into dough and put into a cylindrical mold with the height of 5mm and the diameter of 2 mm.

2.2.2. Sample Adjustment

The small cylindrical sample was put on a square aluminum plate with the dimension of 10*10 mm and the thickness of 0.6 mm. This instrumentplayed the role of a leg. Afterwards, the sample was located at the end of a bar, leading into the spherical furnace.

A spherical furnace Hot Stage Microscope and a light source were installed at one side and a taping camera was installed on the other one. When the cylindrical sample was put on the aluminum plate, it was moved into the furnace and the lighting caused a black and white image which was the shadow of the sample on the camera lens.

What was finally shown on the monitor was a rectangle. When the corner angles of the rectangle were fully sharp, the sampling was optimum (Fig. 1(a) and 1 (b)). The Microscope employed in this research was Olympus TS1400XY connected to a Mettler Toledo Hot Stage.

Hot stage microscope analysis was conducted to evaluate viscosity. In other words, a chart with vertical and horizontal axes was given using hot stage microscope analysis. The horizontal ax represented temperature based on centigrade, and the vertical one in terms of percentage; this showed the maximum of 105%, representing the primary height of the chart, which was calculated to be 100% by the device at the beginning of the analysis when the sample was not yet melted. The height was decreased as the temperature was increased. In fact, there was a slope in this chart which represented the viscosity of the sample. The more falling the slope, the less the viscosity existing at the temperature.

Fig. 1. A schematic of hot stage microscope.

3. Results and Discussion

Considering the melting graph of the reference powder derived from hot stage microscope analysis (Fig. 2), a volume increase was observed at the temperature range of 600 to 1070 °C in this sample. This volume increase might have been caused due to the formation of such gases as CO_2, which left the sample due to the reaction of the primary materials of the reference powder ($Na_2CO_3 \rightarrow Na_2O + CO_2$).

The viscosity of the reference powder remained stable in the temperature range of 1070 to 1130 ºC, thereby proving that there was a kind of viscosity stability in this temperature range. The viscosity of the reference powder was decreased in the temperature

range of 1130 to 1150 ºC, and it was wholly melted at the temperature of 1150 ºC.

MnO was used as a substitute to reduce CaF_2 in the chemical composition of sample 1. Sample 1 contained 2.09 wt. % of F^- and MnO amounts of 6.23 wt. % in the first place; this was then increased to 10.41 wt.% in the chemical composition of this sample. In the melting graph of sample 1 (Fig. 3), a slight increase in the volume due to the emission of CO_2 was noticed because the reaction of primary materials was observed in the temperature range of 600 to 800 ºC. The volume of sample 1 was maintained in the temperature range of 800 to 1125 ºC. This maintenance of the volume suggested that the surface energy of sample 1 did not allow such formed gases as CO_2 of the reaction to quit ($Na_2CO_3 \rightarrow Na_2O + CO_2$).
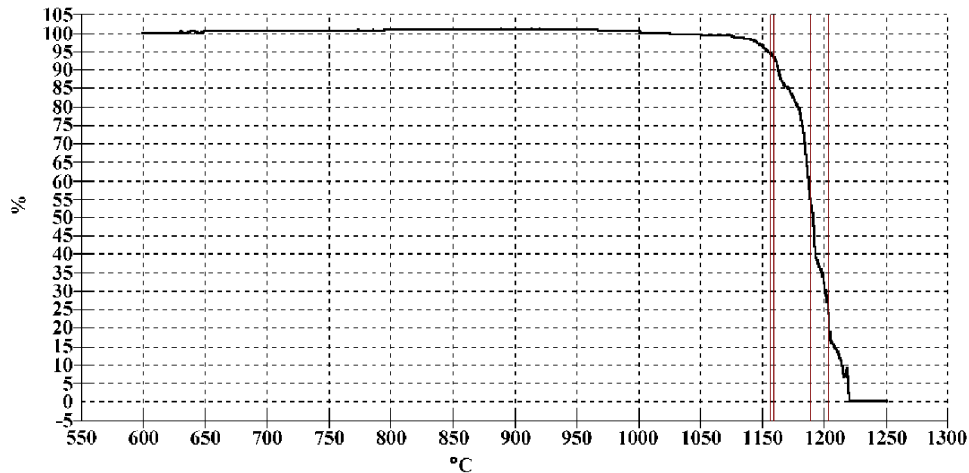
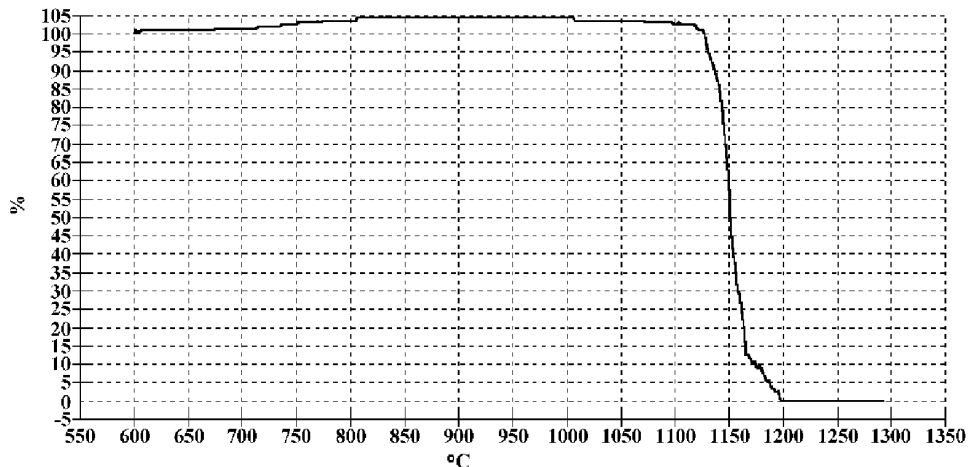Fig. 2. Reference powder melting graph using Hot Stage Microscope Analysis.

Fig. 3. Melting graph of sample 1 containing 2.09 wt.% F^- and 6.23 wt.% MnO using hot stage microscope analysis.

A sharp decrease in the viscosity was observed in the temperature range of 1125 to 1170 ºC, showing that the materials had produced gas up to the temperature of 1125 ºC. From the temperature of 1125 ºC on, the pressing force generated by production and expansion of gases apparently overcame the straining force of the primary materials shell, and the melt was of low viscosity. Viscosity was slightly increased in the temperature range of 1170 to 1200 ºC. Sample 1 was totally lubricating with no viscosity in the temperature range of 1200 to 1300 ºC. Considering the falls and rises of the slopes representing viscosity, it could be concluded that this sample had some viscosity almost similar to that of the reference powder. Fe_2O_3, which is a non-toxic composition, was used as a fluorine-reducing element in the chemical composition of sample 2. However, 1.5 wt. % of Fe_2O_3 existing in the chemical composition of Portland cement clinker was in the chemical composition of this sample. This amount of Fe_2O_3 was increased to 5.7 wt. %. The amount of F^- in this sample was 2.09 wt. %.

By considering the melting graph of this sample (Fig. 4), a slight volume increase of the powder was observed in the temperature range of 600 to 1125 ºC. This volume increase could be due to such gases as CO_2 produced because of the reaction of the primary

materials ($Na_2CO_3 \rightarrow Na_2O + CO_2$).

The slope representing the viscosity sharply fell in the temperature range of 1125 to 1190 °C. The condition of this temperature range in this sample was similar to that of the reference powder. A sudden fall of the viscosity and the complete lubrication of the powder were observed and derived in the temperature range of 1190 to 1200 °C. Li_2O was used as a fluorine-reducing element in the chemical composition of sample 3. This sample contained 2.2 wt. % of F^- and 0.22 wt. % of Li_2O.

Based on the melting graph of this sample (Fig. 5), a slight volume increase of the powder was observed in the temperature range of 600 to 1100 °C. This volume increase could be due to such gases as CO_2 produced because of the reaction of the primary materials. It must be, however, noted that gases quit the sample near the temperature range of 1100 °C, causing the vertical ax of graph to reach 100 % ($Na_2CO_3 \rightarrow Na_2O + CO_2$ and $Li_2CO_3 \rightarrow Li_2O + CO_2$).
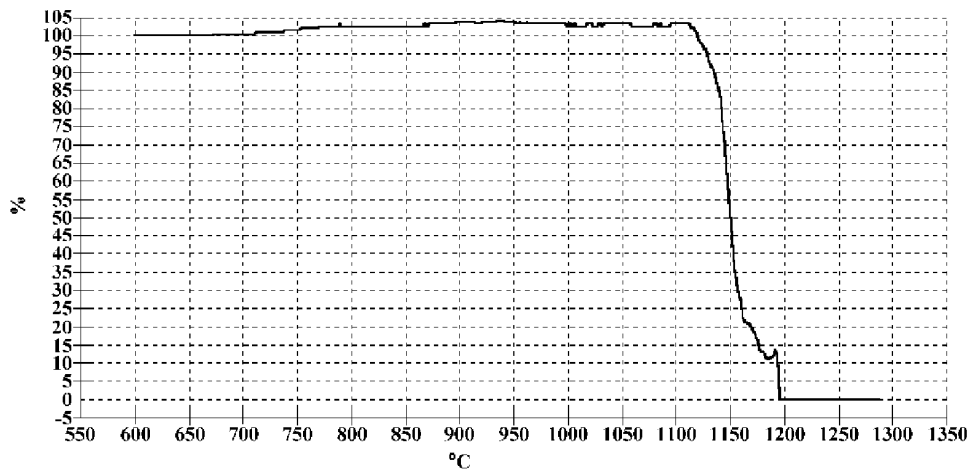

Fig. 4. Melting graph of sample 2 containing 2.09 wt. % F^- and 5.7 wt. % Fe_2O_3 using Hot Stage Microscope Analysis.
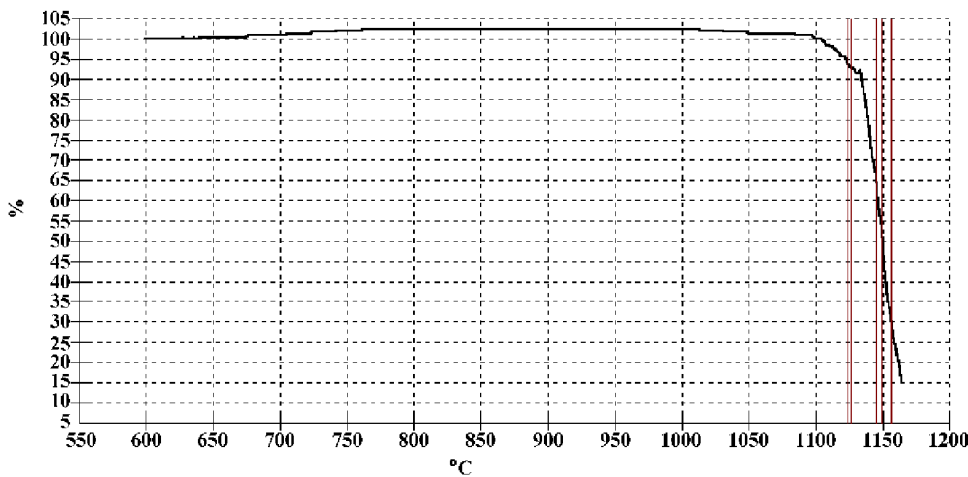

Fig. 5. Melting graph of sample 3 containing 2.2 wt. % F^- and 0.22 wt.% Li_2O using Hot Stage Microscope Analysis.

The viscosity of sample 3 was higher than that of the reference powder in the temperature range of 1100 to 1140 °C. The viscosity was decreased in the temperature range of 1140 to 1160 °C, which was less than that of the reference powder. Considering the melting graph of sample 3 in the temperature range of 1140 to 1160 °C, it could be concluded that Li_2O with the amount of less than 0.2 wt. % was an appropriate lubricating oxide which could be a substitute to reduce

CaF_2 in the chemical composition of this sample.

TiO_2 and ZnO were used as fluorine-reducing elements in the chemical composition of sample 4. This sample was, therefore, a low-fluorine one containing 1.04 wt. % of F^-, 5.2 wt. % of TiO_2 and 2.08 wt. % of ZnO. No volume increase was observed in the temperature range of 600 to 1100 °C in the melting graph of this sample (Fig. 6). This meant that all gases such as CO_2 produced by the reaction of the

primary materials quit the sample prior to reaching the temperature of 600 ºC. The viscosity of this sample had a fall in the temperature range of 1100 to 1130 ºC, thereby showing an increase in the viscosity in comparison to that of the reference powder in the same range of temperature. The viscosity of this sample was decreased slightly in the temperature range of 1130 to 1160 ºC, and the whole powder was melted. In this temperature range, 1130 to 1160 ºC, the viscosity was less than that of the reference powder. The viscosity was sharply decreased in the temperature range of 1160 to 1200 ºC and the whole sample was thoroughly melted at once. The viscosity was very similar to that of the reference powder in this temperature range. Considering the frequent vibrations of the viscosity-representing slope in the melting graph of the sample 4, this sample seemed to have some viscosity similar to that of the reference powder.

A combination of Fe_2O_3 and TiO_2 was used as a substitute for CaF_2 in the chemical composition of sample 5. In other words, CaF_2 was thoroughly omitted from the chemical composition of this powder. This sample contained 1.54 wt. % of Fe_2O_3, which was increased to 4.78 wt. %. In addition, 3.24 wt. % of TiO_2 was also added to this sample. The melting graph of this sample (Fig. 7) showed a slight volume increase in the temperature range of 600 to 1120 ºC due to such produced gases as CO_2 because of the reaction of the primary materials ($Na_2CO_3 \rightarrow Na_2O + CO_2$). The viscosity of the sample 5 was observed to be more than that of the reference powder in the temperature range of 1120 to 1150 ºC. The viscosity was decreased in the temperature range of 1150 to 1170 ºC. At last, the whole powder was completely melted. Sample 5 was a fluorine-free one having some viscosity very similar to that of the reference powder.
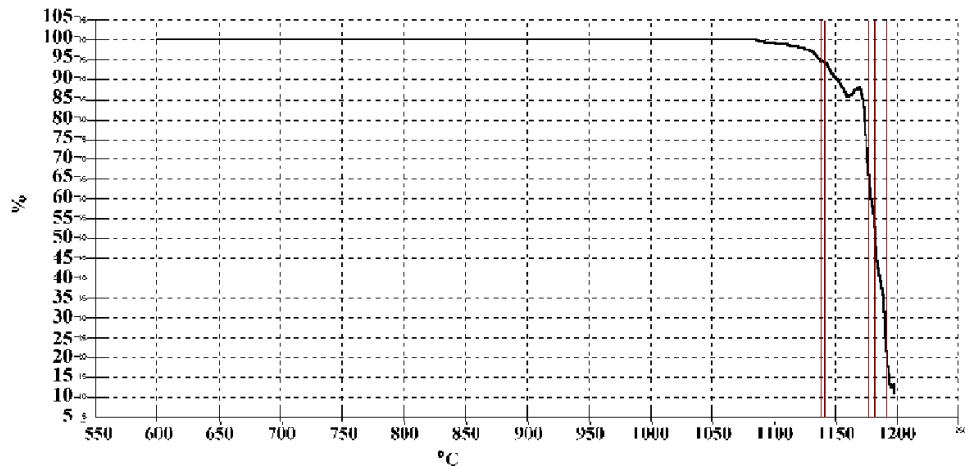

Fig. 6. Melting graph of sample 4 containing 1.04 wt. % F⁻, 5.2 wt.% TiO_2 and 2.08 wt.% ZnO using Hot Stage Microscope Analysis.
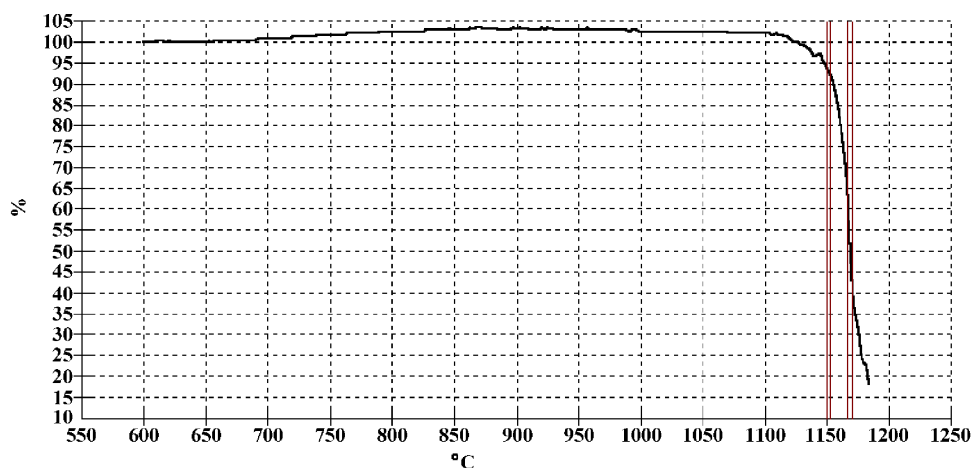

Fig. 7. Melting graph of sample 5 containing 4.78 wt. % Fe_2O_3 and 3.24 wt. % TiO_2 using Hot Stage Microscope Analysis.

4. Conclusion

• By using MnO with amounts of about 4 wt.% (surplus to the existing MnO in the chemical composition of the mold powder), a lower-fluorine sample (sample 1), in comparison to the reference powder, was prepared. This sample could be a recommended alternative to the reference powder currently used in the continuous casting of steel industry.

• By using 4.2 wt.% of Fe_2O_3 (surplus to the existing Fe_2O_3 in the chemical composition of Portland cement clinker in the chemical composition of the mold powder) and 2.09 wt.% of F^-, a low-fluorine sample (sample 2) was prepared that showed some rather similar viscosity to that of the reference powder. This sample could also be a recommended alternative to the reference powder currently used in the continuous casting of steel industry.

• By employing 0.2 wt.% of Li_2O, a low-fluorine sample (sample 3) was prepared that had some viscosity similar to that of the reference powder. Li_2O, which was a lubricating composition, proved to be able to control the viscosity if used in low amounts along with CaF_2.

• By a combination of hematite and TiO_2, a fluorine-free sample (sample 5) was prepared that had some viscosity similar to that of the reference powder. This sample can be an optimized composition because of its viscosity, which was similar to that of the reference powder; therefore, it could be a substitute for the currently used mold powder applied in the continuous casting of steels with high speed.

It must be taken into consideration, however, that these substitutions are recommended according to their viscosity, which was similar to that of the reference powder.

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