The Influence of Hematite on High Speed Continuous Casting of Steel Lubricating Powders: Viscosity and Crystallization

A. Shafieirad [1], A. Arefpour [2*], A. Monshi [3], A. Saidi [4]

Advanced Materials Research Center, Faculty of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran

Abstract

Mold powders used in the continuous casting of steel contain the harmful CaF_2 as a main substance developing toxic gases such as SiF_4 and HF at elevated temperatures. In this study, three samples of I_1, I_2 and I_3, which contained gypsum free Portland cement clinker with different percentages of Fe_2O_3 (5.68, 6.83, 8.02) and F^- (2.09, 1.06, 0), were prepared and their main characteristics were compared with those of the standard and the molten reference powder. The results showed similarity in viscosity between samples I_1, I_2 and the molten reference powder, which was desired. Sample I_3 with no fluorine showed a higher viscosity in comparison to the standard sample and therefore, a complete replacement of CaF_2 with Fe_2O_3 could not be recommended. Furthermore, the XRD of the reference powder, molten reference powder and sample I_2, the SEM of the molten reference powder and sample I_2 and EDS of sample I_2 analyses were also performed. The XRD patterns results demonstrated that by decreasing CaF_2, cuspidine phase was vanished, while other crystalline phases such as gehlenite, fayalite, akermanite, nepheline and Mn_3O_4 were found. In addition, SEM micrographs and EDS analysis of sample I_2 in the white area revealed crystalline particles in the glass matrix. Considering EDS analysis of sample I_2 showed the existence of Mg, Na, Mn, Fe, Si, Al and O. It could be concluded that such crystals as gehlenite, akermanite, nepheline and fayalite were composed in the glass matrix, developing to similar heating properties in the glassy matrix.

Keywords: Mold powder; Viscosity; Fluorine; Hematite.

1. Introduction

Mold powders for the continuous casting of steel production have been used to enhance the final quality of the products [1]. The final quality of the products depends on the viscosity and heat transfer of thermal powders permeating between the mold wall and the solidified steel shell [2]. Mold powders have various functions including protecting the molten meniscus protection against oxidation, providing thermal insulation of the molten meniscus, as well as adequate lubrication between the mold wall and the solidified shell, controlling heat transfer between the mold and the solidified shell, and absorbing impurities from the molten materials [3-5]. Among these, lubrication and heat transfer of mold powder are the two major factors [6, 7]. Mold powders make a slag film between the mold wall and the solidified shell which is usually made up of three layers: molten, crystalline and glass [8]. The composition of mold powders usually includes oxides such as SiO_2, Al_2O_3, CaO and fluorine (CaF_2) compounds [9, 10]. Among these compounds, CaO, SiO_2 and CaF_2 make a crystalline deposit in the slag film called cuspidine [11]. The fluorine in the mold powder adjusts the viscosity and the melting point [5]. Furthermore, fluorine in the mold is a lubricant agent, but its presence also causes corrosion and erosion of the factory equipment; therefore, it is a harmful compound for human and environment [12]. The objective of this work was to decrease fluorine compound level and replace it with the hematite compound. As expected, the results showed that the viscosities of samples with low fluorine were comparable to that of the molten reference powder. Furthermore, XRD patterns, SEM micrographs and EDS analysis of sample I_2 were compared with those of the standard and the molten reference powder in order to ensure an accurate comparison of the crystalline behaviors.

* *Corresponding Author*
Tell: +98 913 101 9125
Email: arefpour.a@gmail.com
Address: Advanced Materials Research Center, Faculty of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran
1. M.Sc.
2. M.Sc.
3. Professor
4. Professor

Table 1. Chemical composition of the reference powder on the basis 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
Fluorine (F^-)	3 – 4
S	< 0.3
H_2O (120 ºC)	< 0.8

2. Materials and Method

2.1. Samples preparation

In order to lubricate and improve the quality of the steel produced in the continuous casting process at Mobarakeh Steel Complex, Iran, a mold powder was used as the reference powder. The chemical composition of this powder is provided in Table 1.

According to the data in Table 1, the reference powder contained carbon. Since the main purpose of this research was to study the effect of hematite on the viscosity of mold powders and compare the viscosities of the lab samples to that of the reference powder, the reference powder was required to be decarburized at

Table 2. Chemical composition of the decarburized reference powder.

Chemical Composition	Weight percentage
CaO	35.99
SiO_2	31.06
Na_2O	8.78
MnO	5.95
Al_2O_3	5.59
MgO	5.58
F	4.5
Fe_2O_3	2.67
SO_3	0.387
TiO_2	0.275
K_2O	0.199
Cr_2O_3	0.075
P_2O_5	0.063
NiO	0.058
CuO	0.028
SrO	0.025
ZnO	0.022
Cl	0.018
ZrO_2	0.012
LOI*	0.63
* LOI: Loss on Ignition	

580 ºC, in the air, for 24 hours [13]. The detailed analysis of the decarburized reference powder is shown in Table 2. This powder was named the original reference powder.

The main compound used to make the samples was Portland cement clinker, whose chemical analysis is given in Table 3. Other substances such as silica (SiO_2), magnesium oxide (MgO), manganese oxide (MnO), sodium carbonate (Na_2CO_3), fluorine (CaF_2) and hematite (Fe_2O_3) were also employed to make the samples.

Since these samples were supposed to be free from impurities such as sulfates, Portland cement clinker was used in the chemical composition of the samples. According to the reference powder (Table 1), chemical composition of the decarburized reference powder (Table 2), chemical analysis of Portland cement clinker (Table 3), and basicity of the reference powder (CaO/SiO_2=0.94), three 100g samples were prepared based on the chemical composition reported in Table 4. So the prepared samples were based on 100 percentage, without calculating the loss on ignition as the total percentage, as given in Table 5.

Each sample was mixed with ethanol (96% purity) in a grinding mill at a rate of 600 rpm for 2 minutes and 30 seconds (the amount of ethanol used was equal

Table 3. 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

Table.4. Chemical composition of the prepared samples on the basis of gram.

	I_1	I_2	I_3
Portland cement clinker	45.65	45.65	45.65
SiO_2	21.29	21.29	21.29
MnO	5.95	5.95	5.95
MgO	4.72	4.72	4.72
Na_2CO_3	14.53	14.53	14.53
CaF_2	4.1	2.05	
Fe_2O_3	4	5	6

Table 5. Chemical analysis of the prepared samples based on weight percentage.

	I_1	I_2	I_3
CaO	33.8	32.76	31.7
SiO_2	32.68	33.19	33.72
Fe_2O_3	5.68	6.83	8.02
Al_2O_3	2.58	2.62	2.67
MnO	6.23	6.32	6.42
MgO	5.84	5.93	6.02
Na_2O	9.03	9.17	9.32
K_2O	0.34	0.35	0.36
F^-	2.09	1.06	---
C	1.72	1.74	1.77
S	0.004	0.004	0.004

to the weight of each powder sample). In order to evaporate the ethanol in the samples, the samples were placed in a drier at 110 °C for three hours.

2.2. Viscosity comparison

When powders appeared to be dried, compacted disc samples 1g in weight (with 13 mm diameter and 2 mm height) were prepared under a pressure of 30 bars using a press operation. A compressed sample of the original reference powder with three other compressed samples were then placed on the top of a groove viscometer plate placed on a slope of 45° (Fig. 1). Finally, the set was placed in a furnace. To prevent the possible breaking of the groove viscometer at high temperature, the whole set was preheated at 400 °C for 30 minutes. After preheating, the furnace temperature was increased from 400 °C to 1150 °C. At 1150 °C, the furnace was turned off and the set was cooled inside it.

*Fig. 1. Schematic illustration of the groove viscometer placed on the 45° slo*pe.

2.3. Crystalline behavior

2.3.1. XRF analysis

In order to determine the chemical analysis of the decarburized reference powder, X-ray Fluorescence instrument, model S4PIONEER, manufactured by Bruker Company in Germany with the accuracy of 0.01%, was employed.

2.3.2. XRD analysis

XRD patterns were conducted in order to identify phases in the reference powder and the molten samples on the grooves of the groove viscometer. In this stage, X-ray diffraction instrument, model D8ADVANCED, manufactured by Bruker in Germany, was employed.

2.3.3. SEM analysis

In order to study the microstructure of the reference powder and the molten samples on the grooves of the groove viscometer, Scanning Electron Microscope, model VEGA2, manufactured by TESCAN Company in Czech Republic, was employed.

3. Results and Discussion

The original reference powder was fired at 1150 ºC and melted on the groove of a groove viscometer. This powder was used as the molten reference powder to compare its viscosity and crystalline behavior to those of the molten prepared samples. Comparison of the viscosity of the molten samples on groove viscometer to that of the molten reference powder is shown in Fig. 2.

Fig. 2. Schematic illustration of molten samples on the groove viscometer.

The results showed that sample I_1 with F- (2.09 %wt.) and hematite (5.06 %wt.) had a viscosity similar to that of the molten reference powder. Additionally, in sample I_2, with the reduction of fluorine to about 1 %wt. and the enhancement of hematite to 6.83 %wt., a similar viscosity was also obtained, as compared to the molten reference powder. In sample I3, however, by the complete elimination of fluorine and its replacement with 8.02 %wt. hematite, the viscosity was increased in comparison to the other three samples: I_1, I_2 and the molten reference powder. Therefore, this option could not be recommended. The comparison of the viscosity of samples I_1, I_2 and I_3 with that of the molten reference powder showed that hematite was a non-toxic compound and acted like fluorine in controlling the viscosity of the mold powders. Therefore, hematite could be a suitable substitute for the partial replacement of fluorine in the chemical composition of the mold powder used in the continuous casting of steel production.

Chemical composition of mold powders plays

a key role in its viscosity. These compositions can be generally divided into two groups: glass-making compositions, which form the structure of glass in a molten powder, such as SiO_2, Al_2O_3, bond-breaking compositions, which cause the lubrication that decreases the viscosity of the powder by breaking the bonds. The instances of the latter are Na_2O, K_2O, Li_2O, CaO, MgO, MnO, hematite, B_2O_3 and the bond breaking composition of fluorine. The effect of some compositions such as TiO_2 can be very complicated. For example, adding TiO_2 up to 6 weight percentage to a mold powder decreases its viscosity and increases it in higher amounts. This proves that TiO_2 acts as a bond-breaking composition in lower amounts, in comparison to the 6 weight percentage, which decreases the viscosity and acts as a glass-making composition in higher amounts, and increases the viscosity [3]. It can be concluded that hematite, like TiO_2, is a bond-breaking composition causing the bridge oxygen to change into the non-bridge one by breaking the bond in the silicate network and consequently, decreasing the viscosity of the mold powder (Fig. 3).

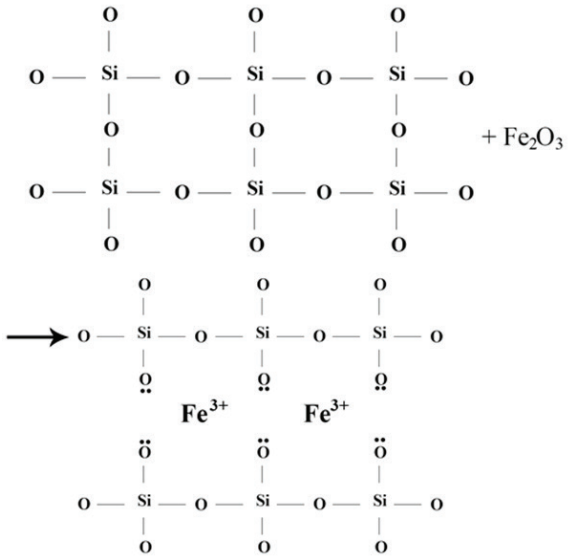

Fig. 3. Bond breaking mechanism of hematite in the composition of the silicate network.

Hematite led to some apt lubrication in samples I_1 and I_2 by breaking the bonds of silicate network and turning the bridge oxygen into the non-bridge one. On the other hand, sample I_3, in which hematite was 8.02% of the weight, showed increased lubrication. It can be, therefore, concluded that hematite in amounts higher than 8 %wt. acts as a glass-making component leading to an increase in the viscosity of the mold powder.

In order to identify the reference powder and compare the crystalline behavior of the molten reference powder with that of sample I_2, XRD, SEM and EDS of the samples were analyzed. The XRD patterns phases of the reference powder were wollastonite ($CaSiO_3$), silica (SiO_2), $MnSiO_3$, aluminum oxide (Al_2O_3), Na_2CO_3, fluorine (CaF_2), $CaMg(SiO_3)_2$ and $CaAl_2O_4$.

The main phase in this powder was wollastonite (Fig. 4). Subsequently, the crystalline behavior of the molten prepared in sample I_2 was compared with that of the molten reference powder. The XRD pattern of the molten reference powder showed the main phases of gehlenite ($Ca_2Al_2SiO_7$), cuspidine ($Ca_4F_2Si_2O_7$) and akermanite ($Ca_2MgSi_2O_7$). In addition, nepheline ($NaAlSiO_4$) and Mn_3O_4 phases were also observed. Data in Fig. 5 shows a schematic illustration of the XRD pattern of this powder.

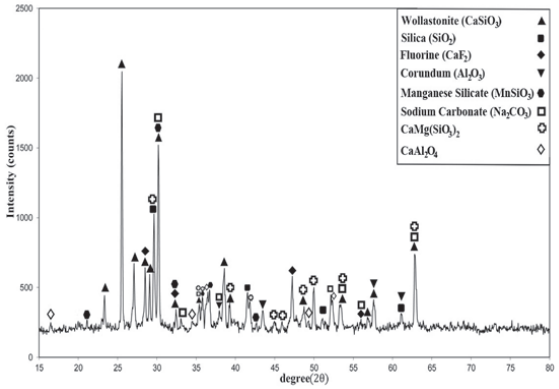

Fig.4. Schematic illustration of the XRD pattern of the reference powder.

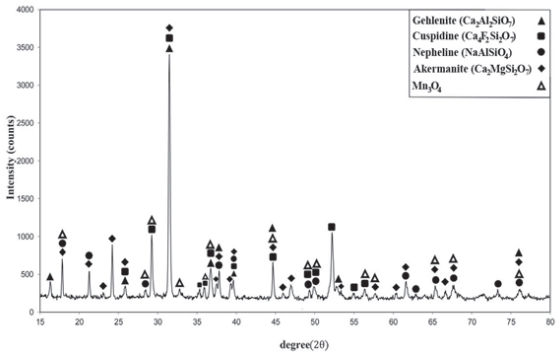

Fig. 5. Schematic illustration of the XRD pattern of the molten reference powder.

The SEM micrographs of the molten reference powder at 1000x and 9000x (Fig. 6(a) and 6(b)) indicated the existence of the crystalline particles in the matrix. By considering the SEM micrographs of the molten reference powder, it can be concluded that the white particles included multiple silicates dispersed inside the glass, which could be good for the mold powder because they optimized the viscosity of the mold powder, and offered favorable conditions for the cooling of ingot.

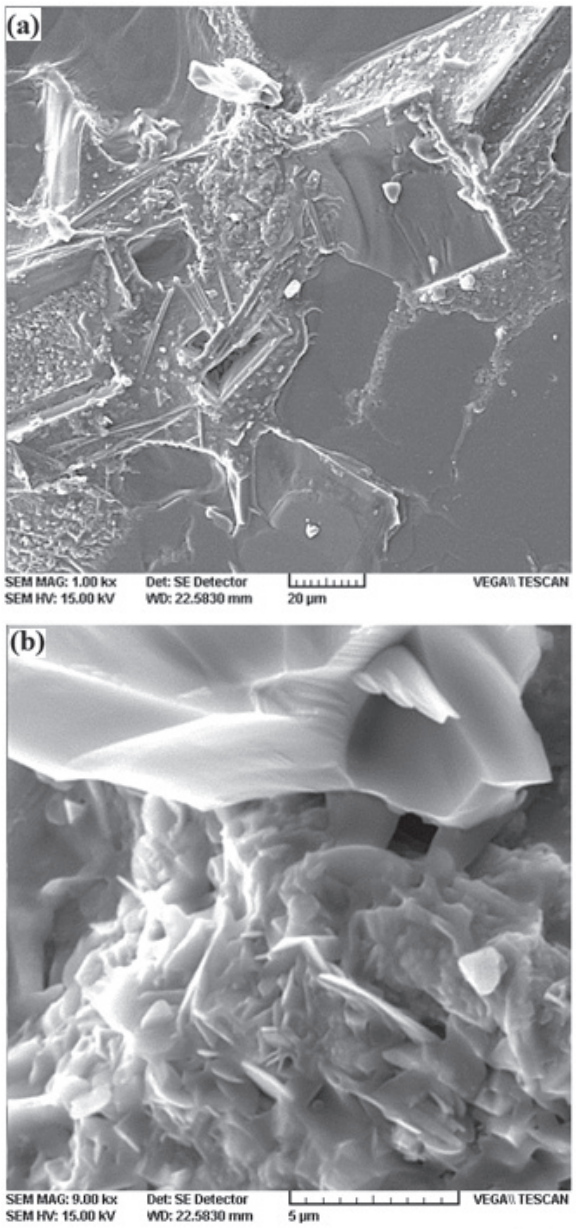

Fig. 6. SEM micrographs of the molten reference powder (a) 1000x and (b) 9000x.

Data in Fig.7 shows a general view of the XRD pattern of sample I_2. The XRD pattern of sample I_2 showed crystalline phases such as gehlenite, akermanite, nepheline and Mn_3O_4, which were also seen in the molten reference powder. Moreover, the crystalline phase of Ca_3SiO_5 was seen in the XRD pattern of sample I_2, indicating the existence of Portland cement clinker in the chemical composition of sample I_2. The XRD pattern of sample I_2 also showed the crystalline phase of fayalite (Fe_2SiO_4) as a result of adding hematite to the chemical composition of sample I_2. The crystalline phase of fayalite had a high tendency to form. On the other hand, it appeared that, because this phase was rather fast to melt, it could have the capacity to absorb a major amount of SiO_2 and decrease it from the crystalline phase of cuspidine to a noticeable amount. That is why the crystalline phase of cuspidine was not seen in the XRD pattern of sample I_2.

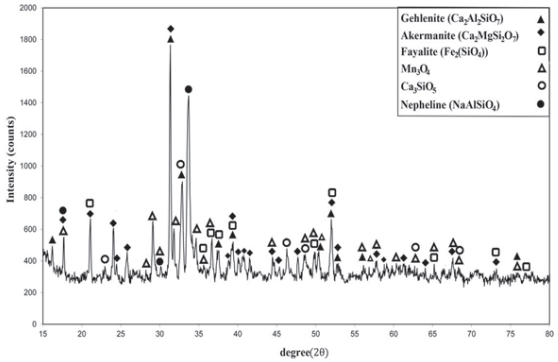

Fig. 7. Schematic illustration of the XRD pattern of sample I_2.

The SEM micrographs of this sample at 1000x and 9000x (Fig. 8(a) and 8(b)), and the EDS analysis of white particles showed fayalite crystals beside gehlenite, akermanite, nepheline, Ca_3SiO_5 and Mn_3O_4 crystals. On the other hand, the EDS analysis of sample I_2 (Fig.9 and Table 6) revealed 8.52 %wt. of

Table. 6. EDS analysis of the white particles of sample I_2.

Norm. C[wt.%]	Series	Element
16.82	K series	Oxygen
0.01	K series	Fluor
7.12	K series	Sodium
2.05	K series	Magnesium
3.31	K series	Aluminum
24.48	K series	Silicon
2.18	K series	Potassium
33.32	K series	Calcium
2.17	K series	Manganese
8.52	K series	Iron

iron. It seemed that the fayalite crystal along with other crystals whose crystalline phases were indicated in the XRD pattern in the glass matrix resulted in the optimized viscosity of the mold powder.

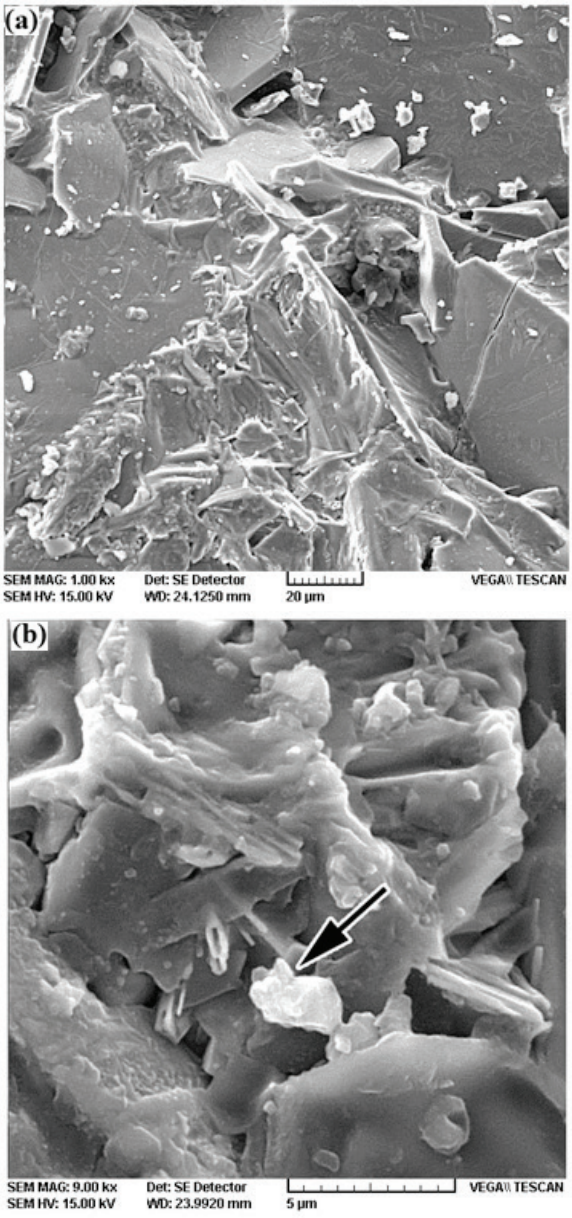

Fig. 8. SEM micrographs of sample I_2 (a) 1000x and (b) 9000x.

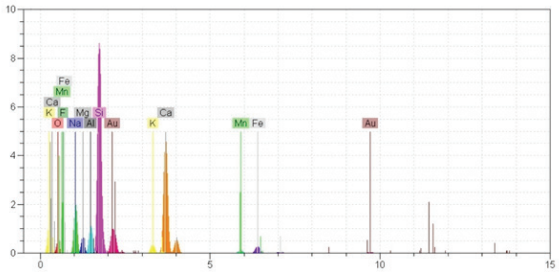

Fig. 9. EDS analysis of sample I_2.

4. Conclusions

The results of this study could be summarized in the three following statements:

- Hematite or Fe_2O_3 are suitable oxide compounds that can be used in mold powders for either reducing or replacing fluorine compound. This finding was primarily based on the results showing that a viscosity similar to that of the molten reference powder was obtained in our study.
- No cuspidine phase was observed in the XRD pattern of sample I_2 due to the reduction of the fluorine; however, other crystalline phases such as gehlenite, akermanite, fayalite Mn_3O_4 and nepheline could be developed to represent similar properties in the mold powder.
- As an environmental advantage, similarity in viscosity and development of some crystalline particles in the glassy matrix can be promising in the replacement of harmful CaF_2 with the non-toxic hematite and the development of new mold powders.

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