Effects of Replacing Fluorine with Sodium and Titanium Oxides on Mold Powders Lubrication in Continuous Casting of Steel

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ABSTRACT

Mold powders are used as raw materials in continuous casting of steel industry. They are mostly composed of aluminum, calcium, silica oxides, alkaline and earth-alkaline oxides along with carbon and fluor. Two of the most important duties of mold powders are the lubrication of the space between mold walls and steel shell, and heat transfer control between steel shell and the copper mold. Fluor is one of the most important constituents of mold powders and is employed to control viscosity in order to obtain favorable lubrication and solidification temperatureinheat transfercontrol. The fluor in the mold powder is added with the aid of some fluorided compounds like fluorine (CaF_2). Using Portland cement clinker and fluorine,this study aimsto make a powder similar to the reference sample. Moreover, groove viscometer studies have been conducted to compare the sample viscosities to that of the reference sample. In addition, XRD as well as SEM analyses were conducted. As a result, the crystalline phase of cuspidine was found in the glass matrix indicating that the chemical compound in sample 1 may be a suitable substitute compared to the reference sample for the mold powder used in continuous casting steel industry.

1. Introduction

Over ninety percent of the world's steel is produced through the process of continuous casting of steel [1]. Continuous casting of steel industry has been one of the most important operation units in steel production throughout the world in order to reach an efficient final product with high quality [2]. In order to reach this level, it is essential to employ mold powder which plays a key role in the stability of continuous casting of steel in all speed ranges [3, 4].

Mold powders are used as raw materials in steel industry and are mainly composed of such oxides as SiO_2, CaO, Al_2O_3, alkaline oxides, earth-alkaline oxides, carbon, and Fluor [5, 6].

Mold powders, or mold lubricants as they are sometimes called, are bound to some duties among which lubricating between mold walls and solidified shell of the steel and controlling heat transfer between the steel shell and the copper mold are two to be mentioned [7]. It should also be noted that mold powders prevent molten steel from oxidation, insulate molten steel to prevent heat loss and absorb impurities from molten steel during continuous casting of steel as well, inadditionto their above-mentioned duties [8, 9].

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Table 1. Composition of the reference powder based on weight percentage

Chemical composition	Weight percent
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°C)	< 0.8

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

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

One of the composing constituents of mold powders is Fluor which helpsincontrolling viscosity and hence obtaining an apt lubrication and control of solidification temperature for controlling heat transfer [10]. Fluor in the composition of the mold powder is added to it through such components as CaF_2 which contain fluoride. Fluorine in the composition of the mold powder creates a crystalline sediment called Cuspidine ($3CaO.2SiO_2.CaF_2$) in mold lubricants which causes a favorable lubrication and the control of the viscosity which are crucial parameters in determining the condition of casting [11, 12].

In this research, Fluorine is employed to produce a powder similar to the reference powder. Additionally, TiO_2 is applied to decrease or thoroughly substitute Fluorine in the composition of the mold powder. Groove viscometer is employed in order to study the viscosity of the powders, and XRD and SEM analyses are applied to study their crystalline behavior.

2. Experimental

Mobarakeh Steel Complex applies a mold powder for high speed continuous casting of steel that is taken as reference powder in this research. Chemical analysis of this powder based on weight percentage is given in Table1. Such materials as SiO_2, MnO, Na_2CO_3, MgO, CaF_2, TiO_2,and Portland cement clinker whose chemical analysis is given in Table 2 were used to make laboratory powder samples. The percentage of the above minerals is according to Table 3. Since in this research the prepared laboratory samples should be free from harmful components of sulfate, Portland cement clinker free from harmful impurities of sulfate was used. Considering the analyses of the reference powder and Portland cement clinker, three 50-gram samples were prepared whose chemical compositions are given in Table 4. It should be mentioned that the chemical compositions of these prepared samples are based on weight percentage and have been calculated without considering any heat loss. In order to homogenize the above-mentioned minerals, ball milling was employed. Ethanol with ninety-six percent puritywith the same weight as the sampleswas added to eachsample and they were mixed with the speed of 600 Rpm in the mill for homogenization. Subsequently, in order to vaporize the ethanol, the samples were put in a drier with the temperature of 110°C for three hours. After the drying, three laboratory

Table 3. Chemical composition of the usedmaterials on the basis ofweight percentage

Materials	Sample 1	Sample 2	Sample 3
Portland cement clinker	45.5	45.7	45.08
SiO_2	21.2	21.3	21.02
Na_2CO_3	14.5	16.25	19.41
MnO	5.93	5.95	5.87
MgO	4.7	4.72	4.7
TiO_2	---	2	3.95
CaF_2	8.2	4.1	---

Table 4. Chemical analysis of the prepared samples based on wt%

	1	2	3
CaO	36.52	34.08	30.63
SiO_2	32.36	32.95	32.6
Fe_2O_3	1.48	1.51	1.5
Al_2O_3	2.56	2.61	2.58
MnO	6.16	6.3	6.21
MgO	5.78	5.9	5.82
Na_2O	8.94	10.2	12.13
K_2O	0.34	0.35	0.35
F^-	4.14	2.1	0
TiO_2	-	2.11	4.17
S	0.004	0.004	0.004
C	1.7	1.94	2.33

samples with the height of 2 mm and diameter of 13 mm as well as the reference sample pressed under 3 Mpa were created. All the samples were then placedon the groove viscometer, and the viscometer was located on a surface with a slope of 45°. All these were put in the furnace. Because of the breaking possibility of the viscometer and the destruction of the samples in high temperature, the temperature of the furnace was first set on 400°C and the samples were pre-heated for 30 minutes. Afterwards, the temperature of the furnace was increased to 1150°C in which the samples were melted on the groove viscometer. The furnace was then turned off and all the contents were left to cool down.

3. Result and discussion

Before studying and discussing the results, it is worth mentioning that one of the most important researches on mold powders in continuous casting of steel was production of a mold powder for steel enriched with reducers by Itoyama et al. in 1994. In addition, the production of a low-fluorine mold powder by Morita et al. in 2002 and the production of a fluorine-free mold powder with TiO_2 in amounts about 1-6 weight percentage by Wen et al. in 2007 [1, 6] should also be mentioned.

Fig. 1 is a schematic demonstrating the molten samples on the groove viscometer. Sample 1, which contains 4.14 wt% (about 8 gr) of Fluor, has a very similar viscosity to that of the molten reference powder. It seems that

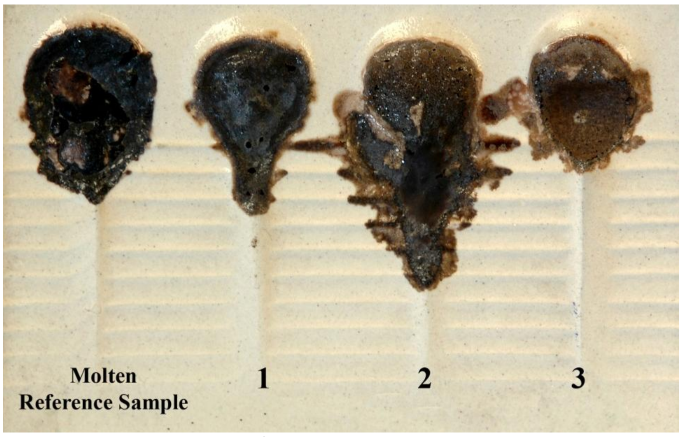

Fig. 1. Schematic illustration of the samples molten on the groove viscometer

sample 1 has shown the effect of Fluorine in the lubrication of the mold powder. In other words, the lubrication of sample 1 is more favorable than that of the molten reference powder. Therefore, it can be concluded that the main task of Fluorine in the composition of the mold powders in continuous casting of steel is controlling the viscosity or creating a favorable lubrication. On the other hand, Fluorine along with SiO_2 and CaO lead to a favorable lubrication between the cooling copper mold and the solidified steel shell with the creation of the crystalline sediment of Cuspidine. This proves that, underthe abovementioned conditions, the quality of the final product is improved and the condition for continuous casting of steel is optimized. Sample 2, in which Fluor was reduced to half and TiO_2 was used instead, caused more lubrication and increased fluidity in comparison to that of the molten reference powder when 2 grams of Fluor (2.1 wt%) and 2 grams of TiO_2 (2.1 wt%) were applied to its chemical composition and the weight percentage of Na_2O was increased 1.26% comparedto sample 1. In other words, it can be said that sample 2 was not comparable to the molten reference powder considering that it caused too much lubrication having Fluorine along with TiO_2 and Na_2O.In sample 3, in which Fluor was completely eliminated and replaced with 4 grams of TiO_2 (4.24 wt%) and a two-percent increase of Na_2O compared to that of sample 2, the molten powder was not fluid on the groove viscometer and the viscosity was much higher when compared to that of the molten reference powder as seen in Fig 1. Hence, it can be concluded that Fluorine obtains more fluidity power than TiO_2. In other words, TiO_2 has acted as a viscose-making component and its application as a substitute for Fluor is not favorable and therefore not suggested.

In order to study the crystalline behavior of the reference powder and the molten reference powder, XRD and SEM analyses were conducted.

XRD analysis of the reference powder revealedwollastonite ($CaSiO_3$), silica (SiO_2), hematite (Fe_2O_3), CaF_2, Al_2O_3, Na_2CO_3, CaMg $(SiO_3)_2$, and $CaAl_2O_4$ phases. The $CaSiO_3$ phase had the highest peak considering the intensityof the peaks compared with other phases. In other words, $CaSiO_3$is the main component of the main composition of the reference powder. Fig. 2 is a schematic of the XRD pattern of the reference powder. SEM images of the sample in magnificationsof 500x and 1000x, shown in Fig. 3a and Fig. 3b, respectively, prove the fact that $CaSiO_3$is the main constituent of the of the main composition of the reference powder.

Considering the composition of the reference powder, which is mainly composed of CaOand SiO_2, Portland cement clinker whose 88 percent is made up of CaO and SiO_2 was employed in the production of the samples.

Subsequently, the reference powder was heated and melted at 1150°C.As it was melted in such high temperature, gehlenite ($Ca_2Al_2SIO_7$), cuspidine ($Ca_4F_2Si_2O_7$), and akermanite ($Ca_2MgSi_2O_7$) phases with a high peak were detectedin the XRD analysis of this

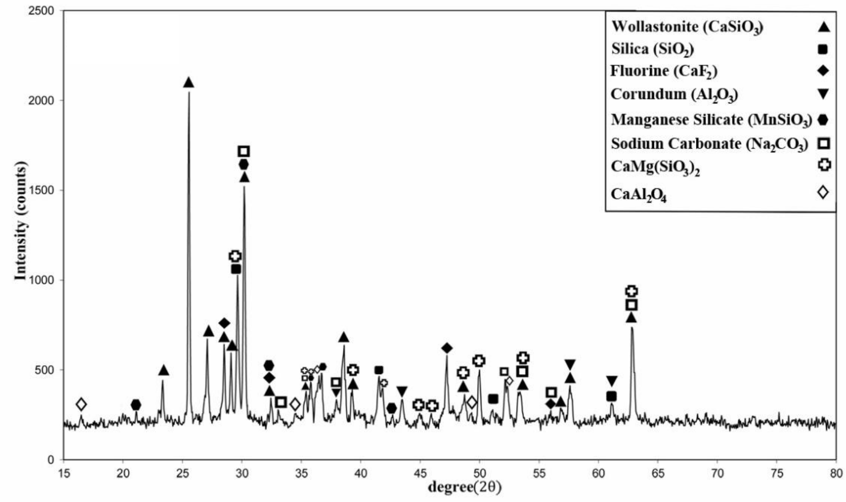

Fig. 2. The XRD analysis of the reference powder

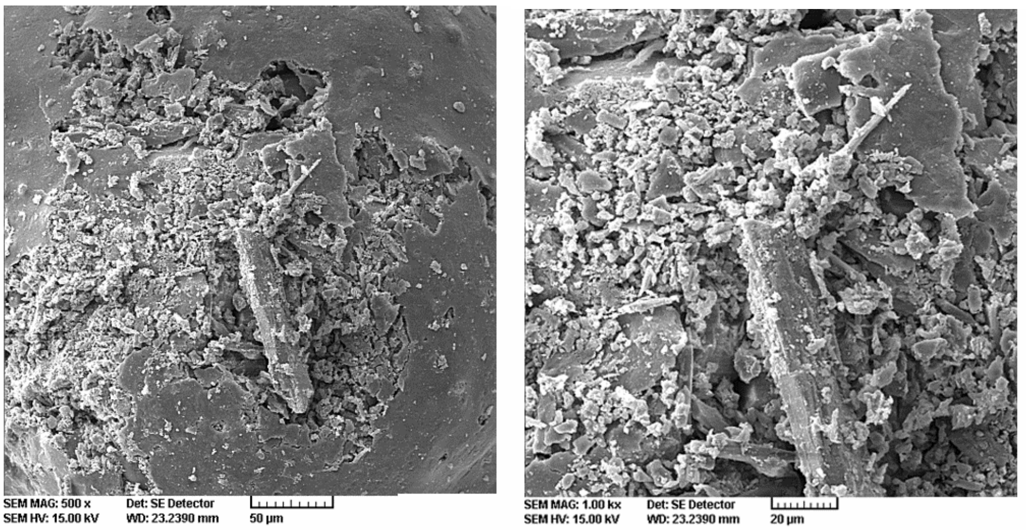

Fig. 3. SEM images of the reference powder(a) 500x (b) 1000x

sample. It should be mentioned as well that in the XRD analysis of this sample, Nepheline and $Mn_3O_4$with a very low peakwere also observed. Fig. 4 is a schematic of the XRD pattern of the molten reference powder. SEM images of this sample in magnificationsof 500x and 1000x,shown in Fig. 5a and Fig. 5b, respectively, prove the existence of crystalline particles in the glass matrix which lead to the control of the viscosity of the mold powder and thus to an optimized condition forcontinuous casting of steel. In other words, the SEM images show the molten powder with an extensive matrix created by the glass-making process. Due to the glass being saturated with SiO_2, several silicates are created during the solidification as shown in the XRD analysis which are of greatimportance to the mold powder because they prevent the viscosity from being too low for the mold powder in the melting temperature of the steel (1600°C) leading to a sudden collapse of the very lubricating molten powder. They also cause a favorable viscosity for the billet to cool down. SEM images reveal the generationof these crystals. XRD analysis of sample 1 shows gehlenite, cuspidine, akermanite, nepheline, and Mn_3O_4 phases whose peaks were in great similarity with those of the molten reference powder. In addition, in the XRD pattern of sample 1, the crystalline phase of Ca_3SiO_5 was also detected which confirms the existence of

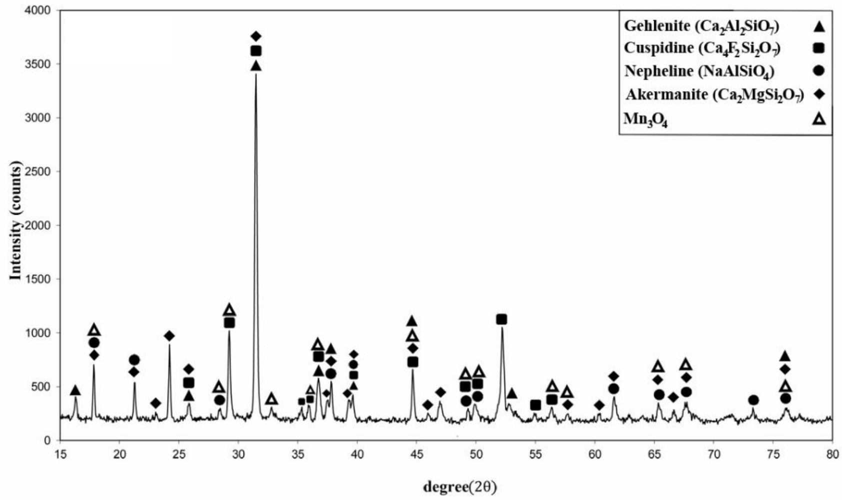

Fig. 4. The XRD analysis of the molten reference powder on groove viscometer

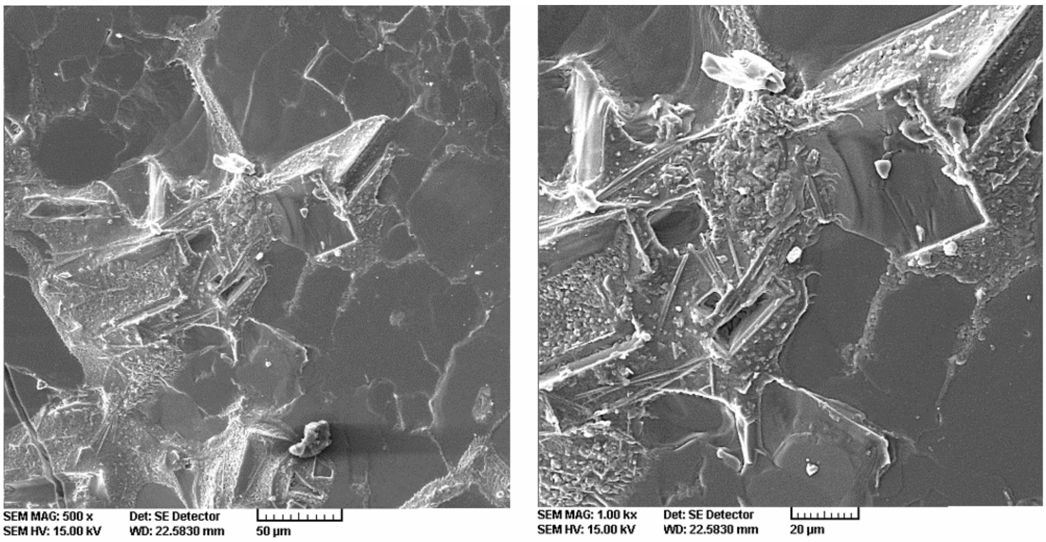

Fig. 5. SEM images of the molten reference powder (a) 500x (b) 1000x

Portland cement clinker in the chemical composition of sample 1. Therefore, it can be concluded that with the creation of the crystalline phase of Cuspidine in sample 1 and the similarity between the crystalline phases of this sample and the molten reference powder, sample 1 can be an apt substitute for the reference powder applied in continuous casting of steel industry. Fig. 6 is a schematic representation of the XRD pattern of sample 1.

4. Conclusion

1. Portland cement clinker is a very suitable composition for mold powders in continuous casting of steel which can be applied as a substitute for wollastonite in the composition of the mold powder.
2. Portland cement clinker along with Fluorine in sample 1 led to a similar viscosity to that of the molten reference powder.
3. TiO_2 along with Fluorine and Na_2O in the composition of the mold powder led to too much lubrication. Therefore, application of all three is not recommended in the chemical composition of the mold powder.
4. Elimination of Fluorine and using TiO_2 and Na_2O as substitutes is not recommended since Fluorine yields better lubrication.
5. Considering the XRD analysis of sample 1, it can be said that CaF_2 causes the creation of

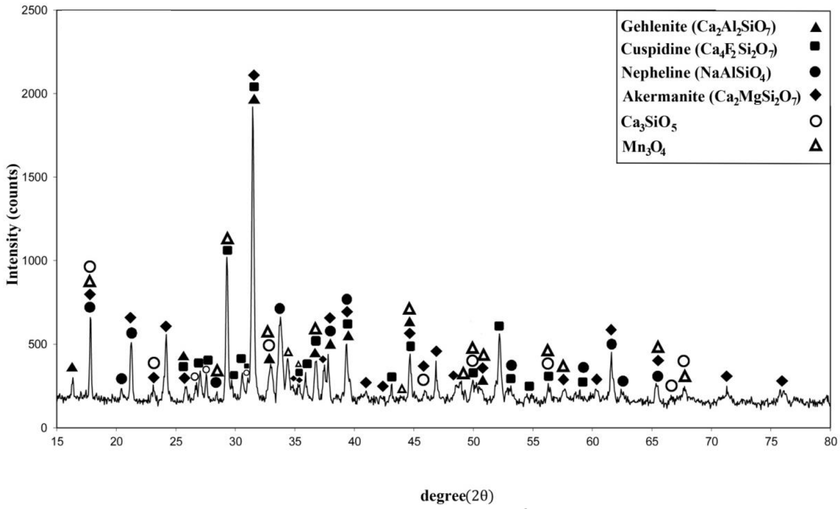

Fig. 6. The XRD analysis of sample 1

Cuspidine phase which leads to the creation of a crystalline sediment resulting in a better control of the viscosity of the mold powder and hence an optimized condition in continuous casting of steel.

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