Fluorine Free Mold Powder

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Abstract

Generally, mold powder for the continuous casting of steel contains fluorine in order to control the slag viscosity and the crystallization temperature. However, from environmental angles, etc., fluorine free mold powder has been required. Fluorine free conversion is possible for slab casting (low carbon, ultra-low carbon, and high carbon grades), bloom casting, billet casting, and beam blank casting, and fluorine free powders are currently being used in these cases. In this paper, the roles and impacts of fluorine in the mold powder and the method of fluorine free conversion are described.

1. Introduction

In general, mold powder consists of SiO_2 and CaO as its main composition, and Al_2O_3, MgO, Na_2O, Li_2O, F and C are added as components to control the viscosity, crystallization temperature and so on. The main roles of fluorine are to control the slag viscosity and crystallization temperature. However, fluorine causes problems including the acceleration of submerged entry nozzle erosion, increased machine corrosion, drainage water contamination and regulations, and so on. For these reasons, a reduction of fluorine in the mold powder has been required. This paper reviews the development of our fluorine free mold powder.

2. Role of Fluorine in Mold Powder

The mold powder is added onto molten steel surface in the mold, and it is melted by heat from the molten steel. The molten slag flows into a gap between the mold wall and the solidified steel shell, and forms a slag film. The flowing molten slag provides lubrication between the mold and the solidified steel shell. At the same time, slag film controls the heat removal rate from the steel shell to the mold.

Generally, lower viscosity is effective in increasing lubrication, and Fluorine has a relatively high contribution to decreasing the powder slag viscosity.

In order to prevent surface cracking, it is also necessary to reduce the heat removal rate. This will form an even solidified steel shell thickness and reduce the shrinkage stress of the steel shell. Enhancing the crystallization in the slag film with increasing crystallization temperature is an effective method to gain lower heat removal. Mold powder is designed to form the Cuspidine ($Ca_4Si_2O_7F_2$) crystal, which has superior heat removal control[1]. However, it is difficult to form Cuspidine in a low fluorine content mold powder because the crystal chemical formula contains fluorine. Thus, controlling the heat removal with low fluorine mold powder is difficult. This fluorine function is particularly important with mold powder for peritectic carbon grades, because the grades are very crack sensitive.

3. Problems of Fluorine in Mold Powder

3. 1 Slag line erosion in the Submerged Entry Nozzle (SEN)

Slag line in the SEN is usually reinforced by using ZrO_2-C materials which is partially stabilized by either CaO or MgO. This gives high erosion resistance against the mold powder slag. Fig. 1 shows the effect of mold powder composition on destabilization and amount of dissolution of CaO-partially stabilized ZrO_2 (C-PSZ)[2]. These experimental results suggest that fluorine accelerates the destabilization of partially stabilized ZrO_2 remarkably. As destabilization of PSZ is proceeded, degrading of ZrO_2 is also accelerated. So high fluorine content mold powder tends to give large erosion during casting[3]. Accordingly, it is expected that the durability of the SEN will be

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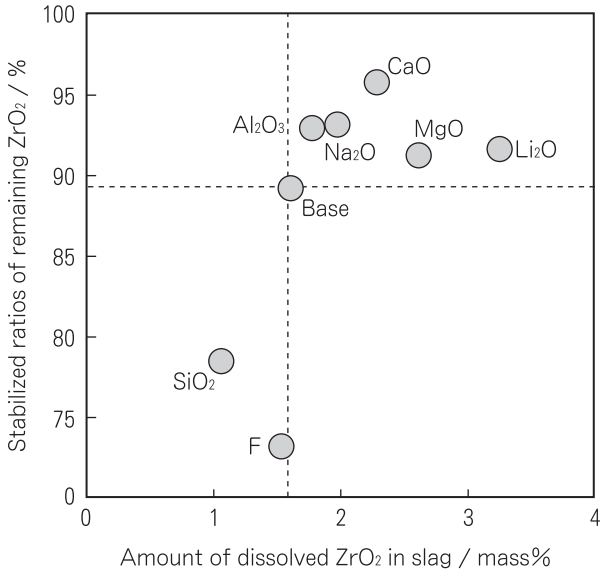

Fig. 1 Amount of dissolved ZrO_2 in Slag and stabilized ratios of remaining ZrO_2.

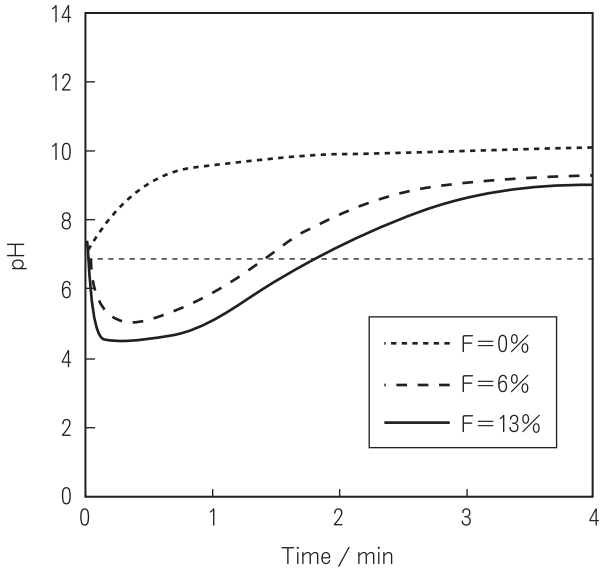

Fig. 2 Influence of fluorine on pH of water.

extended the by using fluorine free mold powder.

3. 2 Corrosion in continuous casting facility

When the slag film comes into contact with secondary cooling water, fluorine in the slag film is dissolved into the water. It yields hydrofluoric acid generation by the reaction in eq. (1), and the cooling water becomes acidic.

$$2F^- + H_2O \rightarrow O^{2-} + 2HF \cdots\cdots (1)$$

Acidic cooling water and/or generated steam corrode the bottom part of mold wall, rolls, and roll stands in the continuous casting facility.

A test was performed by continuously measuring the pH of water exposed to powder slag. For the test 5 grams of mold powder slag melted at 1300℃ were poured into the 25℃ pure water. Fig. 2 shows the results. Mold powder slag samples containing fluorine show the pH drop immediately after pouring the slag into the water, then gradually increasing and becoming alkaline. On the other hand, fluorine free sample shows the pH only increased, without the initial drop. This demonstrates the pH decrease due to the reaction (1) with the dissolution of fluorine, and then the pH increase results from the dissolution of other alkaline components. According to these experimental results, prevention of corrosion of the continuous casting machine is expected by using fluorine free mold powder.

3. 3 Regulation of drainage water

Certain regulations require the neutralizing the acid water that is generated because of Fluorine, and there is a cost involved with this process. Moreover, when drainage acid water is discharged to outside the plant, addressing to the environmental impact is needed. There is an especially high need for fluorine free mold powder in areas where the environmental regulations are more severe.

4. Method of Fluorine Elimination from Mold Powder

It is possible to use other components including CaO, Na_2O, Li_2O, and so on, instead of fluorine to just control the viscosity. This can be done if consideration of other characteristics is unnecessary.

However, fluorine free mold powder does not crystalize Cuspidine. Therefore, forming a replacement for Cuspidine to control the heat removal should be needed. The absence of fluorine is likely to generate other crystals such as Dicalcium silicate (Ca_2SiO_4), Wollastonite ($CaSiO_3$), Gehlenite ($Ca_2Al_2SiO_7$), Na_6SiCaO_6, and so on. These crystals tend to form a high amount of crystal in the solidified slag and the formation is uneven when compared with Cuspidine. Thus, it is difficult to maintain the heat removal control and lubrication with them. Enhancing the glassy phase or increasing the viscosity for suppression of the

crystal growth with increased SiO_2, Al_2O_3 and B_2O_3 are important methods for achieving stable casting operations.

Fluorine free mold powder development has been achieved in bloom, billet and beam blank castings by designing low basicity and high viscosity greater than 1.0 Pa·s. When the slag viscosity increases, the powder consumption is reduced, but it is superior in lubricity by forming a glassy slag film. In addition, as shown in Fig. 3, the heat removal is reduced by using high viscosity powder even though a glassy slag film, and it results in preventing surface cracking.

It is possible to design a Fluorine free mold powder for slab casting (other than medium carbon and peritectic grades) using the addition of B_2O_3 to suppress crystal growing even if the viscosity is low. Low carbon, ultra-low carbon, and high carbon grades have been using relatively high heat removal type mold powders because of lower crack sensitivity as compared with medium carbon grades. Therefore, Fluorine free mold powders can be designed with a B_2O_3 addition that will have similar viscosity and crystallization temperature properties as a conventional type containing Fluorine.

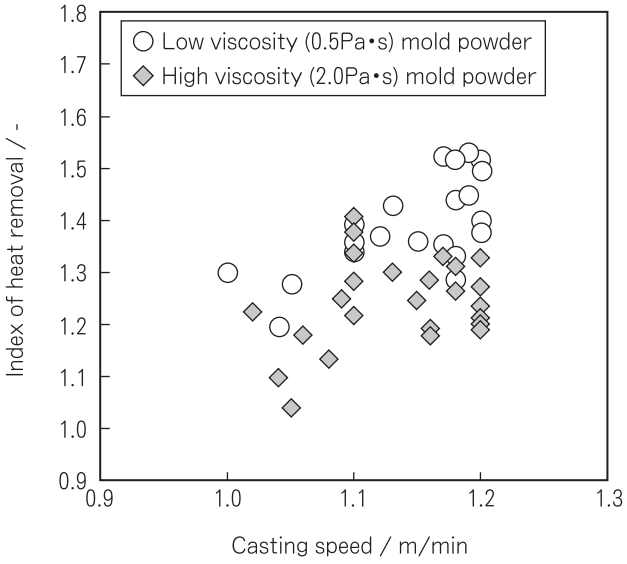

Fig. 3 Reduce heat removal when using high viscosity mold powder.

Fluorine free mold powder for medium carbon peritectic grades on slab casting has not been put in practical use yet due to their difficult nature. This is because these grades are more likely to experience slab cracking, and the slab mold cross-section area is much larger than that of billet, bloom, and beam blank molds. Conventional mold powder for medium carbon grades are low viscosity type and have been aimed to prevent cracking by softer and uniform heat removal with enhanced Cuspidine crystal formation in slag film. However, an alternative crystal to Cuspidine which has excellent heat removal properties has not been found as it stands. Practical application of fluorine free powder for the medium carbon grades with an alternative to Cuspidine will be part of future powder development.

5. Actual Casting Results on Fluorine Free Mold Powders

Table 1 shows examples of newly developed Fluorine free mold powder for low carbon slab casting and bloom

Table 1 Typical property of fluorine free mold powder

	Mold powder A	Mold powder B
Chemical composition / %		
SiO_2	34	39
CaO	32	27
F	0	0
Na_2O	10	2
B_2O_3	4	0
CaO/SiO_2	0.9	0.7
Softening temperature / ℃	1065	1120
Viscosity at 1300 ℃ / Pa•s	0.4	1.3
Crystallization temperature / ℃	1060	-
Application	Slab low carbon steel	Bloom

casting.

Fluorine free mold powders for the slab caster have been designed as a glassy type that has viscosity and crystallization temperature properties equal to conventional Fluorine type powders. Stable casting without any issues has been realized.

The new fluorine free high viscosity (>1.0 Pa·s) mold powders for small size mold have been in wide practical use. The high viscosity product can provide many benefits including improved slab surface quality, reduced erosion in the slag line of SEN, reduction of mold powder consumption, reduction of discharging water treatment cost, and so on.

6. Conclusion

There is a demand for the development of fluorine free mold powder to address environmental regulations, reduce the corrosion of casting facility, and reduce the slag line erosion in the SEN. It is difficult to remove the fluorine from mold powder for the slab casting medium carbon and peritectic grades due to surface crack issues. However, other various uses including slab casting (low carbon, ultra-low carbon, and high carbon grades), bloom, billet, and beam blank casting have been successfully using the newly developed Fluorine free mold powders.

In the future, fluorine free mold powder development will continue in order to meet the needs of continuous casting facilities.

References

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