



Effect of Al₂O₃ on the fluoride volatilization during melting and ion release in water of mold flux



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ABSTRACT

In this study, in view of the hazard associated with the volatilization of fluoride during the melting and ion release in the secondary cooling water from traditional mold flux, the mold flux with a higher Al₂O₃ content was investigated. The volatilization of fluoride during slag melting was monitored by thermogravimetric analysis. The results showed that the tendency to form volatile substances decreased with increasing Al₂O₃ concentration. The leaching and dissolution behaviors of the traditional and high Al₂O₃ content mold fluxes resulting by change in pH and F⁻ concentration were investigated. The leach tests of molten mold flux showed that pH was controlled by the ion exchange processes and varied from 4.0 to 9.5. The F⁻ released from the traditional mold flux was up to 35.4 mg·L⁻¹. Similarly, the F⁻ concentrations and the pH ranges decreased sharply in the beginning and then slightly increased with increasing Al₂O₃ content from 4 mass% to 34 mass%. The ion release ability and pH range were decreased by adjusting the Al₂O₃ content in the mold flux. The formation of volatile fluoride was effectively inhibited when the Al₂O₃ content was controlled in the mass range ~16–34% in the experimental mold fluxes, and the F⁻ concentrations remained within the range ~4–10 mg·L⁻¹. Moreover, the pH varied from 6.5 to 7.5 during the water leaching, thus the harm caused by fluoride volatilization and ion release was significantly inhibited.

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1. Introduction

Mold fluxes play an important role in the continuous casting of steel. These well-tailored mold fluxes usually contain fluoride in the range 4–10 mass% to lower the slag viscosity and liquids temperature to control the precipitation of cuspidine at the mold–strand gap [1]. Fluorides exhibit the best performance as fluxing agents in slags; however, they are undesirable from the environmental point of view. Fluoride is the main environmental concern surrounding the continuous casting of steel because fluoride flux additives (i) emit gaseous HF, SiF₄, NaF etc. in the atmosphere, contributing to acid rain and (ii) are leached from slag film into cooling water, thereby corroding plant equipments [2]. Therefore, the development of environment-friendly mold flux is very important considering these environmental hazards.

To inhibit the pollution caused by the fluoride release, the study of fluoride-free and low-fluoride mold fluxes is of worldwide interest since the early 1990s. Until now, most of the studies [2–7] are focused on the non-fluorine and low-fluorine CaO–SiO₂-based mold flux. However, the removal of fluoride additives from mold fluxes would cause operational problems (such as sticker breakout) or defects (such as

longitudinal cracking), and these problems are particularly severe in middle carbon steel. Therefore, some fluoride is added in many mold fluxes. Hence, the development of alternative mold flux satisfying not only the requirements for continuous casting but also environment-friendly is very necessary. Previous studies indicated that Al₂O₃ could prevent the formation of volatile fluorides [8] and increase the durability of CaO–SiO₂-based glasses [9–11]. However, the effect of Al₂O₃ on fluoride pollution in mold flux has not been systematically investigated. Although traditional mold flux always contains small (<8 mass%) quantity of Al₂O₃, it is too little to exert any significant effects. According to the studies of mold fluxes for Transformation-Induced-Plasticity Steels (Al-TRIP) [12,13], the reacted mold fluxes with 30 mass% Al₂O₃ still meet the demands in the continuous casting process. Therefore, the development of high Al₂O₃ content mold flux based on the traditional one is possible. In this study, we investigated higher Al₂O₃ content (≥10 mass%) mold flux. This novel method without considering the substitute for fluorides can solve the problem caused by the fluoride and possibly replace traditional mold flux by the high Al₂O₃ content one.

In this study, a high Al₂O₃ content mold flux was investigated. Thermogravimetric analysis (TGA) was used to study the formation of volatile fluorides. The chemical state of fluorine for traditional and high Al₂O₃ content mold fluxes was measured using X-ray photoelectron spectroscopy (XPS). To investigate the mechanism of ion exchange processes of traditional and high Al₂O₃ content mold fluxes, the change in F⁻ concentration and pH in the leachate was studied. The aim of this

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Table 1
Designed composition of high Al₂O₃ content mold fluxes.

Powder	Mass%									CaO/SiO ₂	NBO/T
	CaO	SiO ₂	Na ₂ O	Al ₂ O ₃	CaF ₂	MnO	MgO	B ₂ O ₃	Li ₂ O		
CAS-1	32.6	23.4	10.0	10.0	16.4	1.0	3.0	2.0	1.6	1.4	3.1
CAS-2	29.2	20.8	10.0	16.0	16.4	1.0	3.0	2.0	1.6	1.4	2.4
CAS-3	25.7	18.3	10.0	22.0	16.4	1.0	3.0	2.0	1.6	1.4	1.9
CAS-4	22.2	15.8	10.0	28.0	16.4	1.0	3.0	2.0	1.6	1.4	1.5
CAS-5	18.7	13.3	10.0	34.0	16.4	1.0	3.0	2.0	1.6	1.4	1.1

study was to elucidate the effects of Al₂O₃ in mold flux on the formation of volatile substances, pH variation, and ion release in water.

2. Materials and methods

2.1. Sample preparation for TGA

The components of the high Al₂O₃ content mold fluxes (CAS) were selected based on the previous report [12]. To meet the demands of the continuous casting process, the designed mold fluxes with a CaO/SiO₂ ratio of 1.4 and Al₂O₃ content ranging from 10 mass% to 34 mass% were required. The chemical compositions of designed mold fluxes are listed in Table 1. The mold flux powder sample was prepared using chemically pure substances. Li₂O and Na₂O were prepared from Li₂CO₃ and Na₂CO₃ (all materials used for mold flux sample preparation were supplied by Chengdu KeLong Chemical, China). A batch of ~100 g size was prepared, followed by adding a slight amount of absolute ethanol and stirred to form a paste. Absolute ethanol was removed after drying for 3 h at 120 °C followed by crushing the matter. Then, the mold flux powder was grounded and passed through a 75- μ m sieve for analysis by TGA.

2.2. Thermogravimetric analysis

Mold fluxes were added to the top of the steel meniscus in the mold, forming a “powder bed” of mold flux, and then the mold flux powder began to melt forming a liquid pool [14,15]. The volatile fluorides were lost during this process. TGA was used to study the production of volatile fluorides and was recorded using a STA449C NETZSCH thermal gravimetric analyzer (Germany). Sample weighing 10 mg was placed in a Pt crucible and then heated from 30 °C to 1400 °C (the maximum allowable temperature) at the maximum allowable heating rate for the apparatus (20 °C·min⁻¹) under an argon flow rate of 20 mL·min⁻¹. Then the sample was maintained at 1400 °C for 30 min. During the experimental process, the weight variation and the temperature of sample were recorded every 2 s.

2.3. The leach tests of molten mold flux

The mold flux formed a sintered layer and eventually melted forming a liquid flux pool in the mold. Liquid flux from the pool infiltrates into the mold/strand channel and lubricates the newly formed steel shell. Most of the liquid froze forming a solid flux film (ca. 2 mm thick) but a thin liquid layer remained (ca. 0.1 mm thick). In general, the liquid slag film travels with the strand and the solid slag film remains in contact with the mold [14,15]. When the strand entered the secondary cooling zone, the liquid films solidified and fell in the water from the strand under the secondary cooling water. The ions were released in the water from mold flux during this process.

To simulate the release behavior of ions from the mold flux, the leach tests of molten mold flux were performed. Then, the leachate of traditional (CS-1) and high Al₂O₃ content mold fluxes were analyzed and compared. The chemical compositions of designed mold fluxes are listed in Tables 1 and 2. The necessary components were weighed to afford 50 g of mold flux powder, then mixed and transferred to a graphite

crucible. The prepared sample weighing 50 g was heated and melted in the MoSi₂ furnace. The furnace temperature was kept at 1300 °C for 10 min to ensure the complete melting of the sample. Because the temperature of the strand surface and the liquid films just outside of the mold was ~1300 °C, this temperature was selected in the leach tests of the molten mold flux. Then, the molten mold flux was poured into de-ionized water (pH 7.13) with a total volume of 3000 mL. Leachates were obtained at 30, 60, 120, 240, and 480 min later for the analysis of F⁻ concentration and pH. Because only 20 mL was sampled every time, the change in total volume was negligible. After the leach tests of the molten mold flux, the big slag chunk of CAS-1 and CAS-5 was used for XPS analysis. The surface of the slag chunk was cut off to avoid the effect of the leach tests. The aim of XPS analysis was to know the chemical state of fluorine in the traditional and high Al₂O₃ content mold fluxes. The other slag chunk of CS-1 and CAS-5 was ground to powder and examined by X-ray diffraction (XRD).

2.4. The analysis of pH and F⁻ in water

The pH was measured using a pH meter. Fluoride-released into water was measured using a fluoride-selective electrode (MP-523 with pH/ISE meter, Shanghai San-Xin Instrumentation, China). A total ionic strength adjustment buffer (TISAB II) solution was required to ensure that total fluoride ion concentration (free and complexes) was determined. Calibration was performed using the standard solutions.

2.5. XRD

X-ray diffraction was utilized to detect any crystal phase in the samples whose diffractograms were obtained by an X'Pert-Pro diffractometer, in which CuK α radiation was employed for sample analysis. The crystalline phase was identified using the JCPDS indexes in the conventional way.

2.6. XPS of F1s

F1s XPS spectra of the slags were obtained using an X-ray photoelectron spectrometer (PHI-5300/ESCA, Perkin Elmer, USA) equipped with an Al K α X-ray source (1253.6 eV) operating at 3.0 kV and 25 mA. The binding energy was corrected with C1s (284.6 eV) coated on the surface of the slag sample. The surface of the slag sample was etched by an argon ion beam for 30 min to eliminate surface contamination before XPS measurement. The XPS spectra were obtained after the confirmation that the spectra were unaffected by the argon ion beam etching.

Table 2
Designed composition of a traditional mold flux.

Powder	Mass%								CaO/SiO ₂	NBO/T
	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Na ₂ O	MgO	Fe ₂ O ₃	Li ₂ O		
CS-1	26.2	28.5	4.0	14.3	9.5	3.5	3.0	1.4	0.9	3.5

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