

Study on crystallizing properties of mold fluxes in electric field

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Abstract: To improve the surface quality of cast strand, crystallizing behavior and properties of mold fluxes in electric field were investigated. The crystallizing properties of mold fluxes in DC and AC electric field were mainly studied. The experimental results showed that the crystal grain size of mold flux gradually grew larger with voltage rising in DC electric field changing from 1V to 3V, while the crystal grain size gradually became smaller with the same voltage increasing in AC electric field. In DC electric field, the grain growth would be promoted, and the grain would be refined in AC electric field. The crystallization ratio of mold fluxes was effectively promoted in both DC and AC electric field. When the voltage of electric field was 0V, the crystallization ratio was only 28.76%. However, if the voltage of DC or AC electric field was 3V, crystallization ratio was increased to 74.35% and 85.24% respectively. In electric field, there were no new phases of mold fluxes generated, but the amount of main phases were changed, such as cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) and melilite ($\text{Ca}_2\text{Al}[\text{SiAlO}_7]$) phases became the main phases. The amount of main phases were increased with voltage rising in DC electric field from 1V to 3V, while the amount of main phases were gradually reduced with voltage rising in AC electric field from 1V to 3V.

Keywords: Mold fluxes, electric field, crystallizing properties

1. Introduction

Mould electromagnetic technology has been widely used in continuous casting process, a number of investigations have been carried out to improve the strand quality with electromagnetic field. However no investigation was carried out to study influencing of electromagnetic field on properties of mould fluxes between strand and mould¹⁻⁴. As a critical material in continuous casting process, mold flux forms a certain thickness and structural flux film, the crystallization behaviors' plays a critical role in lubrication and heat transfer between strand and mold, and reducing strand surface defects and maintaining good process⁵⁻⁶.

NA et al.⁷ reported that the viscosity of mold fluxes decreased owing to the induction heating action of high frequency electromagnetic field (20kHz), and the dimension of flux channel increased with electromagnetic pressure. OKAZAWA⁸ studied the viscosity change of mold fluxes in electric field, the results showed that the viscosity decreased with direct current and increased with alternating current. Since mold flux belongs to silicate structure system, which is ion structural and conductive at a high temperature⁹, so the thermal and force effect of mold electromagnetic have an impact on crystallization properties of mold fluxes^{10,11}. Therefore, to understand the crystallizing behavior and mechanism of mold fluxes in electromagnetic field is very important. It will be helpful to coordinate the contradiction between lubrication and heat transfer of mod fluxes and apply electromagnetic technology further in continuous casting process. The crystallizing properties of mold fluxes in

different DC and AC electric field were studied in this work, and were analyzed by using mineral phase and XRD.

2. Experimental

2.1 Sample preparation

The chemical composition data of master mold flux samples are listed in Table 1. In order to study the crystallizing properties of mold fluxes in different direct current(DC) and alternating current(AC) electric field, and the influence of basicity on crystallizing properties, DC and AC electric field was applied to molten mold flux respectively, the minimum voltage of electric field was 1V , and the maximum value was 3V, and CaO was added into the samples to change basicity of mold flux from 1.02 to 1.08, experimental schemes are listed in Table 2.

Table 1 Chemical composition of mould fluxes sample(mass%)

CaO	SiO ₂	Al ₂ O ₃	MgO	CaF	Na ₂ O	MnO	FeO	R
39.92	39.08	3.23	4.89	4.35	5.46	2.95	0.12	1.02

Table 2 Experimental schemes

No.	Electric field	Voltage/V	R
1#	—	—	1.02
2#	DC	1	1.02
3#	DC	2	1.02
4#	DC	3	1.02
5#	AC	1	1.02
6#	AC	2	1.02
7#	AC	3	1.02
8#	DC	3	1.04
9#	DC	3	1.06
10#	DC	3	1.08
11#	AC	3	1.04
12#	AC	3	1.06
13#	AC	3	1.08

2.2 Measurement

The experimental device is shown in Fig.1. Before experiment, 140g mold fluxes were firstly charged into graphite crucible and melted at 1300°C in RTW-10 melt phase measuring instrument, then they were quickly poured into the corundum ring of experimental device, meanwhile the two molybdenum wires were charged with current until mold fluxes cooled to room temperature. The crystallized samples of mold fluxes between two molybdenum wires were sliced and polished into thin discs, and the crystallized layer was observed by microscope. Statistical analyses of grain size and crystallization ratio were conducted with image analysis

software. Then crystal samples were made into -200 mesh powder (<0.074mm) and then were analyzed by XRD.

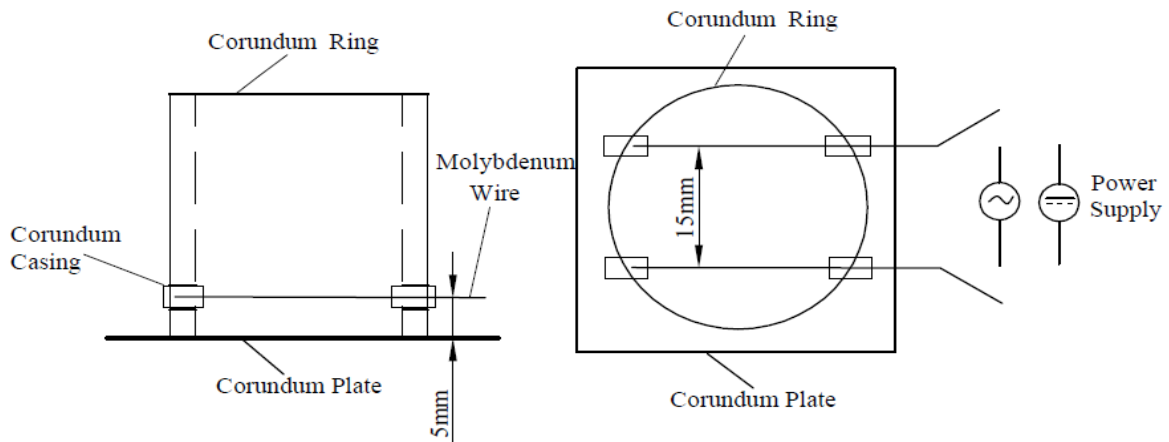


Fig.1 Schematic drawing of experimental device

3. Results

3.1 The effect of electric field on crystal grain size of mold fluxes

The relation between grain size of mold fluxes ($R=1.02$) and voltage in electric field is shown in Fig.2. It can be seen from the figure, the range of voltage was 0 to 3V, the crystal grain size gradually was increased from $64.71\mu\text{m}$ to $69.02\mu\text{m}$ with voltage increasing in DC electric field, while the crystal grain size gradually became smaller with voltage increasing in AC electric field, the grain size was reduced from $64.71\mu\text{m}$ to $58.51\mu\text{m}$. Fig.3 shows the relation between grain size and binary basicity in DC and AC electric field. As illustrated in this figure, with increasing of binary basicity, the crystal grain size was enlarged from $58.51\mu\text{m}$ to $87.07\mu\text{m}$ in AC electric field, and increased from $68.02\mu\text{m}$ to $93.21\mu\text{m}$ in DC electric field. Compared with the same basicity of mold fluxes in AC electric field, the crystal grain size grew much larger in DC electric field.

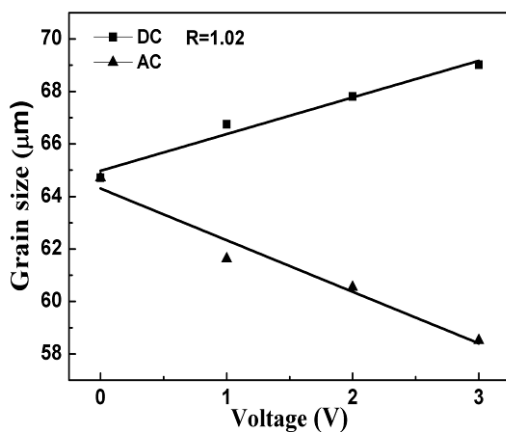


Fig.2 Relation between grain size and voltage

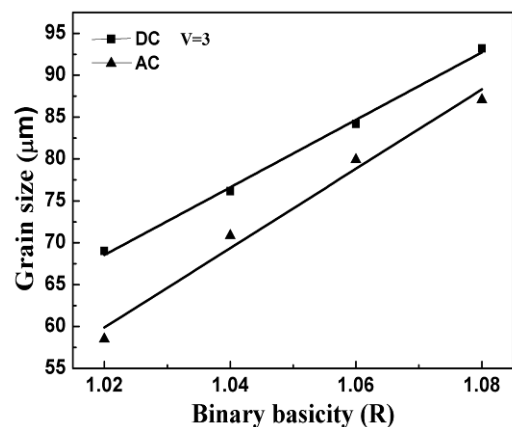


Fig.3 Relation between grain size and binary

basicity

The above experimental results show that the grain growth of mold fluxes will be promoted in DC electric field while the grain will be refined in AC electric field, and the crystal grain size gradually grows larger with binary basicity increasing under the same electric field voltage. Although the applied AC electric field will result in decreasing of crystal grain size, due to the binary basicity being increased and the viscosity of mold fluxes reduced, crystals will still grow up and the crystal grain size of mold fluxes will be increased with binary basicity increasing in AC electric field.

3.2 The effect of electric field on crystallization ratio of mold fluxes

The relation between crystallization ratio of mold fluxes $R=1.02$ and voltage in different electric field is provided in Fig.4. When the voltage of electric field was 0V, the crystallization ratio was only 28.76%. However, if the voltage of DC or AC electric field is 3V, crystallization ratio increases to 74.35% and 85.24% respectively. The crystallization ratio will increase around 15% and 18% respectively when every unit rise in the voltage of DC and AC is conducted. Fig.5 shows the relation between crystallization ratio and binary basicity in DC and AC 3V electric field. As illustrated in figure, with increasing of binary basicity, the crystallization ratio was changed from 74.25% to 79.06% in 3V DC electric field and increased from 85.24% to 94.37% in 3V AC electric field. The crystallization ratio would be increased about 1% and 3% respectively when binary basicity was increased by 0.02 in the DC and AC electric field.

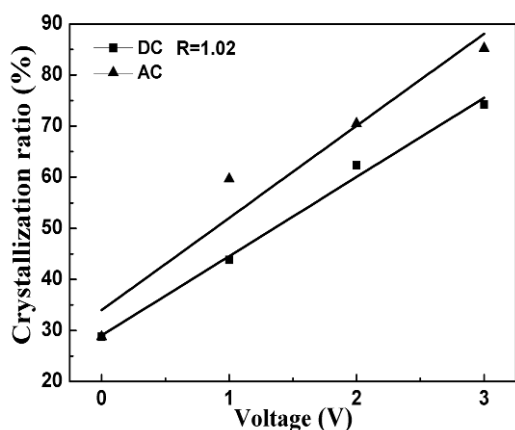


Fig.4 Relation between crystallization ratio and voltage

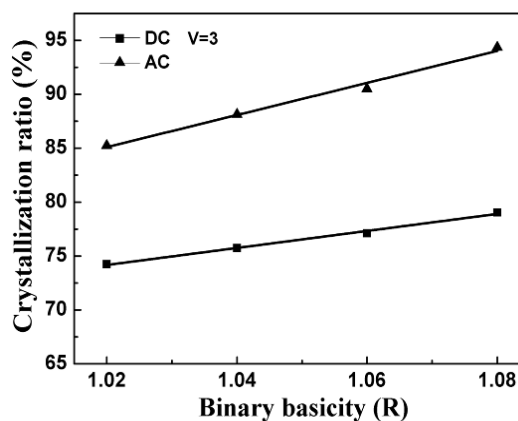


Fig.5 Relation between crystallization ratio and binary basicity

The above experimental results show that the crystallization ratio of mold fluxes was effectively promoted in both DC and AC electric field. In the same binary basicity, the crystallization ratio of mold fluxes in AC electric field will be more than that in DC electric field, and at the same voltage of electric field, crystallization ratio gradually becomes larger with binary basicity being increased. On the other hand, the crystallization ratio can be effectively improved by electric field, the improved effect of electric field is stronger than that of binary basicity changing.

3.3 The effect of electric field on main phase of mold fluxes

The XRD results of 1#~7# crystalline samples in DC and AC electric fields are shown in Fig.6. The crystalline portion of mold fluxes are mainly cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) and melilite ($\text{Ca}_2\text{Al}[\text{SiAlO}_7]$). Compared with 1# crystalline sample without electric field applied, there is no new crystalline phase appeared in the samples with electric field applied, but the diffraction intensity of main phases changed, it illustrated that the amount of main phases were changed.

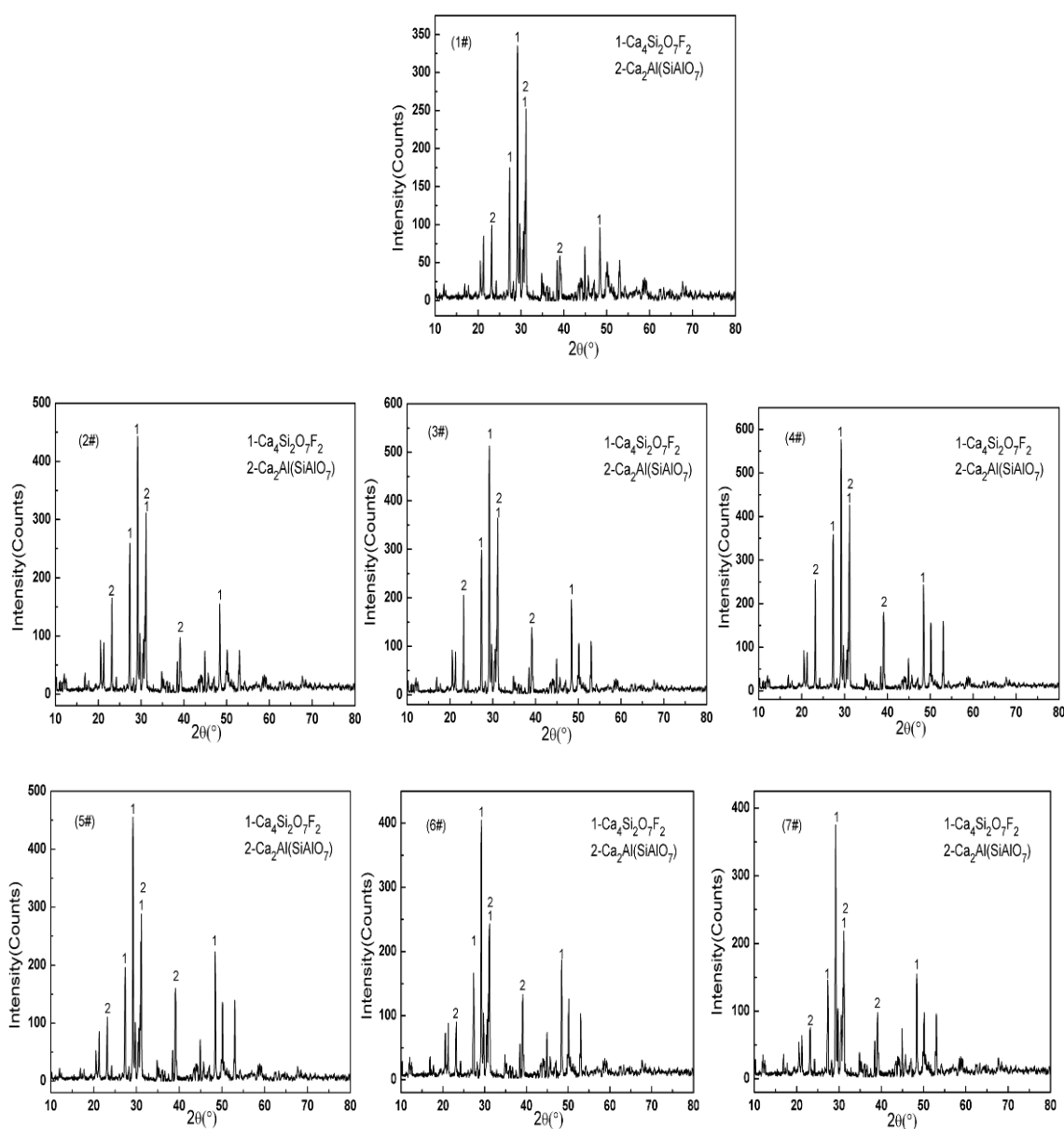


Fig. 6 X-ray pattern of 1#~7# samples

As illustrated in 2#~4# XRD figures, when the voltage of DC increased from 1V to 3V, the amount of cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) and melilite ($\text{Ca}_2\text{Al}[\text{SiAlO}_7]$) become obviously larger than that of 1# sample; the amount of main phases in 2#~4# samples are also more than that of 1# sample, but they gradually decreased with voltage increasing in AC electric field.

4. Discussion

4.1 The effect of DC electric field on crystallization properties of mold fluxes

Silicate crystallization theory¹²⁾ illustrated that molten mold fluxes would be crystallized under super-cooling condition. Under DC electric field, electric dipole moment would be formed in molten slag ions by electric polarization effect. This would make the crystallization parts overcome viscous resistance of molten slag medium and ultimately be accelerated during migration movements along with direction of electric field, thereafter, the conductivity and temperature of molten slag would be increased¹³⁾. In the cooling process, crystallization ratio and time became smaller and shorter with cooling rate increasing¹⁴⁾. However, under DC electric field, the additional energy supplied by the electric field would apply on the crystallization components resulting in smaller super-cooling and longer crystallization time, and leading to crystallized nuclei taking long enough time to grow up.

Additionally, the temperature gradient of interface solidifying front would be reduced by the joule heating effect of DC electric field. Meanwhile, molten slag ions had orderly movement in DC electric field. This made the composition overcooling zone of molten slag solidification front became wider. These would promote the growth of dendrites and the formation of new crystal nuclei in front of fluid phase. While molten slag ions were disseminated and attached by the surface of crystal nucleus, the nuclei would grow up. The crystallization would thereby be promoted by DC electric field.

4.2 The effect of AC electric field on crystallization properties of mold fluxes

The additional energy could also be applied in AC electric field, which would result in super-cooling being reduced and crystallization time being prolonged, leading crystal-nucleation proceeding had enough time to grow up. But AC electric field enhanced molten slag ions to be disordered, and to increase the viscosity of molten slag as well as resistance of ions migration^{8,15)}. As a result it would not be conducive to make ions attach on the crystal nuclei, thus inhibit crystal grain growth. Besides, the disorderly movement of molten slag ions in AC electric field can be seen as a stirring action on molten slag^{10,11)}. When shear force caused by stirring action was much stronger, the dendrite would be fractured, and the growth would be inhibited to result in decreasing of grain size.

On other hand, stirring action caused by AC electric field can produce more uniform temperature and concentration field, which also resulted in decreasing of temperature gradient of solidifying front and constitutional super-cooling, as well as inhibiting of dendrite growth. When shear force was large enough, the

dendrite was fractured into small fragments away from molten slag, which would provide more particles for new crystal nucleus and absorb disorderly ions growing up. Finally the crystallization degree of molten slag was increased.

5. Conclusions

(1) When the voltage of electric field was changed from 1V to 3V, the crystallization particle size of mold fluxes gradually grew larger with voltage increasing in DC electric field, however the crystal size became gradually smaller with voltage increasing in AC electric field. The DC electric field can promote the grain growth of mold fluxes while the AC electric field can make grain be smaller.

(2) The crystallization ratio of mold fluxes was effectively promoted in both DC and AC electric field. When the voltage of electric field was 0V, the crystallization ratio was only 28.76%. However, if the voltage of DC or AC electric was 3V, crystallization ratio would be increased to 74.25% and 85.24% respectively. The crystallization ratio would be increased about 15% and 18% respectively, when voltage of DC and AC conducted was increased by 1V.

(3) There were no new crystallization phases of mold fluxes generated in electric field, but the amount of main crystallization phases would be changed. The amount of cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) and melilite ($\text{Ca}_2\text{Al}[\text{SiAlO}_7]$) phases would be increased with voltage in DC electric field changing from 1V to 3V, while the amount of cuspidine and melilite phases would be gradually decreased with voltage in AC electric field changing from 1V to 3V.

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References

- [1] H.NAKATA, T.INOUE and H.MORI et al. Improvement of Billet Surface Quality by Ultra-High-Frequency Electromagnetic Casting. *ISIJ International.*,2002,42(3),p264-272.
- [2] Ting-ju LI, Kensuke SASSA and Shigeo ASAI. Surface Quality Improvement of Continuously Cast Metals by Imposing Intermittent High Frequency Magnetic Field and Synchronizing the Field with Mold Oscillation. *ISIJ International.*,1996,36(4),p410-416.
- [3] Anyuan DENG, Engang WANG and Jicheng HE. Meniscus Behavior in Electromagnetic Soft-Contact Continuous Round Billet Mold. *Journal of Iron and Steel Research, International.*,2006,13(4),p13-16.
- [4] Zhongming REN, Kang DENG and Guochang JIANG. Development of Electromagnetic Continuous Casting Processing with Soft-Contact Mold. *Journal of Iron and Steel Research.*,2002,2(2),p58-61.
- [5] Jung Wook CHO, Toshihiko EMI and Hiroyuki SHBATA et al. Heat Transfer across Mold Flux in Mold during Initial Solidification in Continuous Casting of Steel. *ISIJ International.*,2002,38(8),p834-842.
- [6] Wanlin WANG and Alan W. CRAMB. The Observation of Mold Flux Crystallization On Radiative Heat

Transfer.*ISIJ International*.,2005,45(12),p1864-1870.

- [7] Xianzhao NA, Xigang WANG and Xingzhong ZHANG et al. Deformation of Initial Solidificated Shell in Soft Contact Continuous Casting Mold under High Frequency Electromagnetic Field. *Journal of Iron and Steel Research*.,200,16(6),p21-26.
- [8] Kensuke OKAZAWA, Masahiro YAMANE and Yuka FUKUDA. Viscosity Change of Molten Oxides by Electric Current Impodition. *The Iron and Steel Institute of Japan*.,2003.89(6),p7~12.
- [9] Jinghao CHI and Yongnian GAN. CC Mold Fluxes. *Shenyang: Northeastern University Press*, 1992.
- [10] Zhicheng HAN. Electromagnetic metallurgy. *Beijing: Metallurgical Industry Press*, 2001.
- [11] Guanglin JIA and Weicheng PANG. Electric Metallurgical Principle and Technology. *Shenyang: Northeastern University Press*, 2003.
- [12] Dongsheng RAO. Physical Chemistry of Silicates. *Beijing: Metallurgical Industry Press*,1980.
- [13] Haiquan WANG, Guohua CHEN. Review on the Orientation and Alignment of Particles Induced by Electric Field.*Journal of HuaqiaoUniversity(Natural Science)*.,2008,29(4),p491-493.
- [14] Jun SHU, Shantong JIN and Li ZHANG et al. Influence of Cooling Rate on Crystallization Properties of Mold Fluxes.*Journal of University of Science and Technology Beijing*.,2001,23(5),p421-423.
- [15] Yu WANG, Zhiwen WEI and Ting GUAN. Research of Molten Slag Viscosity under Electric Field. *CC Mold Fluxes Technology Conference of Chinese Metal Society*.,2009,p100-104.