Mechanism of slag chemical composition change in ESR process

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Abstract: It is found that the slag chemical composition is changed in ESR process with CaF_2 –containing slag. There is a great difference between the initial and the final slag chemical composition in the slag pool. It is of practical and theoretical significance to study the changing mode and mechanism of slag property with the change in ESR composition change for optimizing ESR process. In this paper, simultaneous thermal analyzer (STA) has been used to measure the weight loss of typical slags in CaF_2-CaO-Al_2O_3-SiO_2-MgO slag system, as well as the thermal effect. Experimental tests and theoretical calculation have been carried out to simulate quantitatively the practical results. The results indicated that weight loss rate of slag can be increased with CaF_2, SiO_2, Al_2O_3 and MgO content increase, and decreased with CaO content increase. Evaporation of SiF_4, AlF_3, AlOF is found in coexistence. The regression equation of weight loss and conductivity with chemical composition is obtained. A model of slag chemical-composition change has been proposed to quantitatively estimate the change in ESR process.

Keywords: electroslag refining, slag weight loss, mechanism of slag chemical composition change, simulation calculation

1. Introduction

Slag plays an important role in metal melting, refining, and solidification process in electroslag remelting (ESR). It is known that the slag chemical composition will change in smelting process with CaF_2-based slag that is commonly used, especially the slag(ANF-6) with the chemical composition of 70%CaF_2-30%Al_2O_3 [1,2]. The data of chemical composition change from practical operating process are listed in Table 1.

Table 1. Slag chemical composition change form practical operating process

Slag sample		Chemical composition，mass%					Steel grade
		CaF_2	Al_2O_3	CaO	SiO_2	MgO	
ANF-6	Original	68.85	29.54	-	1.61	-	GH136
	final（1）	61.03	19.64	8.96	5.91	1.27	
	final（2）	60.21	21.35	7.82	7.10	1.66	
Complex slag	original	68.69	19.69	9.55	1.64	0.23	SHSS-1
	final	58.23	19.58	12.66	6.43	2.82	

From Table 1, it can be seen that CaF_2 and Al_2O_3 contents decrease, and CaO, while SiO_2 content increases obviously during the refining. As a result, the properties of these slags including melting point, component activity, electrical conductivity, viscosity, density, surface tension and other physical and chemical properties would change. These changes would finally effect on the quality of the ingot and products. So study on the mechanism of slag composition changes in the electroslag refining process and the relevant effect will be of important significance to process control, process optimization and the pollution control of fluorides.

2. Research Content and Experimental Scheme

Theoretically, there are four reasons for the slag composition changes in the electroslag refining process [1,2,3,5]. The first is the evaporation of various volatiles in the slags, mainly the fluorides. The second is the reaction between the slag and the metal,such as the oxidation of silicon. The third is the segregation of slag components in solidification and the fourth is transfer and dissolution of inclusion. The first and second reasons are taken as the main reasons for the slag composition changes， and the evaporation of various fluorides in the slag has been studied in this paper.

Typical slag systems from operating practice were chosen and the slag was prepared with chemical agents in the experimental tests. The fluoride content was selected with different levels involving：high-fluoride slag (ANF-6), fluoride slag (M-1), low-fluoride slag (L-3) and fluorine-free slag (F-2). The chemical composition data of slags are listed in Table 2.

Table 2 Chemical composition data of typical electroslags

Slag No.	Chemical composition (mass%)			
	CaO	Al_2O_3	SiO_2	CaF_2
F-2	50	43	7	
L-3	37	40	8	15
M-1	30	20	8	42
ANF-6		30		70

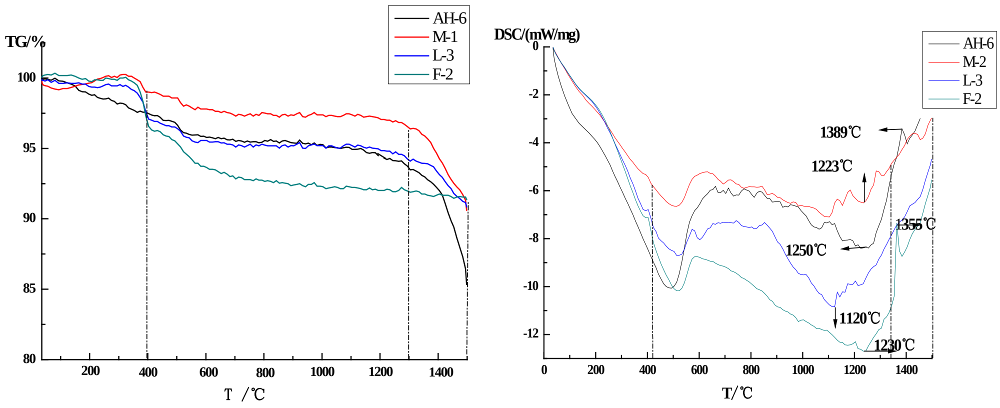
The experimental measurements of weight loss were carried out with 449cJup5ter simultaneous thermal analyzer(STA) and alumina crucible was used to hold the slag powder. In a test, the weight change and energy change of each slag sample with time and temperature were recorded automatically. They are demonstrated in TG and DSC curves. Four-point probe is employed to measure the conductivity of the molten slags. Based on the experimental results, simulation calculation was carried out and compared with the results from practical operations.

3. Experimental results and analysis

3.1 Wight losses of some typical slags

Some TG and DSC curves obtained from the experimental measurements of the slag samples are illustrated in Fig.1. From Fig.1, it can be found that TG and DSC curves of different slags is of the same trend with different slags. In the temperature range between 380 and 450 ℃ in the figure, a obvious weight loss and exothermic reaction appears，then the curves become into relatively gentle changing state. When temperature was above 1300 ℃, slag samples apart from F-2 experienced rapidly weight loss and exothermic peak appeared in DSC curves in correspondence. From the experimental results at 1450 ℃, the evaporation rates of the slags is in an order of ANF-6＞M-1＞L-3＞F-2.

In the temperature range between 380 and 450 ℃, it could be found the weight change degree related with the content of CaO in the slags. According to relevant data, the reaction of $Ca(OH)_2$ decomposition could be inferred.



（a） TG （b）DSC

Fig.1 TG and DSC curves of slag samples

Above 1300℃, the cause of the weight loss of samples could be generally considered by the reaction(s) between oxides and CaF_2 in the CaF_2-CaO-Al_2O_3-SiO_2-MgO slag system, which generated volatile fluoride(s). This can be especially true when CaF_2 in melt coexists with acidic oxides like SiO_2, Al_2O_3 etc. The relevant reactions are listed in Table 3. By thermodynamic analysis, the order of evaporating tendency could be as: MgF_2＞SiF_4＞AlF_3＞AlOF in standard state. With the activity increase of reactants, the order may be changed, for instance, the activity of SiO_2 can be obviously changed with the addition of CaO and reaction (1) in Table 3 can be inhibited.

The slope of TG curves can reflect the evaporation speed to some content. When the temperature got up to 1400℃, the evaporation speed of slag ANF-6, M-1 and L-3 reached 0.68, 0.39 and 0.24 %/min respectively.

Table 3. Evaporation reaction and the thermodynamic data

Item No.	Reaction	K_p		
		1000K	1500K	1800K
1	$SiO_{2(s)}+2CaF_{2(s)}=SiF_{4(g)}+2CaO_{(s)}$	4.37×10^{-15}	2.24×10^{-9}	3.82×10^{-7}
2	$Al_2O_{3(s)}+3CaF_{2(s)}=3CaO_{(s)}+2AlF_{3(g)}$	1.94×10^{-34}	1.97×10^{-17}	2.45×10^{-12}
3	$CaO_{(s)}+AlF_{3(g)}+CaF_2(s)=2CaF_{2(g)}+AlOF_{(g)}$	2.33×10^{-39}	2.41×10^{-20}	3.01×10^{-14}
4	$MgO_{(s)}+CaF_{2(s)}=MgF_{2(g)}+CaO_{(s)}$	4.07×10^{-15}	1.69×10^{-7}	3.72×10^{-5}

3.2 Chemical Composition Change of ANF-6 in Smelting Process

To obtain the relation between slag weight loss and chemical composition, ANF-6 is selected as the typical basic slag . The range of chemical composition change in operating practice is taken as a reference, which involves the contents: CaF_2 50-65 mass %, CaO 6-15 mass％, SiO_2 5-8 mass％, Al_2O_3 18-30 mass％ and MgO 1-7 mass％.

Based on the TG results, a regression equation of CaF_2-CaO-Al_2O_3-SiO_2-MgO slag system at 1450 ℃was obtained as follows.

$$W=12.36-5.68F+3.91C-11.16S-5.152A-3.6M, \quad \% \qquad (1)$$

where W denotes weight loss rate ,%; F, C, S and A are the contents in mass fraction respectively for CaF_2 , CaO , SiO_2 as well as Al_2O_3 respectively, %.

It can be seen that the weight loss are shown to be increased with the increase of CaF_2, SiO_2, Al_2O_3 and MgO content, and to be decreased with the decrease of CaO content. The components cross impact is neglected in the regression equation.

From chemical reaction（2）, the weight loss and conductivity data from the operating practice (200kg ingot, ANF-6 slag) and the corresponding results by calculation with regression equation are compared. The results are shown in Fig.2 and Table 4.

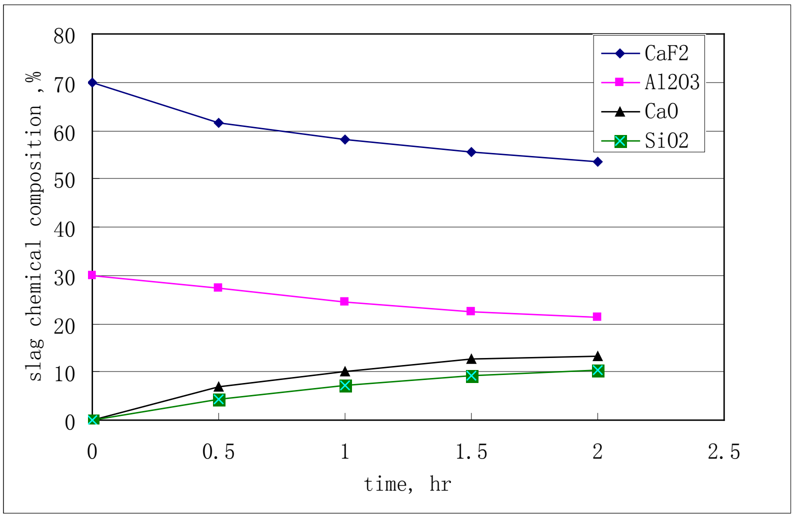


Fig.2 the calculated results in ESR process

Table 4 Comparison of composition and conductivity change

	Slag type	Slag chemical composition /mass %					Conductivity/ S/cm
		CaF_2	Al_2O_3	CaO	SiO_2	MgO	
ANF-6	Initial	70	30	0	0	0	2.394
	Final, Calculated	53.5	21.4	13.2	9.1	0	2.195
	Final, Practical	60.21	21.35	7.82	7.10	1.66	2.292

It can be seen that the changing trends of calculated composition values and practical data were in coincidence. Calculated CaO and SiO_2 contents were higher and CaF_2 content was lower than the practical data. This may imply there would be other evaporation reactions, such as the formations of SiF_4 and AlOF besides AlF_3. Evaporation of MgF_2 can be neglected due to the lower MgO content in slag. So the reaction (1) and (3) in Table 2, as well as the kinetic reason, should be taken into account. Further work should be taken into consideration though it is complicated. However, according to the data from the practical operation, the weight loss rate of ANF-6 slag is about 7mass%, CaF_2 and Al_2O_3 content is decreased about 9.97mass% and 5.36mass% respectively, CaO and SiO_2 increase about 3.0mass%

and 5.4mass% respectively. Such changes can cause the difference of electroslag properties in ESR process, and should be pay attention in the industrial operating practice.

3.3 Effect of Slag Composition Change on Conductivity

The conductivity of slags with the content range of CaF_2 50-65mass %, CaO 6-15mass％, SiO_2 5-8mass％, Al_2O_3 18-30mass％ and MgO 1-7mass％ were measured using four-point probe technique. The regression equation of conductivity(κ) with slag component content from experimental results was obtained as follows.

$$\kappa = 2.294 + 0.031F + 0.013C - 0.077S - 0.069A + 0.034M \quad \text{, s/cm} \qquad (2)$$

From Eq.(2), it can be seen that conductivity decreased with the increasing of Al_2O_3， SiO_2 content, and rised with CaF_2, MgO and CaO content increasing. To slag ANF-6, the conductivity can decrease from 2.394 S/cm to 2.295 S/cm.

From the present study, the following statements could be drawn. In ESR practice, if constant voltage and current operation are adopted, a consumable steel electrode will insert deeper in the slag pool with the conductivity decrease and high-temperature zone, therefore the heat loss from furnace mouth will be changed [1,2,4]. As a result, the solidification structure of the ingot will be changed accordingly.

4. Conclusions

TG/DSC measurements along with electrical conductivity testing with four-point probe technique for four kinds of ESR slag were carried out. The experimental results were correlated with the composition changes at high temperature. The obtained relations were used to compare with the data from ESR operating practice. The following conclusions are drawn from the present study.

1) The composition change of molten slag pool can be deduced from formation of volatile fluoride. In the present study at 1400℃, the evaporation rate of slag ANF-6 reached 0.68 %/min. As a result, CaF_2 and Al_2O_3 content would be reduced, and CaO content would be increased.
2) In the experiments, evaporations for SiF_4, AlF_3, AlOF coexisted. Their contribution to the weight loss should be further investigated.
3) The regression equations of weight loss and conductivity with chemical composition at 1450 ℃ were obtained as follows:

   W=12.36-5.68F+3.91C-11.16S-5.152A-3.6M ,%

   $\kappa = 2.294 + 0.031F + 0.013C - 0.077S - 0.069A + 0.034M$,s/cm
4) The properties of the slag can be effected by chemical composition change, and the smelting process as well as quality of final product can be effected accordingly.

Acknowledgements

The authors would like to thank National Natural Science Fund of China for the finacial surpport on No.51174155 . Thanks to Shannxi Key Discipline of Metallurgical Physical-chemistry for the support.

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