A study on the process of removing sulfide in steel surface layer by molten salt electrolysis

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Abstract: A study on the desulfurization of solid steel samples with sulfur content of 0.4% under conditions of electrolysis in molten CaF_2 was experimentally carried out at 820, 850 and 880^0C respectively. The effects of temperature, electrolysis voltage, and time of the electrolysis process were experimentally examined. The analysis of the results formed the basis of optimized technological parameters. The present investigation indicated that properly increase the temperature, and the voltage would be favorable for facilitating the desulfurizaion process. In addition, to extend the time of the electrolysis treatment would enable the reduction of sulfur content in the surface layer and interior of the samples more significant, and would increase the depth of desulfurization layer. All this effects can be explained by the diffusion of sulfide ions driven by the electrochemical potential gradient in the bath of molten CaF_2. On the basis of the above-mentioned experiments along with the analysis, optimized conditions for removing sulfide in steel surface layer by molten salt electrolysis have been proposed.

Keywords: Molten salt electrolysis, sulfide inclusions, steel, diffusion, kinetics

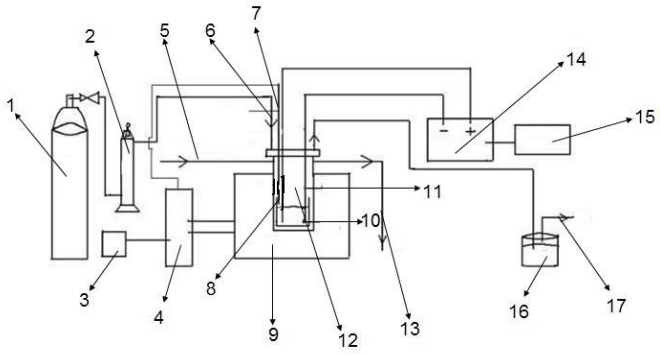
1. Introduction

The traditional desulfurization process mainly includes pre-desulfurization of hot metal and deep desulfurization of molten steel. The main operation there is to make the desulphurization agent react with the sulfur in molten steel or hot metal, as the result, the desulphurization-product bearing slag is formed. The content of sulfur in the steel can be decreased by skimming the sulfur-rich slag. The demand to some special grades of steel and the requirement to the surface sulfur content have become stricter. The deep desulfurization of traditional desulfurization process is obviously not very economical. How to reduce the sulfur content in surface layer of steel materials becomes an eager problem to solve. In this paper, the approach that removing the sulfide inclusions on the surface layer of steel material by molten salt electrolysis was proved to be a feasible and effective way [1,2]. From the experimental results, optimized technological parameters for the electrochemical reduction process are proposed in the present paper. Finally, mechanism of process kinetics in desulfurization is proposed on the basis of the diffusion driven by the gradient of electrochemical potential.

2. Experiments

The apparatus used for the experiments is shown in Fig.1. The reactor for the experiments was placed in electrical resistance furnace. As shown, the cooling device, the import and export devices of argon gas were on top of the furnace. The steel sample with a uniform sulfur content of 0.4wt% was used as cathode, high-density graphite carbon rod was used for anode. An hydrous calcium chloride($CaCl_2$) was slowly heated up to 400 ℃, and kept

muffle furnace. The cathode and anode were suspended above the molten salt to preheat. The argon gas was introduced at the same time. The cathode and graphite carbon rod were inserted into molten salt when the molten salt temperature reached 850 ℃. The electrolytic voltage was 2V and 3V respectively. The time for an electrolytic run was 10min, 1h, 6h and 20h respectively. The mass fraction of sulfide in the steel surface was calculated by the quantitative metallographic method after electrolysis.



1—Argon cylinders; 2—Drying tower; 3—Power supply; 4—Temperature control unit; 5—Cooling water; 6—Argon 7—Thermocouple; 8—Graphite anode; 9—Tubular furnace; 10—Steel sample; 11—Iron chromium wire cathode 12—Electrolytic cell; 13—Platoon walk; 14—DC regulated power supply; 15—A laptop computer to record data 16—Vitriol oil 17—Evacuation

Fig.1 Schematic presentation of experimental set-up

3. Experimental results and discussion

3.1 Effect of electrolysis temperature on the diffusion of sulfur in the samples

The electrolysis time of 60min was determined, and electrolysis voltage was 3V, the effect of electrolysis desulfurization temperature on the diffusion of sulfur was studied. Fig.2 shows the distribution curves of sulfur concentration measured at 820℃, 850℃ and 880℃. As it was shown in Fig.2, with the increasing temperature, the sulfur concentration in the steel surface layer was decreased, and the depth of desulfurization was increased. Due to the desulfurization which proceeded in solid steel, the desulfurization can be attributed to the solid diffusion [3] of sulfide ions in steel driven by the electrochemical potential gradient, involving the chemical potential and electrical potential gradient.

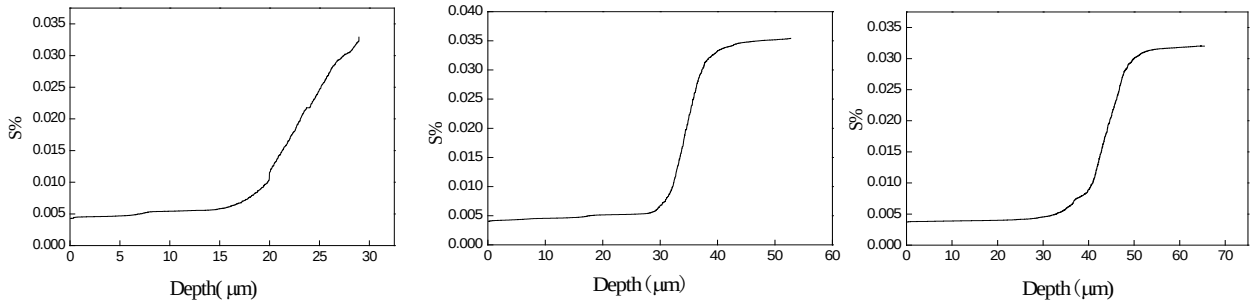


Fig. 2 Distribution of sulfur content in samples electrolyzed under different temperatures

The experimental sulfur concentrations at different depths are listed in Table 1 for the three temperatures. As the deFrom Table 1 one could see that the desulfurization layer was increased with the rising temperature. This could be resulting from the facilitated diffusion of sulfide ions at relatively higher temperature.

Table 1 Effect of electrolysis temperature in samples on the sulfur diffusion

Temperature（℃）	Depth x（μm）	Sulfur Concentration（%）
820	16.489	0.0064
	18.486	0.00823
	19.484	0.00955
	20.485	0.01297
	22.49	0.01803
	24.49	0.02313
850	30.498	0.00725
	31.501	0.00854
	32.492	0.01118
	33.51	0.01526
	34.503	0.01977
	35.51	0.02391
	36.506	0.02782
	37.504	0.03037
	38.500	0.03207
880	35.496	0.00614
	37.503	0.00755
	39.508	0.00841
	41.498	0.01143
	43.499	0.01717
	45.498	0.022
	47.500	0.02722
	49.509	0.02963
	50.498	0.0303

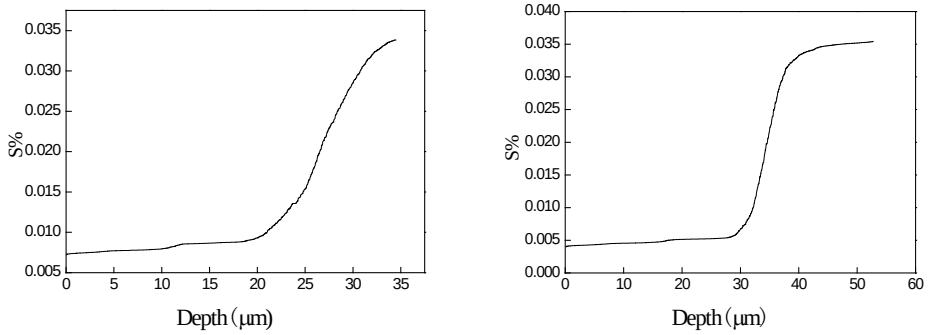
Due to the volatile feature of the molten salt, the higher the temperature was, the stronger the volatility was. From the consideration both in speeding up desulfurization and reducing the volatilization, the experiments were chosen to carried out at 850℃. With this condition, the process was carried out smoothly, and provided better economic effects.

3.2 Effect of electrolysis voltage on the diffusion of sulfur

Apart from the effect of temperature, other electrolysis parameters would inevitably affect the concentration distribution of sulfur in the steel samples. Under the electrolysis temperature of 850℃ and electrolysis time for 60min, the sulfur distribution curves in samples electrolyzed at voltages of 2V and 3V are shown in Fig.3, the corresponding data are shown in Table 2. It could be seen from the Fig.3 and Table 2, that with the voltage increase, the sulfur content in the samples surface layer and interior region was reduced more sharply.

The effect of electrolysis voltage on the desulfurization process can be reasoning from change in the driven force to

the diffusion. Because any change in electrolysis voltage would change in the electrical potential, and in turn would change the electrochemical potential. With the increasing electrolytic voltage, the diffusion process would significantly speed up. It shows that a larger electrolysis voltage could help to improve desulfurization the in the samples.



（a）2V　　（b）3V

Fig.3 Distribution of S in samples electrolyzed at different voltage and at 850^0C

Table 2 Effect of electrolysis voltage in samples on the diffusion of sulfur

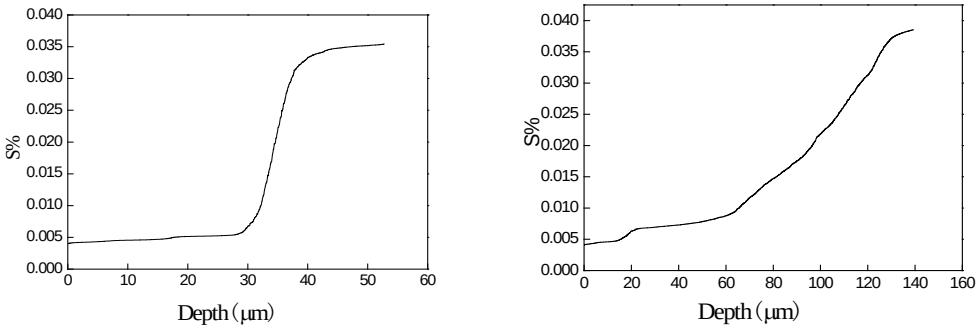
Voltage（V）	Depth x（μm）	Sulfur Concentration（%）
	20.503	0.00957
	21.502	0.01055
	22.499	0.01172
	23.496	0.01319
2V	24.499	0.01443
	25.499	0.01662
	26.508	0.01993
	27.499	0.0229
	28.499	0.02528
	30.498	0.00725
	31.501	0.00854
	32.492	0.01118
	33.510	0.01526
3V	34.503	0.01977
	35.510	0.02391
	36.506	0.02782
	37.504	0.03037
	38.500	0.03207

In addition to the effects of temperature and electrical voltage, the experimental results also showed that the sizes of sulfide inclusions in steel were affected by the size of electrolysis voltage. When the electrolysis voltage was low, the size and number of sulfide inclusions in steel were not changed obviously. However, with an electrolysis voltage increase, the shape of sulfide inclusions in the steel was changed from irregular morphology to small spherical or

rounded spots, and the number of inclusions was significantly reduced. Nevertheless, the electrolysis voltage must be confined in a reasonable range. If the electrolysis voltage of molten salt was exceeded to the breakdown voltage, the decomposition reaction of molten salt occurred, which was negative to the entire process. So under a pre-condition of no CaF_2 to decompose, an appropriate choice of a high voltage in the desulfurization process was beneficial.

3.3 Effect of electrolysis time on the diffusion of sulfur

Under the conditions of electrolysis temperature of 850℃ and electrolysis voltage of 3V, the effect of electrolysis time on the sulfur concentration distribution was studied. Fig.4 demonstrates the sulfur distribution curves in samples during 60min and 120min of electrolysis. As shown in Fig.4, the sulfur content reducing degree was lowered down with the extension of electrolysis time. Apart from the reduction of the surface concentration, the diffusion layer was also deepened and the total content of sulfur in the samples was significantly reduced.



（a）60min　　（b）120min

Fig.4 Distribution of S in samples electrolyzed at different time

Table 3 Effect of electrolysis time in samples on the diffusion of sulfur

Time（min）	Depth x（μm）	Concentration（%）
60	30.498	0.00725
	31.501	0.00854
	32.492	0.01118
	33.51	0.01526
	34.503	0.01977
	35.51	0.02391
	36.506	0.02782
	37.504	0.03037
	38.500	0.03207
120	101.493	0.02241
	102.496	0.02277
	103.498	0.02308
	104.503	0.02351
	105.494	0.02397
	106.498	0.02441
	107.503	0.02493
	108.506	0.0255

4. Conclusions

A study on solid steel sample desulfurization under conditions of electrolysis in molten CaF_2 was experimentally carried out at 820, 850 and 880^0C respectively. The effects of electrolysis voltage and time were also experimentally examined. The diffusion of sulfide ions driven by the gradient of electrical potential was used to explain the mechanism of these effects. The following conclusions can be down from the investigation.

(1) With the rising temperature, the total content of sulfur in the samples reduced, the desulfurization layer and diffusion thickness were becoming thicker. This could be resulting from increasing diffusion coefficients of sulfide ions with the rising tenpeerature.

(2) With the voltage increase, the total sulfur content in the samples was reduced, the desulfurization layer and diffusion thickness were increased. The effect of voltage change could be due to the change of electrical potential, which in turn changed the electrochemical potential, i.e the driven force to the diffusion readily. To properly increase voltage was favorable for promoting desulfurization.

(3) With the extension of time, the content of sulfur in the samples significantly reduced. Apart from the reduction of the surface concentration, the depth of desulfurization increased.

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