Applied Chemical Engineering (2019) Volume 2 Issue 2
doi:10.24294/ace.v1i2.428

Study on Phase Transformation and Desulfurization Ability during Refining with Flux Additions of B_2O_3 and CaF_2 into CaO-Based Desulfurizer

Chih-Chun Hsieh[1*], Cheng-Han Wu[2], Weite Wu[2*]

[1] Department of Materials Science and Engineering, National Chung Hsing University, Address: No.1, Julun Rd., Gangshan Dist., Kaohsiung City 820, Taiwan. E-mail: jeromehsieh@gmail.com

[2] Department of Materials Science and Engineering, National Chung Hsing University, 250 Kuo-Kuang Rd., Taichung 402, Taiwan. E-mail: wwu@nchu.edu.tw

ABSTRACT

CaF_2 aids melting and desulfurization, but can also cause environmental pollution. Thus, it has become important to discuss the phase transformation and find a substitute for CaF_2. A CaO-based desulfurizer with various flux additions of B_2O_3 and CaF_2 is investigated during the refining process. The purpose of this study is to discuss the phase transformation and desulfurization ability and during refining with B_2O_3 and CaF_2 using a high frequency furnace. Experimental results indicate that the melting temperature of CaO-Al_2O_3-SiO_2 series desulfurizer becomes lower when more B_2O_3 and less CaF_2 are added. On the other hand, the desulfurization ability can be affected within 15 min when various proportions of B_2O_3 and CaF_2 are added. The desulfurization ability is better with a high content of B_2O_3 desulfurizer within a 15 min period. However, the desulfurization ability is not affected by the proportion of B_2O_3 and CaF_2 for a long melting period (30 min).

Keywords: Compounds; Oxides; Recycling; Phase Transformation; X-Ray Diffraction

1. Introduction

In recent years, some steel companies' use of arc furnace steel-making processes has grown rapidly, leading to an increasing demand for scrap steel. It is difficult to produce high-quality steel with arc furnace steel-making, because the scrap steel contains large amounts of impurities. Therefore, the refining process in arc furnace steel-making is very important.

The ladle furnace (LF) technique not only easily adjusts to the temperature of the molten steel, but also randomly increases various alloy elements or compounds. Therefore, the ladle furnace is the most commonly used equipment for refining molten steel[1-2]. Great amounts of desulfurization slag are produced after refining desulfurization. Most steel plants discard this desulfurization slag, resulting in industrial cost and environmental pollution; the recycling of the desulfurization slag can reduce environmental pollution.

Many recent investigations have focused on the recycling of desulfurization slag. According to these papers[3-6], the desulfurization slag has been partly applied to the raw materials of cement, road repair and construction, due to the stability of its physical and chemical properties and nontoxic characteristics. Some researches[7-9] have also pointed out that desulfurization slag contains residual Free-CaO. Therefore, it is worth discussing the effect of recycling desulfurization slag on the sulfur content of molten steel.

Hino et al.[10] have confirmed that the effectiveness of desulfurization flux is related to its chemical composition. In a CaO-Al_2O_3-MgO ternary slag system, the desulfurization ability is proportional to the CaO/MgO at the constant of Al_2O_3. The decay of the desulfurization ability is attributed to the increscent of

doi: 10.24294/ace.v1i2.428

SiO_2 and Al_2O_3 in a CaO-SiO_2-Al_2O_3 ternary slag system. Furthermore, a few researches have focused on recycling desulfurization slag.

Regarding the compositional design of the desulfurizer, both a high CaO content and a low melting point are desired, but very difficult to achieve. Therefore, the addition of flux into a desulfurizer is necessary during the refining process. The flux additions have two advantages: (1) decreasing the melting point, and (2) accelerating the desulfurization reaction. CaF_2 flux is often used in desulfurizers because of its good desulfurization effect. However, the addition of CaF_2 corrodes the refractory of the furnace liner, decreasing desulfurization efficiency. Also, toxic gas will be released when the CaF_2 flux is used, and may harm many people, animals and plants[5]. As described above, finding a substitute for CaF_2 is very important for ecological protection.

The purpose of this study is to discuss the desulfurization ability during refining with the addition of two fluxes: B_2O_3 and CaF_2, into a CaO-based desulfurizer. The substitution of B_2O_3 for CaF_2 is also discussed in terms of melting point and desulfurization ability.

2. Experimental procedures

Low carbon steels (S15C) with a specific weight of 500 g was selected as the experimental material and placed in a high frequency furnace crucible. Then, 0.685 g FeS was added to increase the S content of the molten steel. After the FeS is melted, Al bars (2.1g) were placed in a high frequency furnace crucible for deoxidation, with the main purpose being to decrease the partial pressure of the oxygen of the molten steel. This procedure can enhance desulfurization. Finally, some compositions of desulfurizer (CaO, Al_2O_3, SiO_2, MgO, CaF_2, and B_2O_3) were placed in a high frequency furnace crucible. The reaction times of desulfurization were 15 and 30 min. In this study, experimental analyses can be divided into slag analysis, steel analysis and refractory analysis.

After melting, the slag and steel ingots were analyzed. For the slag analysis, the phase identification was examined using an XRD (SIEMENS D5000), and composition was analyzed using an XRF (PANalytical PW2640), a C/S analyzer (Leco CS230) and a wet chemical analytical technique. The chemical composition of the steel ingots was performed using a spark discharge spectrometer (Oxford ARC-MET8000).

In this study, desulfurization was studied with a CaO-based desulfurizer, the composition of which was designed according to the CaO-Al_2O_3-SiO_2 ternary phase diagram (**Figure 1**[11]). A lower melting point and higher CaO content were considered in order to satisfy the condition of desulfurization. Therefore, the based composition of desulfurizer (55%CaO-35%Al_2O_3-10%SiO) was used in this study. On the other hand, 8% MgO was added to replace the 8% Al_2O_3 in order to protect the refractory of the furnace liner.

The compositions of desulfurizer can be divided into five groups (A~E). The compositions of A~B groups were 59.78%CaO-20.65%Al_2O_3-10.87SiO_2-8.69MgO and 55%CaO-19%Al_2O_3-10SiO_2-8%MgO-8% CaF_2. The groups of C~E had 2% B_2O_3, 5% B_2O_3, and 8% B_2O_3 added, respectively, and 2% CaF_2, 5% CaF_2, and 8% CaF_2 reduced, respectively. Detailed compositions of the A~E groups are listed in **Table 1**. The melting points of desulfurizers for the five groups are examined using a TGA/DTA simultaneous thermal analyzer (LINSEIS STA PT1600).

3. Results and discussion

3.1 Melting point examination of desulfurizer

The melting points of A~E groups can be analyzed using a TGA/DTA simultaneous thermal analyzer. **Figure 2** shows the DTA thermal analysis results of the five groups. An endothermic peak was detected between 450 ^{o}C and 480 ^{o}C, and this peak was a reaction peak of water of crystallization of CaO. However, another endothermic peak was also observed at a temperature range from 1245 ^{o}C to 1404 ^{o}C, and this repre-

Figure 1. $CaO\text{-}Al_2O_3\text{-}SiO_2$ ternary phase diagram.

Specimen	Content of compound (wt.%)					
	CaO	**Al_2O_3**	**SiO_2**	**MgO**	**CaF_2**	**B_2O_3**
A	59.78	20.65	10.87	8.69	0	0
B	55	19	10	8	8	0
C	55	19	10	8	6	2
D	55	19	10	8	3	5
E	55	19	10	8	0	8

Table 1. Chemical composition of desulfurizer

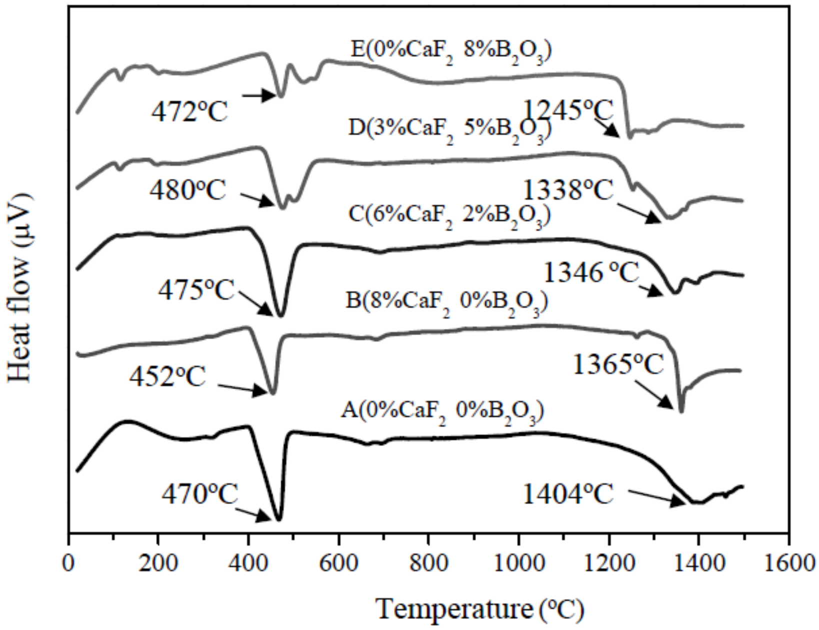

Figure 2. Thermal analyzed results of desulfurizers.

sented the melting points of desulfurizer for the five groups. Furthermore, the melting points had decreasing tendencies for desulfurizers of groups A~E. The melting points decreased from 1,404 ^{o}C to 1,245 ^{o}C when B_2O_3 contents increased from 0% to 8%. In regard to the melting point, the B_2O_3 can replace the CaF_2, and is a better flux in desulfurization than CaF, because B_2O_3, CaO, Al_2O_3, and MgO can form low melting point eutectic compounds. The CaF_2 and Al_2O_3 MgO can also form low melting point compounds, but the melting point of eutectic compound in B_2O_3 is lower than that in CaF_2. As stated above, the melting point of the desulfurizer can be decreased to 1245 ^{o}C.

3.2 Compositional analysis of steel ingot

The chemical compositions and desulfurization ratios of steel ingots after 15 and 30 min of melting times are shown in **Tables 2** and **3**, and **Figure 3**. It indicates that the desulfurization ratio has no obvious change after 30 min. However, the desulfurization ratio exhibits a variation after 15 min. The desulfurization ratio of group A without a flux addition is lower after 15 min than other desulfurization ratios of groups B~E. However, other desulfurization ratios of groups B~E are very close, which means that the flux additions can promote the desulfurization ability within a short time. On the other hand, the desulfurization ratio of group A can be increased to 12.4%, while those of groups B~E can only be raised to 5~7% after 15 min; this means that group A does not show excellent desulfurization ability within 15 min. Furthermore, groups B~E indicate better desulfurization ability within 15 min, so the increment of desulfurization ratios is limited over 15 min.

Groups	**Content of compound (wt.%) (15 min)**									
	CaO	**F-CaO**	**Al_2O_3**	**SiO_2**	**MgO**	**MnO**	**C**	**S**	**B**	**T-Fe**
A	22.489	0.086	22.458	33.562	3.616	16.903	0.028	0.039	0.009	1.119
B	20.017	0.059	23.293	36.281	3.578	16.556	0.030	0.050	0.018	1.056
C	21.879	0.061	29.492	34.475	3.968	15.742	0.027	0.049	0.152	1.026
D	19.924	0.057	25.781	34.063	3.324	14.802	0.026	0.052	0.320	1.217
E	23.252	0.057	21.205	33.871	3.425	13.181	0.021	0.050	0.523	1.033

Table 2. Chemical composition of slag at 15 min

Groups	**Content of compound (wt.%) (30 min)**									
	CaO	**F-CaO**	**Al_2O_3**	**SiO_2**	**MgO**	**MnO**	**C**	**S**	**B**	**T-Fe**
A	19.591	0.059	17.705	39.362	2.796	16.188	0.027	0.054	0.012	1.135
B	18.129	0.043	19.258	41.930	2.396	17.804	0.029	0.055	0.008	1.141
C	23.105	0.040	17.934	41.190	3.358	12.320	0.027	0.055	0.124	1.284
D	21.857	0.037	18.337	40.450	3.042	14.182	0.025	0.058	0.295	1.004
E	20.604	0.038	21.585	39.600	3.031	14.550	0.022	0.059	0.508	1.177

Table 3. Chemical composition of slag at 30 min

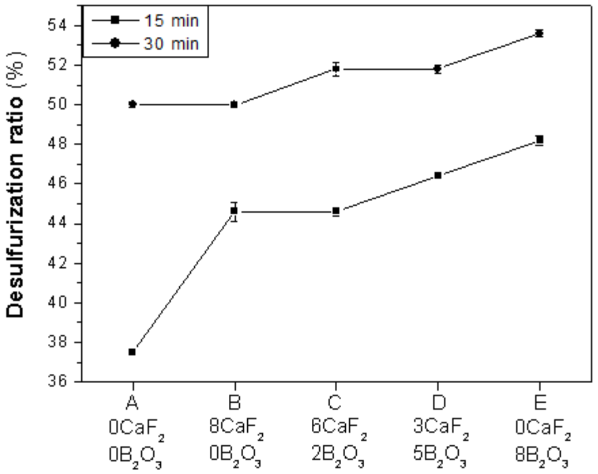

Figure 3. Relationship between the desulfurization ratios and desulfurizers at 15 min and 30 min.

The desulfurization ratios of groups B~E with flux additions of B_2O_3 and CaF_2 show no obvious change. However, the desulfurization ratios of higher B_2O_3 content (groups D~E) after 15 min melting were higher than that of lower B_2O_3 content (groups A~C). This result indicates that the B_2O_3 flux additions can increase the desulfurization ability within 15 min, and shrink the difference of desulfurization ratios between 15 and 30 min. This means that the desulfurization reaction is almost finished after 15 min, so the desulfurization reaction time can be increased. Therefore, B_2O_3 can substitute CaF_2 for improving desulfurization.

3.3 Compositional analysis of slags

The compositions and the S contents of slags after 15 and 30 min of melting are shown in **Figure 4**. The S content in group A is lower than groups B~E because the flux does not help the rapid dissolution of CaO after 15 min of melting. However, the S contents are very close with flux additions after 15 and 30 min of melting. This is because the fluxes can improve the rapid dissolution of CaO. Groups B~E display good desulfurization ability after 15 min of melting. Therefore, the desulfurization ability in slag will be limited over 15 min of melting. The difference of S contents becomes very small when the contents of B_2O_3 are higher (groups D~E).

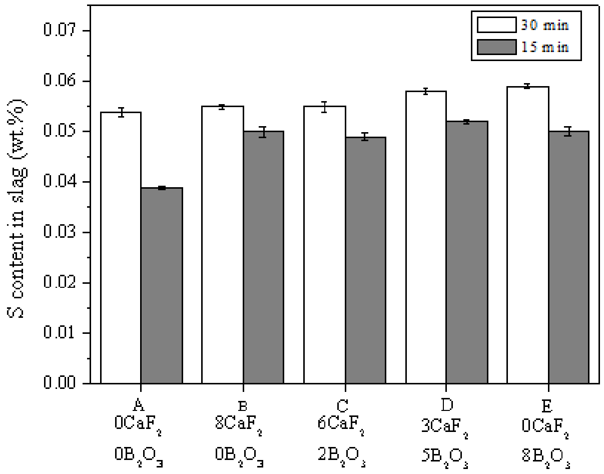

Figure 4. Relationship between the S contents in slag and desulfurizers at 15 min and 30 min.

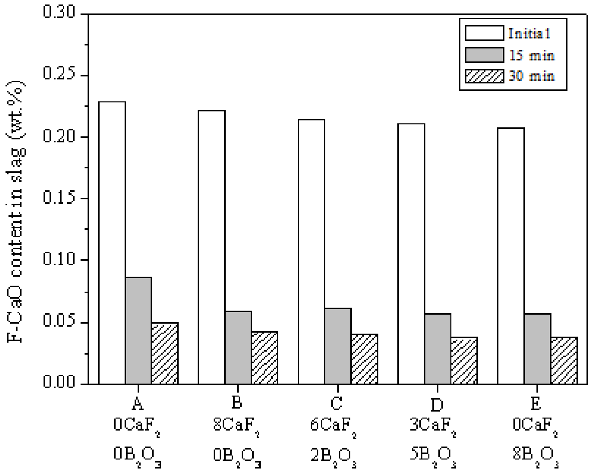

Figure 5. Relationship between the Free-CaO in slag and desulfurizers at 15 min and 30 min.

Figure 5 shows the Free-CaO contents in slag with different melting times. The contents of Free-CaO without flux addition are higher than that with flux addition after 15 and 30 min because a lot of unreacted CaO is present without a flux addition and the desulfurization reaction does not proceed adequately in the desulfurizer. However, there are lower Free-CaO contents in groups B~E than in group A. Less unreacted CaO is present in groups B~E, so the desulfurization reaction can be completed. The desulfurization has a similar effect with flux additions of B_2O_3 and CaF_2 after 15 and 30 min. However, the desulfurization effect of B_2O_3 is better than that of CaF_2. Hence, the B_2O_3 promotes the rapid desulfurization of CaO.

3.4 Relationship between desulfurization ratio and Free-CaO content

Figure 6 combines **Figures 3** and **5**. The relationship between the desulfurization ratio of a steel ingot and the amount of Free-CaO slag is shown in **Figure 6**; it shows that the desulfurization ratio of the steel ingot and amount of CaO slag have a linear relationship, and their correlation can be represented as Equation (1). The desulfurization ratio can be increased when the used amount of CaO is increased. This means that the desulfurization ability can be improved when higher Free-CaO contents are consumed during the desulfurization. Therefore, Free-CaO is an important compound for the desulfurization reaction.

$$\text{Desulfurization ratio (\%)} = 0.7135 + 286.96[\text{F-CaO(wt.\%)}] \tag{1}$$

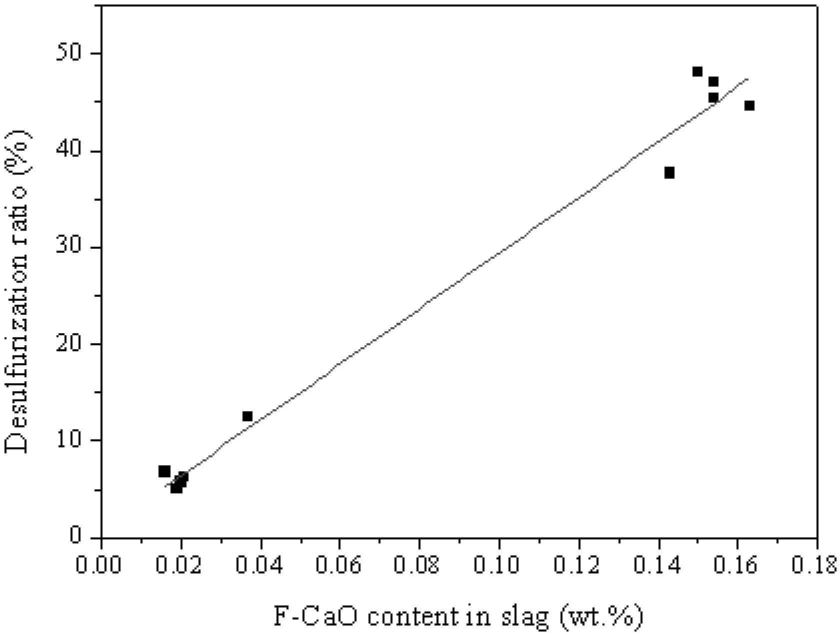

Figure 6. Relationship between the desulfurization ratios and Free-CaO contents.

3.5 Phase transformation of CaO-CaF2 and CaO-B2O3 at high temperature

The CaO-B_2O_3 (1:1) was mixed and heated to 1,650 °C with a heating rate of 5 °C/min via a high temperature furnace in order to understand the fluxing mechanism of CaO under high temperature. Following this, the high temperature compounds were analyzed using the XRD.

Figure 7 shows the compounds of the CaO and CaF_2; no new precipitate was found after heating. Hence, the fluxing mechanism of CaO did not result from the precipitation of low melting point compounds. The diffraction peaks of the $CaAl_2O_4$ and $CaAl_4O_7$ compounds were detected, with two peaks derived from the Al_2O_3 crucible.

In **Figure 8**, the diffraction peaks of $Ca_2B_2O_5$ were examined; this compound was a low melting point compound[12]. The compounds of $Ca_2B_2O_5$ can help with the rapid dissolution of CaO during melting as well as to achieve a fluxing effect. Therefore, the desulfurization reaction can also be accelerated. It can be proven that the addition of B_2O_3 and CaO into the desulfurizer can be reacted as a compound of low melting point, $Ca_2B_2O_5$. Similarly, the diffraction peaks of $CaAl_2B_2O_7$ and Al_2O_3 were also derived from the Al_2O_3 crucible.

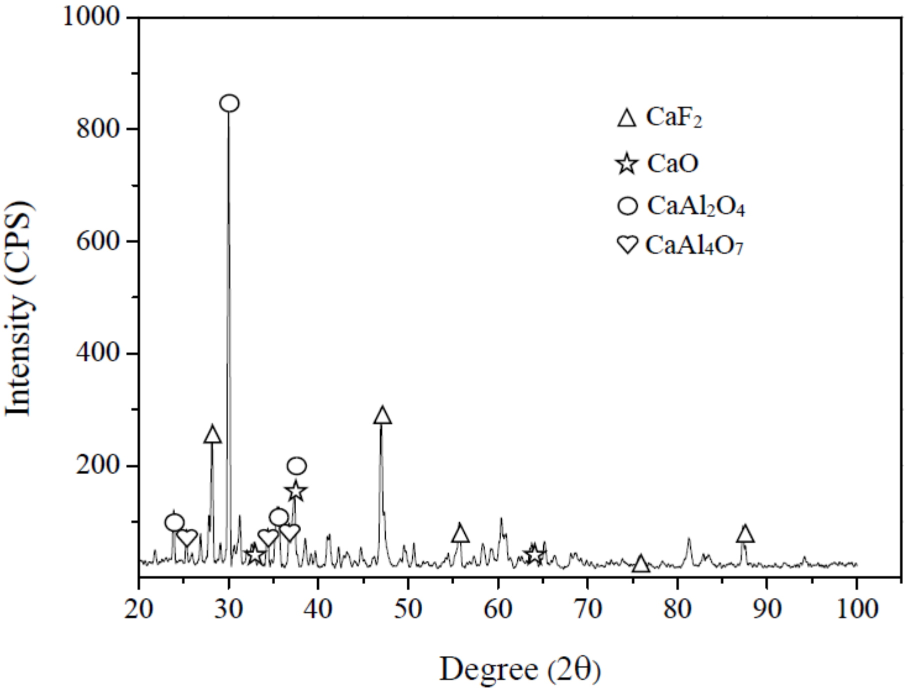

Figure 7. XRD diffraction pattern of CaO-CaF_2.

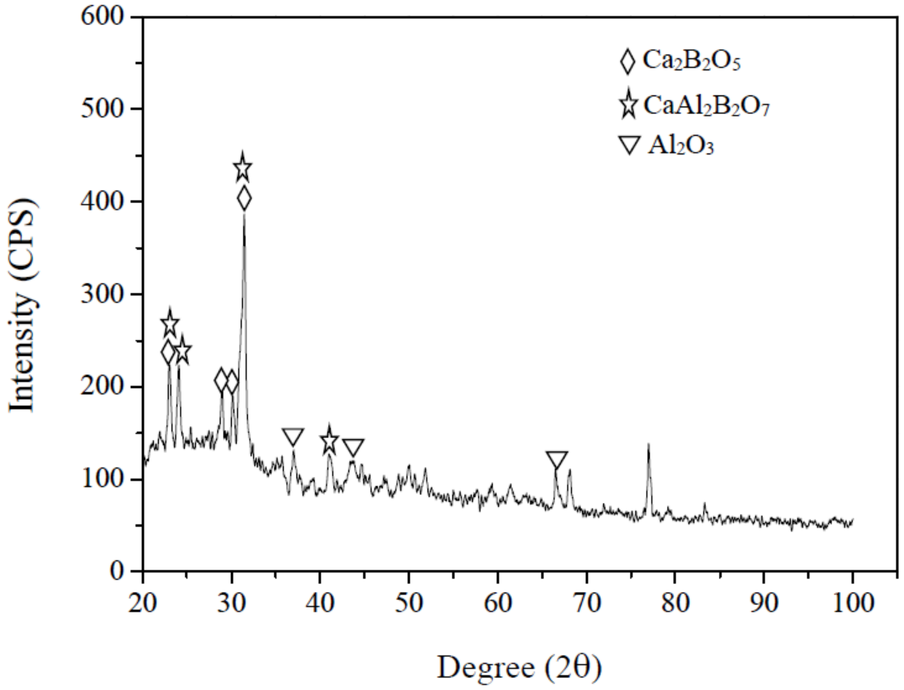

Figure 8. XRD diffraction pattern of CaO-B_2O_3.

4. Conclusions

This study discusses the phase transformation and desulfurization ability for a CaO-based desulfurizer with different flux contents of CaF_2 and B_2O_3. Some significant results can be summarized as follows:

1) In the CaO-based desulfurizer, the CaF_2 content is lower when the B_2O_3 content is higher, which leads to a lower desulfurizer melting point, especially with 8% B_2O_3. The desulfurizer melting point (8% B_2O_3) was the lowest of all contents.

2) Different ratios of CaF_2 and B_2O_3 can affect the desulfurization ability within a short time, and the desulfurizer (8% B_2O_3) shows excellent desulfurization ability within a short time.

3) The desulfurization ability of CaO-based desulfurizer is not affected by CaF_2 and B_2O_3 contents for a long desulfurization time, but the Free-CaO can dominate the desulfurization ability of the CaO-based desulfurizer.

4) A linear relationship between the desulfurization ability of the CaO-based desulfurizer and the Free-CaO content of the desulfurizer exists as follows: Desulfurization ratio (%) = 0.7135 + 286.96 [Free-CaO (wt.%)].

Conflict of interest

The authors declared no conflict of interest.

Acknowledgements

The authors are obligated to thank the National Science Council of the Taiwan, R.O.C. for the financial support under the projects numbered NSC 100-ET-E-005-001-ET, NSC 100-2811-E-005-001, and 100-EC-17-A-08-S1-117.

References

1. Wang H, Li G, Li B, *et al.* Effect of B2O3 on melting temperature of CaO-based ladle refining slag. Journal of Iron and Steel Research International 2010; 17(10): 18–22.
2. Hong X, Zheng Q, Jiang G, *et al.* In: Kanagy DI (editor). Proceeding of 84th Steelmaking Conference; 2001 Mar 25–28; Baltimore, Maiyland. Association for Iron & Steel Technology; 2001. p. 715.
3. Chen YL, Chang JE, Shih PH, *et al.* Reusing pretreated desulfurization slag to improve clinkerization and clinker grindability for energy conservation in cement manufacture. Journal of Environmental Management 2010; 91(9): 1892–1897.
4. El-Mahllawy MS. Characteristics of acid resisting bricks made from quarry residues and waste steel slag. Construction and Building Materials 2008; 22(8): 1887–1896.
5. Durinck D, Engström F, Arnout S, *et al.* Hot stage processing of metallurgical slags. Resources, Conservation and Recycling 2008; 52(10): 1121–1131.
6. Kuo YM, Huang KL, Wang CT, *et al.* Effect of Al_2O_3 mole fraction and cooling method on vitrification of an artificial hazardous material. Part 1: Variation of crystalline phases and slag structures. Journal of Hazardous Materials 2009 169(1–3): 626–634.
7. Das B, Prakash S, Reddy PSR, *et al.* An overview of utilization of slag and sludge from steel industries. Resources, Conservation and Recycling 2007; 50(1): 40–57.
8. Li HJ, Suito H, Tokuda M. Proc. 1st. Int. Conf. on Processing Materials for Properties, 1993. ISIJ international 1995; 35(9): 1079–1088.
9. Nakai Y, Kikuchi N, Iwasa M, *et al.* Development of slag recycling process in hot metal desulfurization with mechanical stirring. Steel Research International 2009; 80(10): 727–732.
10. Hino M, Kitagawa S, Ban-Ya S. Sulphide capacities of CaO-Al_2O_3-SiO_2Slags. Tetsu-to-Hagané 1993; 79(1): 34–40.
11. Sutcu M, Akkurt S. Utilization of recycled paper processing residues and clay of different sources for the production of porous anorthite ceramics. Journal of the European Ceramic Society 2010; 30(8): 1785–1793.
12. Yu X, Shi Q, Zhai R, *et al.* Influence of B2O3 on melting haracteristics of CaO-Al2O3-SiO2-MgO-CaF2 pentary slag series. Special Steel 2006; 27(4): 5–7.