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Effect of Slag Adjustment on Inclusions and Mechanical Properties of Si-Killed 55SiCr Spring Steel

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Abstract: The effects of the Al_2O_3 content and basicity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-10 wt.}\%$ MgO refining slag on inclusions removal in 55SiCr spring steel were investigated. The viscosity of slag was studied using a viscometer, while the microstructure investigation involved using a water-quenching furnace and a Fourier-transform infrared spectrometer. The influence mechanism of the slag adjustment on inclusions was explored through thermodynamic calculations and kinetic analysis. The results indicated that the viscosity of the molten slag increased gradually with the content of Al_2O_3 increasing due to it increasing the degree of polymerization of the slag network structure, especially the $[\text{AlO}_4]^{5-}$ and $[\text{Si-O-Si}]$ structures. In contrast, the viscosity of molten slag experienced the opposite pattern, with the basicity of molten slag increasing. This was due to the fact that Ca^{2+} can significantly reduce the degree of polymerization of a slag network structure, especially the percentages of the $[\text{SiO}_4]^{4-}$, $[\text{AlO}_4]^{5-}$ and $[\text{Si-O-Si}]$ network structures. Finally, the changes in physical properties and structure of slag significantly affected the removal effect of the inclusions in molten steel. As a result, the number, size distribution, composition distribution and morphology of the inclusions displayed significant changes when the content of Al_2O_3 increased from 3 wt.% to 12 wt.% and the basicity of the slag gradually increased from 0.5 to 1.2.

Keywords: 55SiCr steel; spring steel; refining slag; non-metallic inclusions; high temperature viscosity



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1. Introduction

High strength, fatigue resistance and impact resistance are important properties of spring steels [1,2]. Non-metallic inclusion is one of the most important factors that cause fatigue fractures in spring steel [3,4]. Inclusions with high hardness and melting points, such as alumina and spinel, often act as crack sources of fatigue failure [5–7]. The total oxygen (T.O) of steel, as well as the type, number, size, morphology and distribution of inclusions in steel, play essential roles in spring steel cleanliness, and an improvement in cleanliness can effectively prolong the fatigue life of the steel [8–10].

Ladle furnace (LF) slag refining is a widely used technology to control inclusions in spring steel production [11,12]. Appropriate optimization of the refining slag composition can reduce the T.O and the number and size of inclusions in spring steel, as well as control the composition of inclusions located in the low melting area [13,14]. Zhang et al. [15] studied the low-melting-point region (at 1673 K) in a $\text{MnO-CaO-SiO}_2\text{-Al}_2\text{O}_3$ system with the largest area when the Al_2O_3 content in this system was 25 wt.%. He et al. [16] showed that the inclusions are plastic at the end of the refining process, the basicity ($R = \text{wt.}\% \text{CaO} / \text{wt.}\% \text{SiO}_2$) of refining slag is in the range of 1.0–1.2 and the Al_2O_3 content of slag is in the range of 3–9 wt.%. Yang et al. [17] showed that the inclusions located in the low-melting-point region when the basicity was in the range of 1.00 to 1.19 had a C/A value ($\text{wt.}\% \text{CaO} / \text{wt.}\% \text{Al}_2\text{O}_3$) above 9 at 1673 K. Similar results were mentioned in other studies [18–20].

Wu et al. [21] studied the effect of refining slag with low basicity on the inclusions in 55SiCr suspension spring steel. The results indicate that the composition of

the CaO–SiO₂–Al₂O₃ ternary system inclusions is located at the center of the low-melting-point zone, and the plastic deformation ability of the inclusions is good. Nevertheless, the authors did not study the influence of viscosity and structure of refining slag on removing non-metallic inclusions in spring steel.

Du et al. [22] studied the influence of refining slag with high basicity on inclusions in 55SiCr suspension spring steel. The results showed that the number of inclusions decreased sharply as the basicity of the slag gradually increased, and the diameter of most of the inclusions was less than 10 µm. Similarly, the authors did not study the influence of the alkalinity of refining slag on its viscosity and structure.

Non-metallic inclusions have significant effects on many mechanical properties of suspension spring steel, including the strength, plasticity, toughness and fatigue properties. Li et al. [23] studied the effect of inclusions on the tensile fracture properties of 55CrSi spring steel. The results demonstrated that interior inclusions have a significant effect on the ductility and a minimal effect on the tensile strength of spring steel. However, the authors only selected the samples obtained under a single smelting condition as the research object, and the change rules of mechanical properties of spring steel treated with refining slag with different compositions have not been studied.

As for the influence of basicity and Al₂O₃ content on the inclusions in spring steel, most researchers only made a one-sided analysis from the perspective of thermodynamics. Few researchers elaborated on the influence of basicity and Al₂O₃ content on inclusions in steel from the perspective of dynamics according to their influence on the physical properties and structure of slag. Therefore, in this study, the effects of basicity and Al₂O₃ content on the viscosity and structure of slag were studied in detail, and their effects on the removal of inclusions in steel were explored. In addition, the effects of inclusions on the mechanical properties of spring steel are discussed.

2. Materials and Methods

2.1. Materials

The effect of the Al₂O₃ content and basicity in refining slag on the inclusions in spring steel was investigated in a MoSi₂ high-temperature resistance furnace. Table 1 shows the main chemical composition of the 55SiCr spring steel.

Table 1. Chemical compositions of the 55SiCr spring steel (wt.%) used in this experiment.

Elements	C	Si	Mn	Cr	Ni	P	S	V
Range	0.55–0.59	1.40–1.60	0.60–0.80	0.60–0.80	0.20–0.30	≤0.012	≤0.008	0.08–0.20
Target	0.57	1.50	0.70	0.70	0.25	≤0.012	≤0.008	0.15

2.2. Experimental Equipment and Procedure

Seven sample types were created by treating different synthetic LF refining slags with four different Al₂O₃ contents of 3.0 wt.%, 5.0 wt.%, 8.0 wt.% and 12.0 wt.% and four basicities of 0.5, 0.8, 1.0 and 1.2, as shown in Table 2.

Table 2. Chemical compositions of the low-basicity refining slag (wt.%).

Heat	CaO	SiO ₂	MgO	Al ₂ O ₃	R
1 [#]	38.7	48.3	10.0	3.0	0.8
2 [#]	37.8	47.2	10.0	5.0	0.8
3 [#]	36.4	45.5	10.0	8.0	0.8
4 [#]	34.7	43.3	10.0	12.0	0.8
5 [#]	28.3	56.7	10.0	5.0	0.5
2 [#]	37.8	47.2	10.0	5.0	0.8
6 [#]	42.5	42.5	10.0	5.0	1.0
7 [#]	46.3	38.7	10.0	5.0	1.2

Note: R = CaO/SiO₂.

Experiments were carried out in a MoSi₂ high-temperature resistance furnace. An argon atmosphere was kept in the experiments all the time, blowing from the bottom of the furnace tube to the top. The experimental procedures were carried out as follows. First, a 1.00 kg steel rod was placed into a MgO crucible with a 60×10^{-3} m inner diameter and an 80×10^{-3} m depth. Then, the crucible was placed in a graphite crucible to prevent liquid metal from leaking. After the whole crucible was placed in the chamber, the power was switched on and the furnace was heated to the experimental temperature of 1873 K. Alloys were added into the molten steel when the temperature reached 1873 K, and the molten steel was deoxidized using Si. After that, 0.05 kg of synthetic LF refining slag powder was put into the surface of the molten steel. The refining time was constant at 45 min for all of the experiments.

A direct reading spectrometer was utilized to detect the compositions of Si, Mn, Cr, V, Mo, Ni, Al, P and S. For C and S, an infrared C/S analyzer was applied. Furthermore, a LECO[®] TC 500 O₂/N₂ analyzer was selected to detect O and N. The ASPEX (FEI Company, Hillsboro, USA) was used to indicate the number, size and compositional distribution of the inclusions. Finally, SEM-EDS was selected to analyze the morphology of the inclusions.

The sample treatment method for inclusion observation and mechanical properties is shown in Figure 1. A cylindrical ingot was cut into two semi-cylinders along the diameter. One was forged and a heat treatment was conducted for a tensile test, and the other was used to acquire samples for inclusion observation. The forging process started at 1200 °C after heat preservation for 2 h, and was finally air-cooled to room temperature. The cross-section of the forging cylinder had an 18 mm diameter. Forged steel was austenized at 880 °C for 30 min and oil-quenched to room temperature, followed by tempering at 450 °C for 120 min. The atmosphere of the heat treatment process was air. For the mechanical property characterization, tensile tests were conducted on a Shimadzu AGS-X100KN (Shimadzu, Kyodo, Japan) electronic tensile testing machine following standard GB/T 228.1-2010 (ISO 6892-1:2009, MOD) [24].

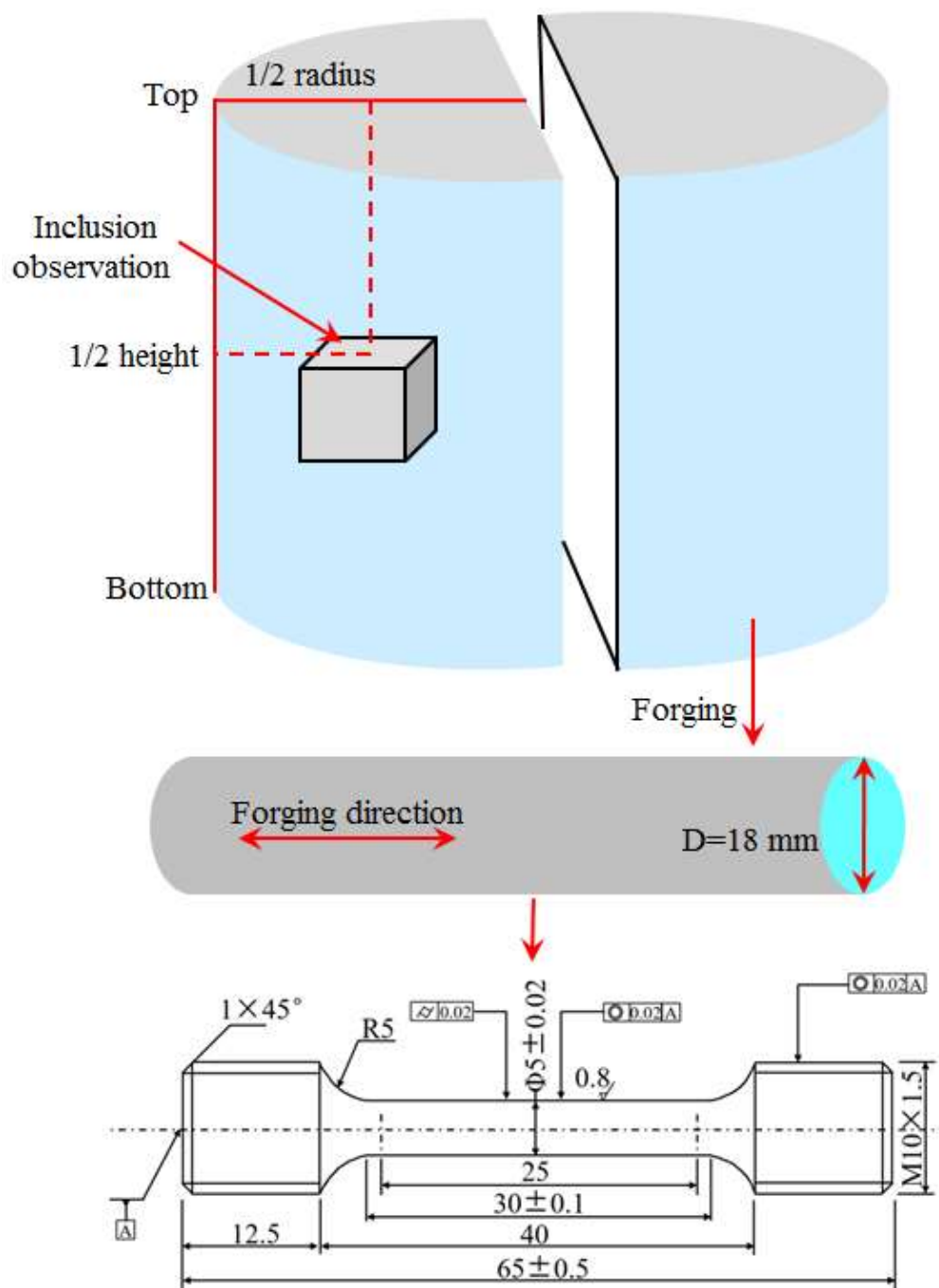


Figure 1. Sample treatment method for the inclusion observation and mechanical properties testing.

2.3. Equipment and Specific Experimental Steps for the Viscosity Measurements of Refining Slag

In this study, a Brookfield DVT rotary viscometer was selected to measure the viscosity of the slag. A schematic diagram of the equipment is shown in Figure 2. The error range of the viscosity measurement was $\pm 1\%$, and the reproducibility of the experimental data was $\pm 0.2\%$. The crucible material used in the experiment was molybdenum, and the size of the crucible was $\Phi 31 \text{ mm} \times 61 \text{ mm}$. The material of the adopted rotor was molybdenum, and its size was $\Phi 17 \text{ mm} \times 25 \text{ mm}$, with an angle of 120° at the top and tail of the rotor. During the experiment, the distance between the top of the rotor and the molybdenum crucible was 3 mm. In order to ensure that the slag liquid level did not exceed 3–5 mm from the tail of the rotor during the experiment, 65 g of slag was weighed for each experiment.

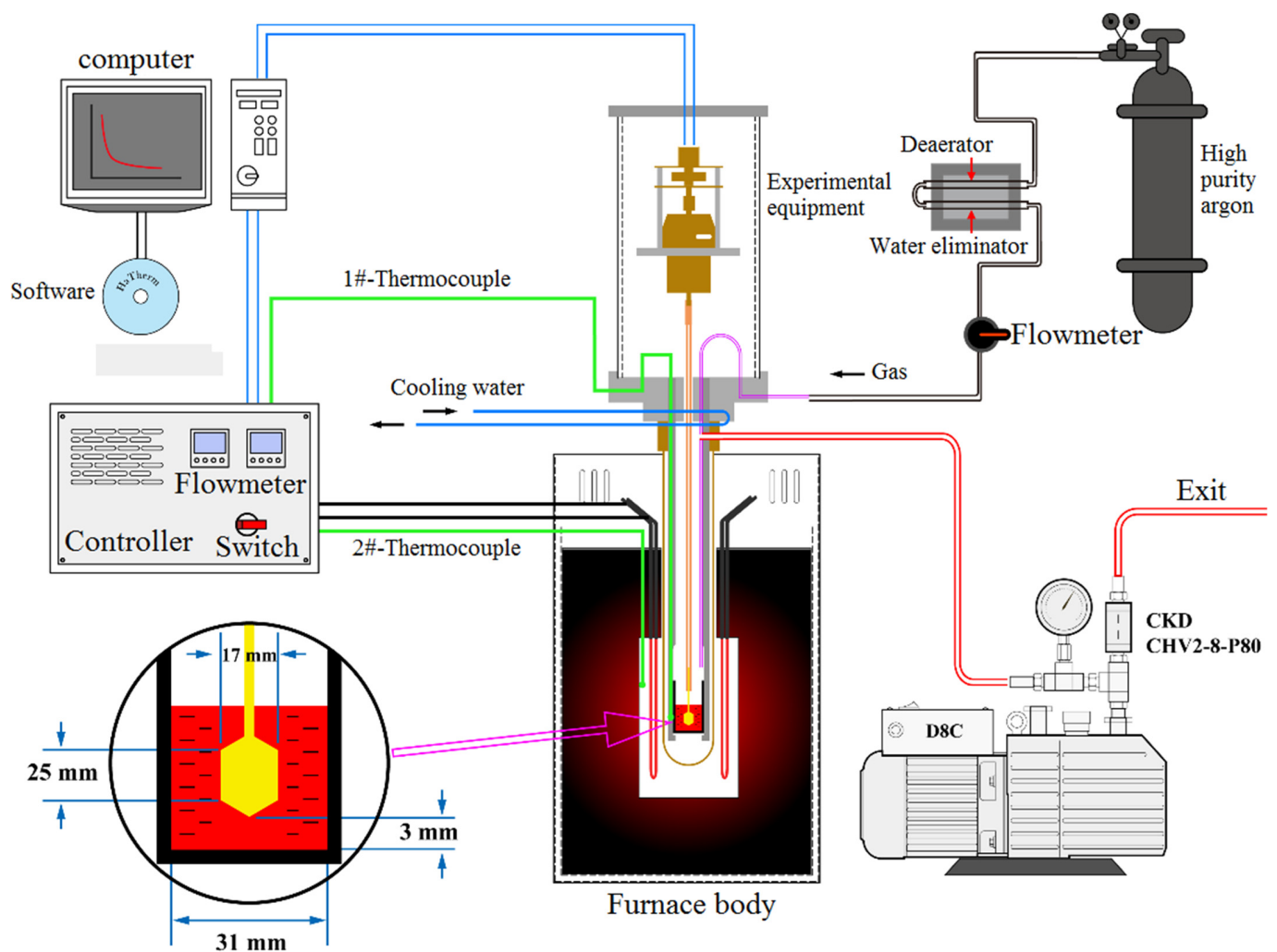


Figure 2. Diagram of the high-temperature viscometer and its auxiliary device.

The detailed steps of the viscosity test were as follows: (1) Preparation of experiment: 65 g of slag was prepared and put into the molybdenum crucible after the compression. (2) Zero adjustment of the viscometer: the viscometer was left to idle for the zero calibration without hanging the rotor. (3) Power on and temperature increase: after the zero calibration, the equipment was sealed, the power was turned on, the temperature was increased and the vacuum pumping began to work. After a vacuum was achieved, the shielding Ar gas was introduced at the flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$ (to prevent the rotor fluctuation caused by excessive air flow and experimental error). Cooling water was fed into the circulation when the furnace temperature reached 673 K. (4) Measuring the viscosity: the temperature was kept constant for half an hour when the temperature reached 1873 K, and then the rotor was lowered to 3 mm from the bottom of the molybdenum crucible and the slag viscosity was measured at the speed of $100 \text{ r} \cdot \text{min}^{-1}$, where viscosity data was recorded every 10 s and continued for 5 min. (5) Viscosity measurement during the cooling process: the temperature was decreased by 20 K each time after the viscosity at 1873 K was measured. The temperature was kept constant for 10 min, and then the viscosity of the slag was measured at this temperature at the speed of $100 \text{ r} \cdot \text{min}^{-1}$. (6) Finally, the temperature was increased again to 1773 K, and the rotor was lifted to stop measuring the viscosity when the torque was greater than 100%. The viscometer was powered off and cooled down. The switches of the Ar gas and cooling water were closed when the furnace temperature reached 873 K and 673 K, respectively.

2.4. Apparatus and Specific Experimental Steps for the Structure Measurement of Refining Slag

A schematic diagram of the water bath quenching equipment is shown in Figure 3. The graphite crucible (20 mm diameter, 40 mm height) containing the refined slag sample was hung in the furnace with platinum wire while ensuring it was located in the constant temperature zone. A basin of ice water was placed at the vertical bottom of the furnace. The power was turned on and the switches for the cooling water and argon gas were turned on at the same time. The temperature increased gradually following the program that was set in the equipment. The furnace was kept at a constant temperature for 1 hour when the temperature reached 1873 K, and then the switch for the platinum wire was released to make the graphite crucible quickly fall into the ice water at the bottom of the furnace. The slag could maintain its structure in the molten state because the liquid refining slag was rapidly cooled from 1873 K to 273 K.

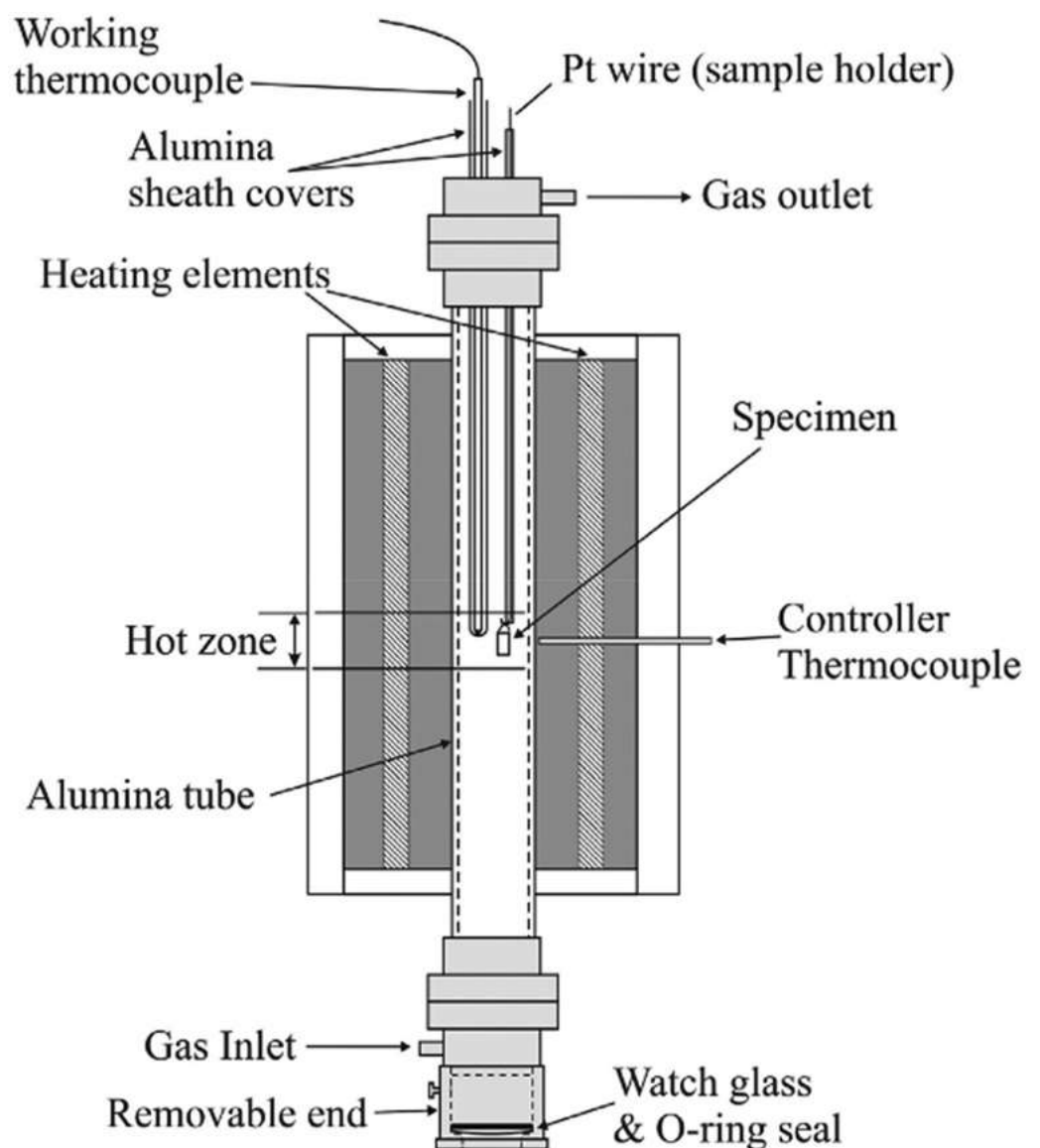


Figure 3. Schematic diagram of the vertical resistance furnace used in the water quenching experiment.

The refining slag was dried after it was removed from ice water, and then it was ground to a particle size below 200 mesh. Finally, the structure of the refining slag was detected using Fourier-transform infrared spectrometry (FTIR).

3. Results and Discussion

3.1. Number and Size of Inclusions

The chemical compositions of the 55SiCr steels are shown in Table 3.

Table 3. Chemical compositions of the 55SiCr steels (wt.%).

	C	Si	Mn	Cr	Ni	V	T.O	N	[Al]s	P	S
1 [#]	0.577	1.446	0.729	0.732	0.267	0.172	0.0016	0.0039	0.0012	0.0084	0.0053
2 [#]	0.582	1.480	0.741	0.746	0.252	0.163	0.0019	0.0028	0.0013	0.0077	0.0058
3 [#]	0.570	1.478	0.713	0.715	0.276	0.163	0.0021	0.0032	0.0014	0.0076	0.0050
4 [#]	0.556	1.498	0.683	0.697	0.251	0.162	0.0023	0.0027	0.0015	0.0092	0.0064
5 [#]	0.560	1.452	0.705	0.716	0.257	0.158	0.0020	0.0034	0.0013	0.0075	0.0056
2 [#]	0.582	1.480	0.741	0.746	0.252	0.163	0.0019	0.0028	0.0013	0.0077	0.0058
6 [#]	0.575	1.427	0.750	0.721	0.266	0.163	0.0017	0.0034	0.0013	0.0072	0.0050
7 [#]	0.564	1.512	0.676	0.716	0.248	0.152	0.0015	0.0036	0.0012	0.0096	0.0060

The T.O and [Al]s contents increased from 0.0016 wt.% to 0.0023 wt.% and from 0.0012 wt.% to 0.0015 wt.%, respectively, as the content of Al₂O₃ increased from 3 wt.% to 12 wt.%. In contrast, the T.O content decreased from 0.0020 wt.% to 0.0015 wt.% as the basicity increased from 0.5 to 1.2.

The number and size distribution of inclusions in the 1[#]~7[#] steel samples is shown in Table 4. Obviously, the quantity density gradually increased from 8.81 to 8.96, while the percentage of inclusions with sizes smaller than 5 µm increased from 61% to 77% with increasing Al₂O₃. In contrast, the quantity density gradually decreased from 8.92 to 8.54, while the percentage of inclusions with a size smaller than 5 µm decreased from 76% to 55% as the basicity increased.

Table 4. Results of the inclusions in the 1[#]~7[#] cast samples.

No.	Total Number	Area (mm ²)	Quantity Density
1 [#]	705	80	8.81
2 [#]	692	80	8.65
3 [#]	701	80	8.76
4 [#]	717	80	8.96
5 [#]	714	80	8.92
2 [#]	692	80	8.65
6 [#]	687	80	8.56
7 [#]	683	80	8.54

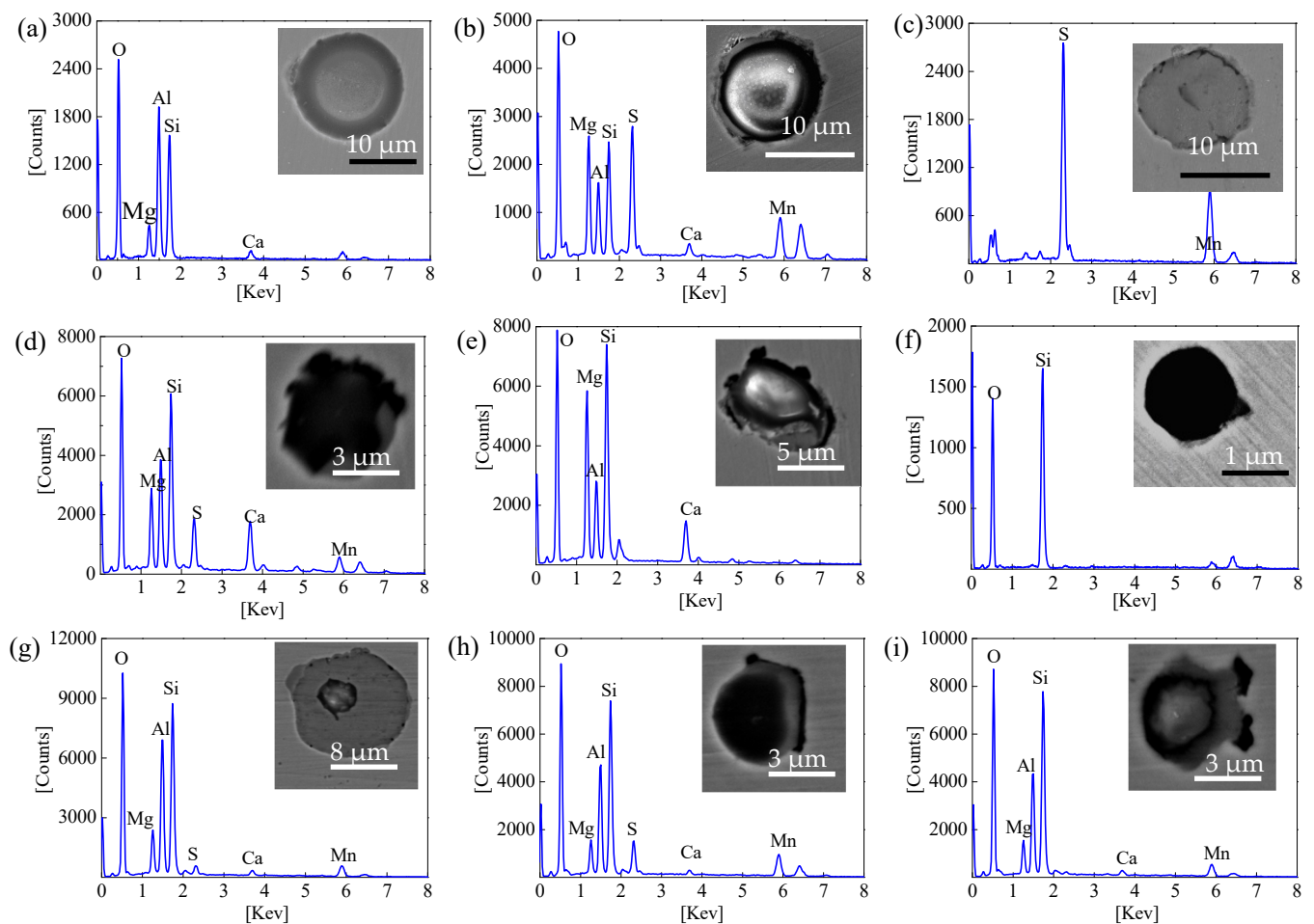
The size distribution of the inclusions in the 1[#]~7[#] steel samples is shown in Table 5. For the 1[#]~4[#] samples with different Al₂O₃ contents, the percentage of inclusions with a diameter larger than 10 µm decreased from 13% to 4%. In contrast, the percentage of inclusions with a diameter smaller than 2 µm increased from 20% to 33%. For the 2[#], 5[#], 6[#] and 7[#] samples with different basicities, the percentage of inclusions with a diameter larger than 10 µm increased from 6% to 19%. In contrast, the percentage of inclusions with a diameter smaller than 2 µm increased from 31% to 17%.

Table 5. The size distribution of the inclusions in the 1[#]–7[#] steel samples (percentage).

	<1 μm	1–2 μm	2–5 μm	5–10 μm	10–15 μm	>15 μm
1 [#]	2	18	41	26	7	6
2 [#]	3	22	41	23	6	5
3 [#]	5	24	44	21	4	2
4 [#]	7	26	44	19	3	1
5 [#]	6	25	45	18	4	2
2 [#]	3	22	41	23	6	5
6 [#]	2	18	40	24	10	6
7 [#]	1	16	38	26	11	8

3.2. Composition and Morphology of Typical Inclusions

SEM-EDS was selected to analyze the composition and morphology of the inclusions. Several randomly selected inclusions were tested and analyzed regarding the composition of the inclusions. The mapping method of typical composite inclusions was carried out to accurately analyze the elemental distribution and structure of the structural inclusions. According to the results, four kinds of typical inclusions were observed in the steel samples, namely, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnS}$, MnS , and SiO_2 , as shown in Figure 4.

**Figure 4.** Cont.

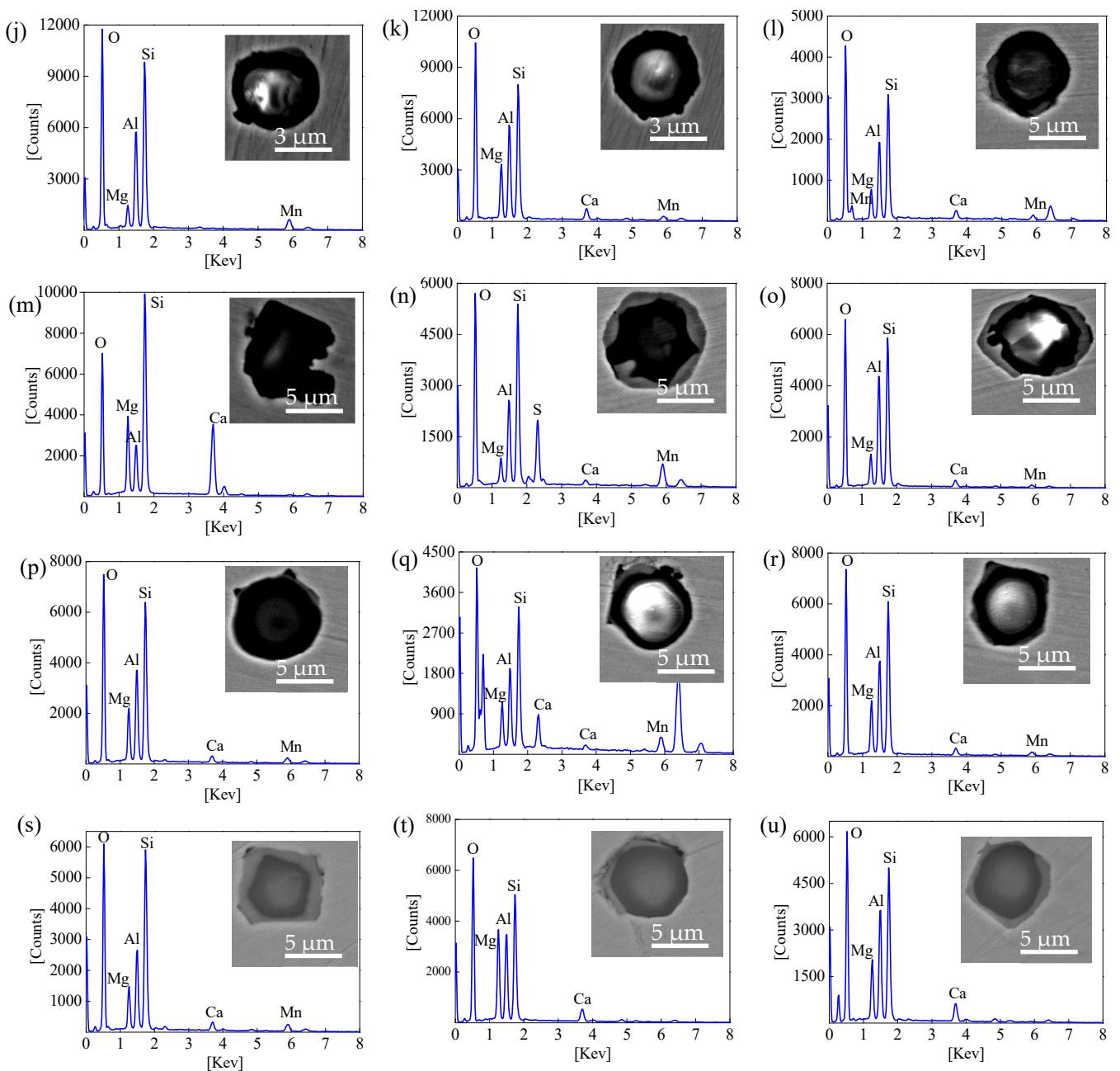


Figure 4. The typical inclusions in steel samples. 1[#]: (a–c); 2[#]: (d–f); 3[#]: (g–i); 4[#]: (j–l); 5[#]: (m–o); 6[#]: (p–r); 7[#]: (s–u).

Most of the compounds contained oxide inclusions, especially the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ inclusions with a diameter of $10\text{ }\mu\text{m}$. The MnS inclusions generally formed during solidification with a diameter larger than $5\text{ }\mu\text{m}$. In contrast, the SiO_2 inclusions had a smaller diameter of approximately $1\text{ }\mu\text{m}$.

The multi-component composite inclusions were generally uniform; that is, the elements in the inclusions were evenly distributed in the whole inclusion without delamination, as shown in Figure 5. Generally, these inclusions would not cause obvious harm to spring steel. In addition, the structure of the layered composite inclusions was usually a homogeneous composite with a layer of MnS inclusions wrapped around the edges. This kind of inclusion will be separated during the hot rolling and cold drawing of spring steel due to the composition and plasticity of the inner and outer layers being different; they would appear as long strips along the rolling direction or drawing direction.

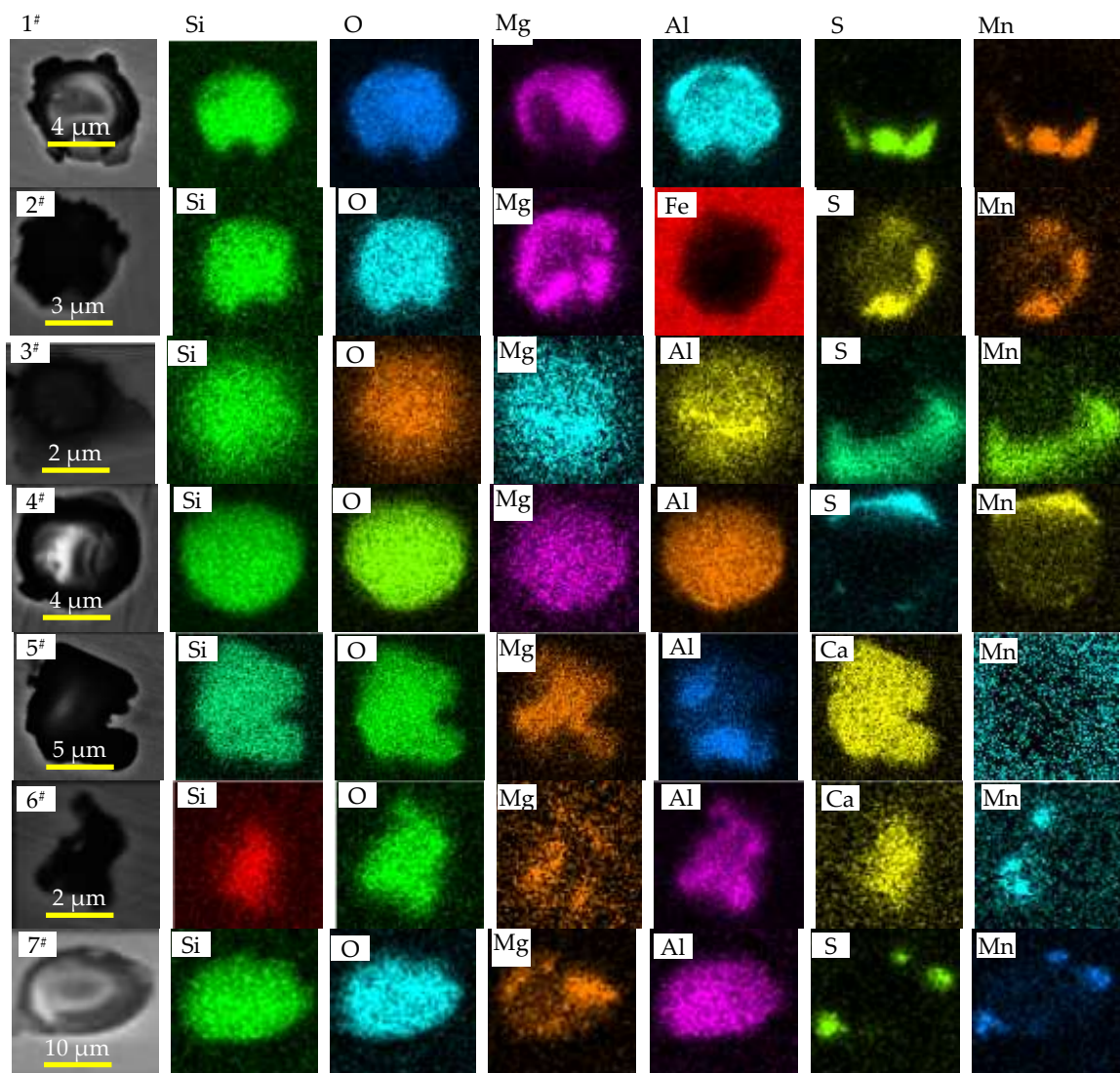


Figure 5. Elemental mapping of inclusions in steel samples.

3.3. Composition Distribution of Typical Inclusions

The composition distribution of inclusions overlaid on a phase diagram with different Al_2O_3 contents and different basicities in the refining slag are shown in Figures 6 and 7, respectively. The “small symbols” are the compositions of each inclusion in a ternary phase diagram, and the “colored square” is the average composition of all the inclusions in the 1[#]~7[#] steel samples. The detail composition of typical inclusions in samples were shows in Table 6.

Figure 6 shows that the content of $\text{Al}_2\text{O}_3(\text{inc})$ in the inclusions and aluminosilicate inclusions had a tendency of increasing with the content of $\text{Al}_2\text{O}_3(\text{slag})$ increasing in the slag. The compound oxide inclusions were mainly concentrated in low-melting-point regions for all of the steel samples. In detail, the average contents of inclusions were $\text{SiO}_2(\text{inc})$: 48.27%, $\text{CaO}(\text{inc})+\text{MgO}(\text{inc})$: 34.39%, $\text{Al}_2\text{O}_3(\text{inc})$: 17.34%; $\text{SiO}_2(\text{inc})$: 48.87%, $\text{CaO}(\text{inc})+\text{MgO}(\text{inc})$: 30.01%, $\text{Al}_2\text{O}_3(\text{inc})$: 21.12%; $\text{SiO}_2(\text{inc})$: 53.46%, $\text{CaO}(\text{inc})+\text{MgO}(\text{inc})$: 17.44%, $\text{Al}_2\text{O}_3(\text{inc})$: 29.10%, $\text{SiO}_2(\text{inc})$: 49.63%, $\text{CaO}(\text{inc})+\text{MgO}(\text{inc})$: 18.40% and $\text{Al}_2\text{O}_3(\text{inc})$: 31.97%.

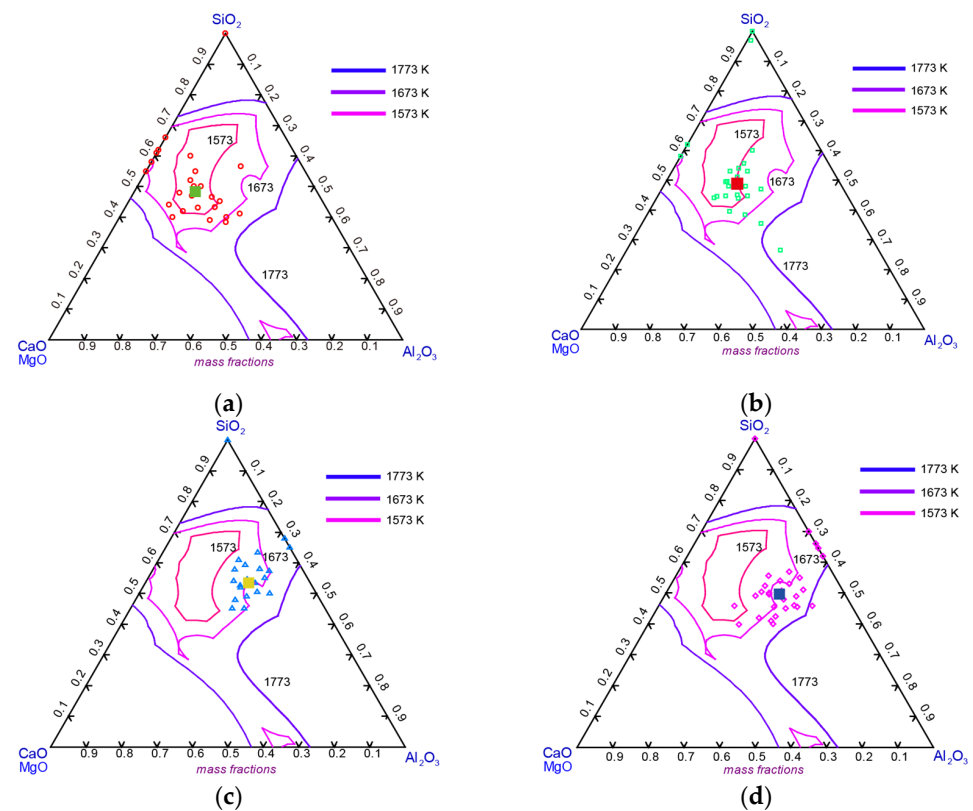


Figure 6. Inclusion distribution overlaid on a phase diagram with the refining slags at fixed Al_2O_3 contents of (a) 3 wt.%, (b) 5 wt.%, (c) 8 wt.% and (d) 12 wt.%.

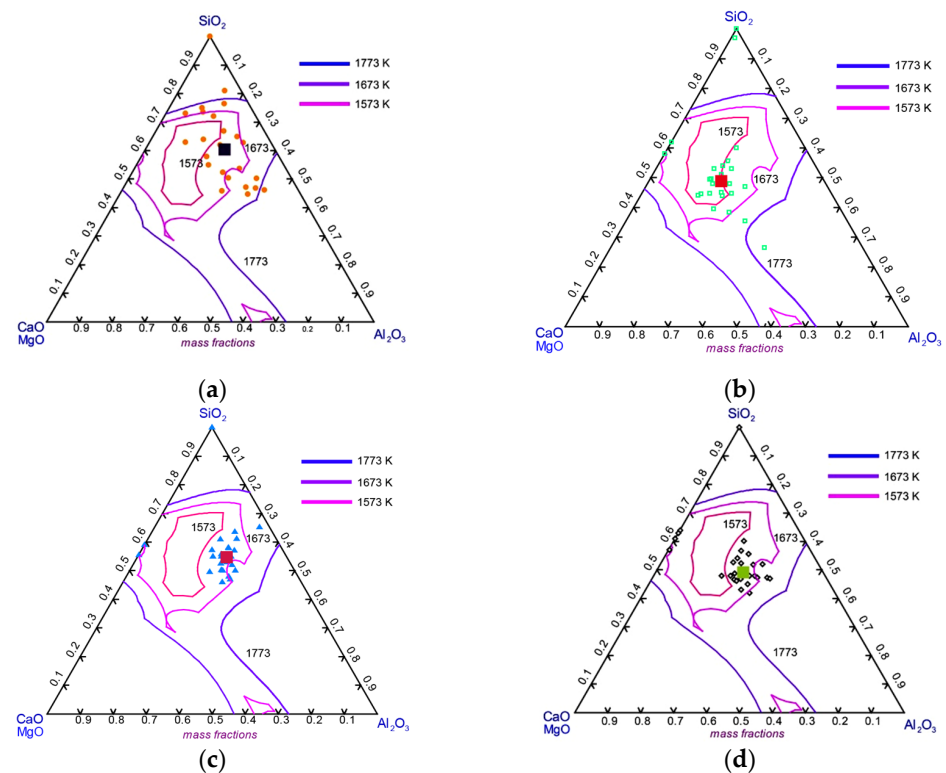


Figure 7. Inclusion distribution overlaid on a phase diagram with the refining slags with different basicities of (a) 0.5, (b) 0.8, (c) 1.0 and (d) 1.2.

Table 6. Chemical compositions of typical inclusions in the experimental steel samples (mass fraction, %).

Exp.	No.	Size (μm)	CaO	Al ₂ O ₃	SiO ₂	MgO	MnO
1 [#] (3wt.% Al ₂ O ₃ , R = 0.8)	1	5.7	3	28	35	19	15
	2	6.3	1	30	40	28	1
	3	4.8	4	21	43	32	0
	4	7.1	1	30	37	29	3
	5	6.5	8	26	45	21	0
	6	2.3	5	23	51	11	10
	7	4.2	8	25	43	24	0
2 [#] (5wt.% Al ₂ O ₃ , R = 0.8)	1	3.3	15	21	38	13	13
	2	2.9	4	45	27	24	0
	3	5.8	1	31	32	26	10
	4	7.6	4	15	25	21	35
	5	4.7	10	17	43	27	3
	6	4.1	8	15	40	27	10
	7	4.2	4	20	45	31	0
3 [#] (8wt.% Al ₂ O ₃ , R = 0.8)	1	5.2	2	18	44	5	31
	2	6.6	2	24	46	6	22
	3	4.3	2	24	54	7	13
	4	2.8	6	31	49	12	2
	5	4.7	5	26	40	13	16
	6	5.2	3	27	51	9	10
	7	6.7	2	23	57	6	12
4 [#] (12 wt.% Al ₂ O ₃ , R = 0.8)	1	3.7	0	26	56	5	13
	2	4.6	6	26	49	12	7
	3	4.1	5	29	50	16	0
	4	6.3	3	25	40	16	16
	5	5.5	2	23	33	13	29
	6	3.7	5	27	52	8	8
	7	4.3	3	31	49	11	6
5 [#] (5 wt.% Al ₂ O ₃ , R = 0.5)	1	5.6	2	19	49	5	25
	2	4.2	1	26	34	6	33
	3	2.9	1	19	41	5	34
	4	4.7	1	24	26	5	44
	5	4.4	3	27	40	7	23
	6	5.1	2	20	33	6	39
	7	6.0	2	35	44	9	10
6 [#] (5 wt.% Al ₂ O ₃ , R = 1.0)	1	5.2	2	24	50	0	24
	2	6.0	4	25	51	12	8
	3	4.9	4	24	53	10	9
	4	4.1	1	27	53	16	3
	5	3.8	3	25	55	10	7
	6	2.6	1	19	38	6	36
	7	5.5	4	22	53	9	12
7 [#] (5 wt.% Al ₂ O ₃ , R = 1.2)	1	3.3	1	21	52	24	2
	2	4.7	9	22	44	16	9
	3	5.8	6	27	50	13	4
	4	2.8	1	20	29	9	41
	5	6.0	12	22	48	10	8
	6	4.6	3	18	52	9	18
	7	2.7	3	25	47	25	0

Figure 7 shows that most inclusions were located in the low-melting-point region, the inclusions distribution was dispersed in the 5[#] steel sample with a basicity of 0.5 in the slag, and the inclusions distribution was concentrated in the 2[#], 6[#] and 7[#] steel samples with basicities of 0.8, 1.0 and 1.2 in the slag, respectively. In detail, the average contents of inclusions in these steel samples were SiO_{2(inc)}: 60.26%, CaO_(inc)+MgO_(inc): 15.49%,

$\text{Al}_2\text{O}_{3(\text{inc})}$: 24.25%; $\text{SiO}_{2(\text{inc})}$: 48.87%, $\text{CaO}_{(\text{inc})}+\text{MgO}_{(\text{inc})}$: 30.01%, $\text{Al}_2\text{O}_{3(\text{inc})}$: 21.12%; $\text{SiO}_{2(\text{inc})}$: 54.56%, $\text{CaO}_{(\text{inc})}+\text{MgO}_{(\text{inc})}$: 18.27%, $\text{Al}_2\text{O}_{3(\text{inc})}$: 27.17%, $\text{SiO}_{2(\text{inc})}$: 49.06%, $\text{CaO}_{(\text{inc})}+\text{MgO}_{(\text{inc})}$: 24.34% and $\text{Al}_2\text{O}_{3(\text{inc})}$: 26.60%.

3.4. Mechanical Properties of the Experiment Steels

The mechanical properties of the experimental steels are shown in Table 7. It is obvious that the tensile strength gradually increased from 1357.83 MPa to 1437.04 MPa as the content of Al_2O_3 in the slag increased from 3 wt.% (1[#]) to 12 wt.% (4[#]). In contrast, the reduction in area and elongation slightly decreased from 27.58% and 10.24% to 24.31% and 9.36%, respectively.

Table 7. Mechanical properties of the experiment steels.

No.	1 [#]	2 [#]	3 [#]	4 [#]	5 [#]	2 [#]	6 [#]	7 [#]
R_m (MPa)	1357.83	1390.64	1397.40	1437.04	1442.12	1390.64	1386.41	1367.84
Ψ (%)	27.58	25.52	25.24	24.31	24.23	25.52	25.78	27.32
δ (%)	10.24	9.60	9.56	9.36	9.32	9.60	9.63	9.96

The fracture morphologies are shown in Figure 8. From the macroscopic appearance of the fractures, the fractures of the four samples were typically cup-shaped and were divided into a fiber area, radiation area and shear lip area from the center to the edge. The radiation areas of the fractures of samples 1[#] and 2[#] were relatively flat, and there were few secondary microcracks, showing certain brittle fracture characteristics. In particular, many long and deep but directionless cracks appeared in the radiation area of sample 1[#], as shown in the white triangle area in the figure. In addition, the area of the radiation area tended to gradually increase; in contrast, the area of the shear lip gradually decreased. Moreover, the shape of the radiation area also gradually changed from an irregular shape and ellipse to a more regular circle. Finally, the number of secondary microcracks in the radiation area of the fracture surface of samples 3[#] and 4[#] significantly increased, radiating from the center to the edge along the radial direction. Furthermore, the length and depth of the secondary crack gradually became more uniform.

Comparing the microstructures of the four steel samples' fractures, it was found that they all contained three kinds of microstructures, namely, secondary microcracks, tear dimples and fine equiaxed dimples. There was no significant difference in the fracture morphology of the four steel samples.

The tensile strength decreased gradually from 1442.12 MPa to 1367.84 MPa as the basicity of slag increased from 0.5 (5[#]) to 1.2 (7[#]). In contrast, the reduction in area and elongation slightly increased from 24.23% to 27.32% and from 9.36% to 9.96%, respectively.

The fracture morphologies of samples 5[#], 2[#], 6[#] and 7[#] are shown in Figure 9. By comparing the macro morphology of these four samples, it can be seen that all the fracture morphologies were typical cup-shaped vertebrae, which was their common point. The 5[#] sample had the largest radiation area, and the shape tended to be a regular circle. Secondary microcracks with high density were evenly distributed in the radiation area. This indicated that the sample's structure was relatively uniform. The radiation area of sample 2[#] was an irregular oval with a small area. In contrast, the shear lip area was large. Moreover, the fracturing of the 2[#] sample was relatively flat, with only a small number of secondary cracks, which generally presented the characteristics of brittle fracture. The fiber area at the fracture of the 6[#] sample was near the center of the circle, and the shape of the radiation area was a regular circle with a large area. The regularity of the fracture morphology of sample 7[#] was the worst, where the fiber area was far away from the center of the circle, the morphology of the radiation area was irregular, and the radiation area was very uneven with a large number and distribution of long and deep cracks. In addition, the area of the shear lip was large.

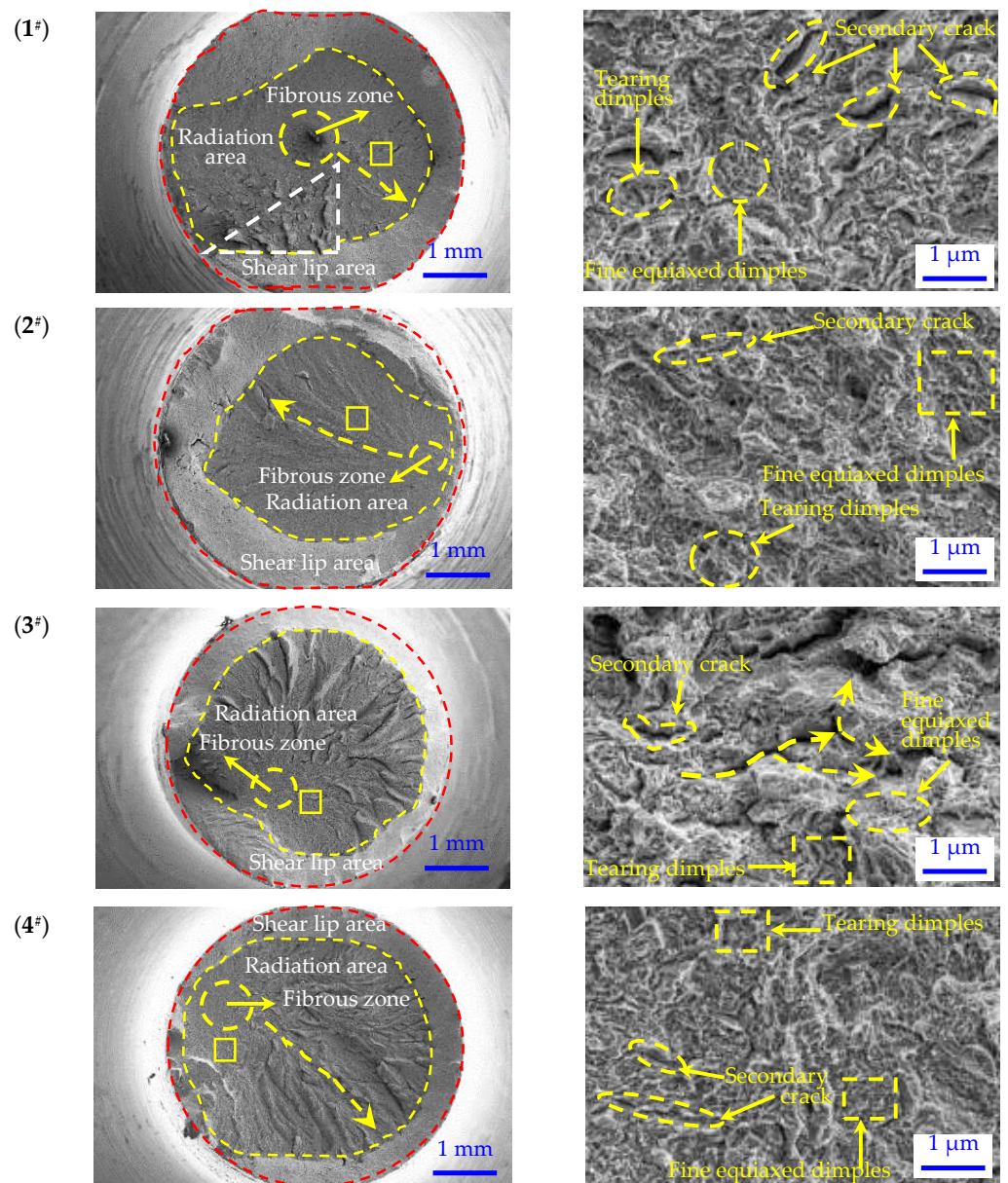


Figure 8. Micro and macro fracture morphologies of the steel samples.

When comparing the microstructures of the four steel samples' fractures, it was found that they all contained three kinds of microstructures, namely, secondary microcracks, tear dimples and fine equiaxed dimples. With the increase in alkalinity, the microstructure at the fracture surface of the samples changed greatly: the number and size of secondary microcracks gradually increased, there were high-density large and deep holes in the fracture of the 6[#] sample (these holes were likely caused by large hard inclusions), and there were not only large and deep holes but also many cleavage planes at the fracture of sample 7[#].

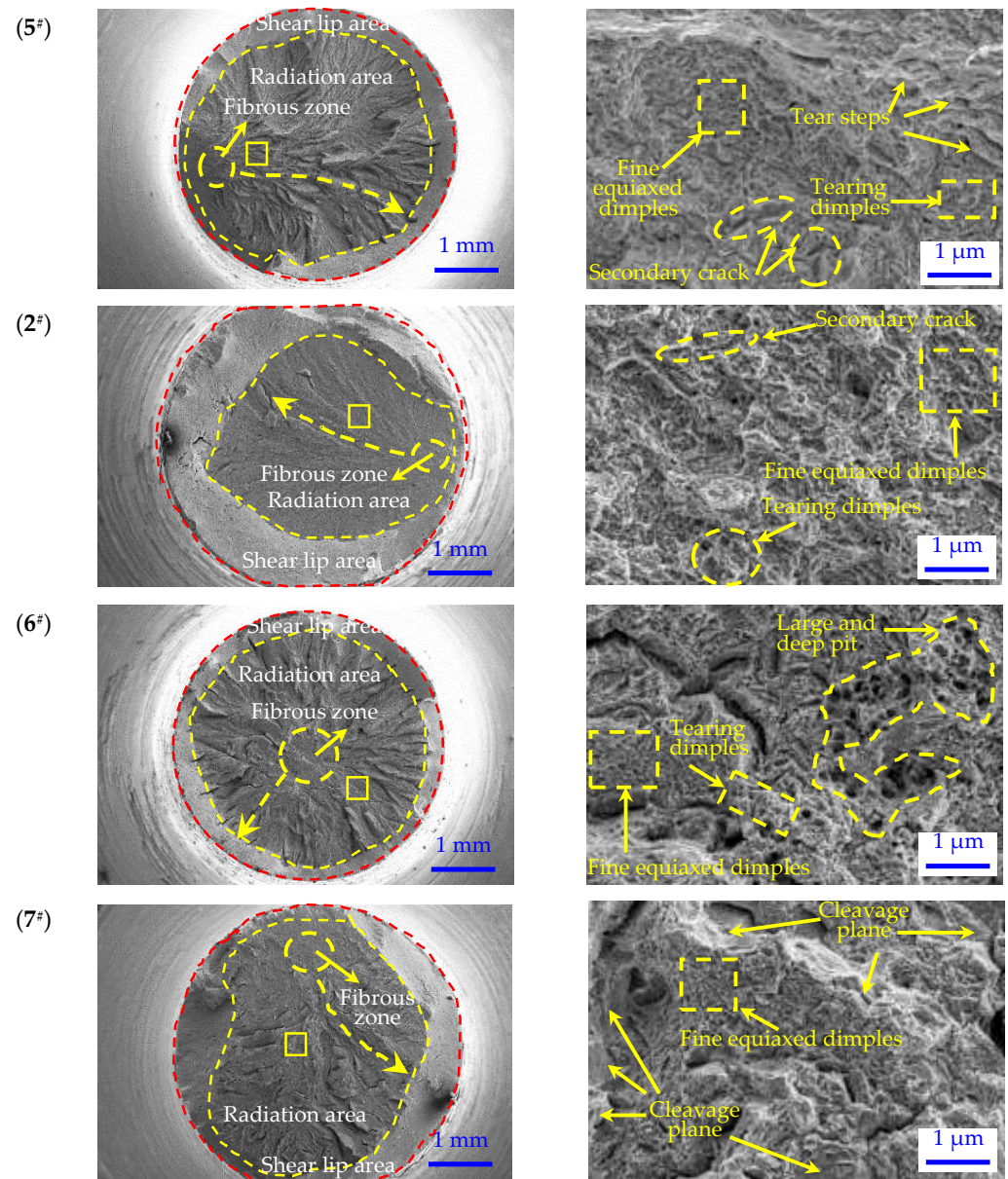


Figure 9. Micro and macro fracture morphologies of the steel samples.

3.5. Thermodynamic Calculations of Isoactivity Lines

The calculation of the component activity of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ (10 wt.%) quaternary inclusion system was mainly completed by the phase diagram module in Fact-sage software. This part mainly calculated the isoactivity lines of CaO , SiO_2 and Al_2O_3 when the reaction reached equilibrium at 1873 K. The results are shown in Figure 10. It was obvious that the value of a_{SiO_2} decreased sharply from 0.7 to 0.02 as the value of R gradually increased. In contrast, the values of a_{CaO} and $a_{\text{Al}_2\text{O}_3}$ increased from 0.00001 to 0.01 and from 0 to 0.05, respectively. Within the low-melting-point zone, the value of a_{SiO_2} was one order of magnitude larger than that of a_{CaO} , which meant that the content of SiO_2 in the generated inclusions was significantly higher than that of CaO , which was consistent with the experimental results.

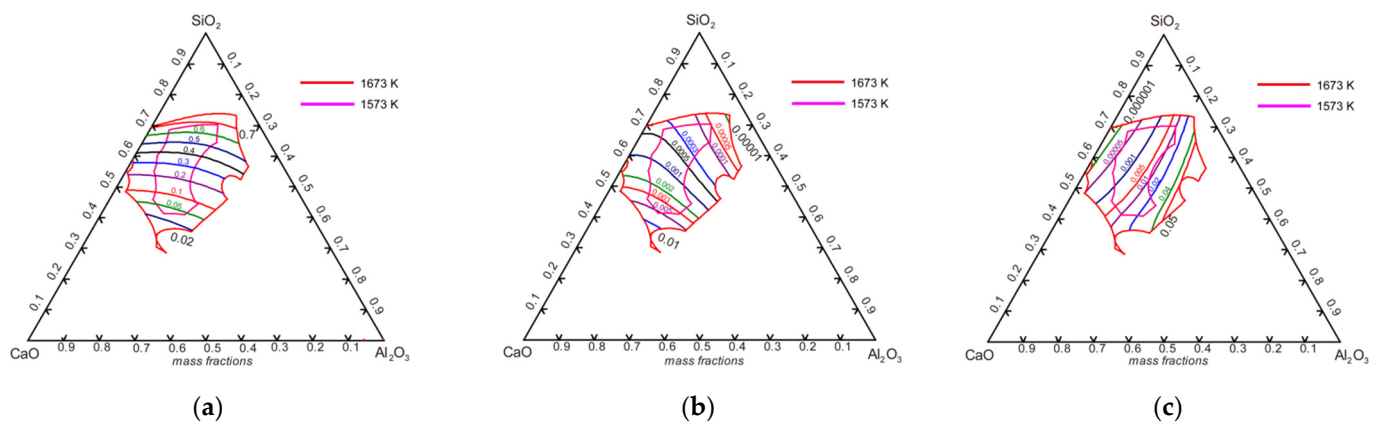


Figure 10. The isoactivity lines of SiO_2 , CaO and Al_2O_3 at 1873 K: (a) SiO_2 ; (b) CaO ; (c) Al_2O_3 .

The contents of [O] and [Al] in steel have an important influence on the number, size and morphology of inclusions. Too high of a content of [O] will produce a large number of oxide inclusions and too high of a content of [Al] will produce brittle and hard inclusions with edges and corners, such as Al_2O_3 and $\text{MgO} \cdot \text{Al}_2\text{O}_3$, which will seriously endanger the mechanical properties of spring steel. Therefore, the isooxygen (Iso-[O]) line and isoaluminum (Iso-[Al]) line were calculated to determine the ranges of [O] and [Al] contents where low-melting-point inclusions were formed.

The Equilib module and Phase Diagram module in Fact-sage software were used to calculate the Iso-[O] line and Iso-[Al] line when the 55SiCr molten steel was in equilibrium with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ quaternary inclusions. The chemical composition of 55SiCr steel is shown in Table 1. The activity coefficients of C, Si, Mn, Cr, Ni, V, Al, O, S, P and other elements were mainly used in the calculation. The activity coefficients f_i of each element can be calculated according to Equation (1).

$$\lg f_i = \sum e_i^j [\%j] \quad (1)$$

where f_i is the activity coefficient of element i and e_i^j is the interaction coefficient of element j with i , as shown in Table 8.

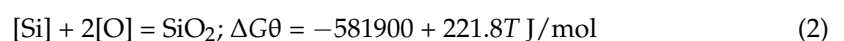
Table 8. Interaction coefficients of elements in molten steel at 1873 K [25].

$i \backslash j$	Al	Si	Mn	O	P	S	C	Cr	V	Ni
Al	0.043 [26]	0.0056	0.0065	−1.867 [27]	0.0033	0.030	0.091	0.0120	/	−0.017
Si	0.058	0.1100	0.0020	−0.230 [28]	0.1100	0.056	0.180	0.0003	0.025	0.005
O	−3.900 [29]	−0.1310	−0.0210	−0.200	0.0700	0.133	0.450	0.0459	−0.300	0.006

(1) The isooxygen (Iso-[O]) line

The chemical reaction of [Si] and [O] in molten steel is shown in Equation (2) [25] and Equation (3) can be derived from it.

The activity value of SiO_2 in Figure 10 and the relevant data in Tables 1 and 6 were substituted into Equation (3) to calculate the isooxygen (Iso-[O]) line of 55SiCr molten steel and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ quaternary inclusions in molten steel at 1873 K. The results are shown in Figure 11a. It was obvious that the oxygen content in the low-melting-point region near the calcline in the phase diagram was 0.0015 wt.%~0.0085 wt.%, with a large controllable range.



$$[\%O] = \left(\frac{a_{\text{SiO}_2}}{K \times f_{\text{Si}} \times [\%Si] \times f_{\text{O}}^2} \right)^{1/2} \quad (3)$$

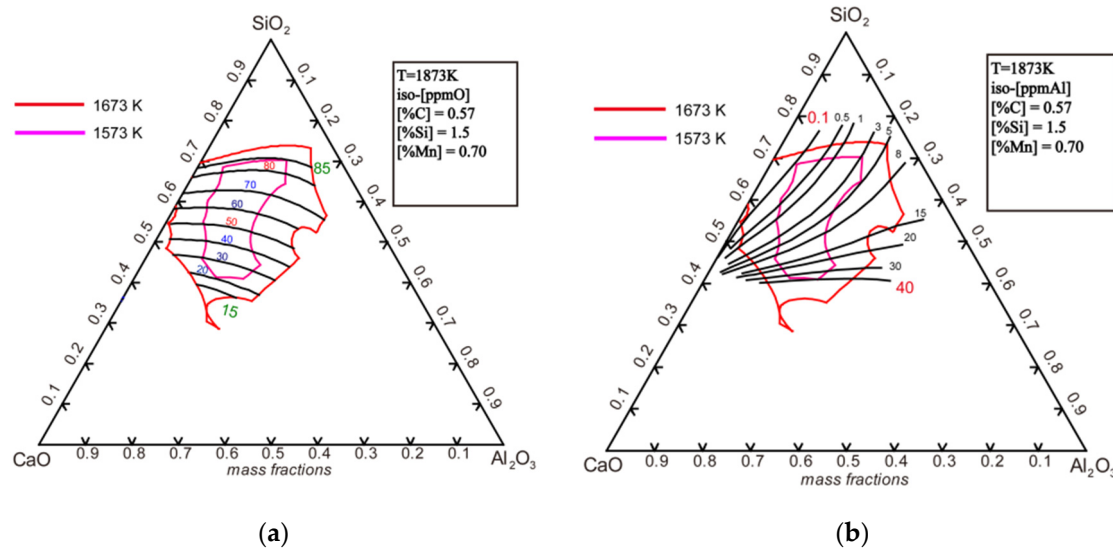
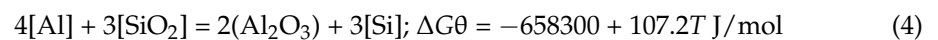


Figure 11. Isoactivity lines of the equilibrium between the molten spring steel 55SiCr and CaO–SiO₂–Al₂O₃–MgO inclusions at 1873 K. (a) Iso-[O] lines and, (b) iso-[Al].

(2) The isoaluminum (Iso-[Al]) line

The chemical reaction of [Al] and [O] in molten steel is shown in Equation (4) [30] and Equation (5) can be derived from it.

The activity value of SiO₂ in Figure 10 and the relevant data in Tables 1 and 6 were substituted into Equation (5) to calculate the isooxygen (Iso-[Al]) line of 55SiCr molten steel and CaO–SiO₂–Al₂O₃–MgO quaternary inclusions in molten steel at 1873 K. The results are shown in Figure 11b. It was obvious that the oxygen content in the low-melting-point region near the calcline in the phase diagram was 0.00001 wt.%~0.0040 wt.%, with a small controllable range. Thus, the content of [Al] in steel needs to be strictly controlled at a very low level in order to obtain low-melting-point inclusions in the smelting process of low alkalinity refining slag combined with silicon deoxidation.



$$[\%Al] = \left(\frac{a_{\text{Al}_2\text{O}_3}^2 \times f_{[\text{Si}]}^3 \times [\%Si]^3}{a_{\text{SiO}_2}^2 \times f_{[\text{Al}]}^4 \times K} \right)^{1/4} \quad (5)$$

In this study, the content of T.O in all steels was about 0.0020 wt.% and the content of all [Al] was about 0.0015 wt.%. Therefore, the inclusions in all of the group steels can be controlled in the low-melting-point region, which is consistent with the actual test results.

For the group made up of the 1[#]–4[#] steels, the compositions of inclusions were consistent with those of refining slag when the three phases of steel–slag–inclusion reached equilibrium. Therefore, the content of [Al]s in the molten steel and the Al₂O₃ content of inclusions in steel increased gradually as the Al₂O₃ content in the slag gradually increased.

For the group made up of the 5[#], 2[#], 6[#] and 7[#] steels, the activity of SiO₂ gradually decreased with the increasing alkalinity of the slag, which inhibited the progress of the reaction shown in Equation (4); as a result, the T.O content and the total number of inclusions in steel decreased gradually. In addition, the content of CaO in inclusions increased gradually with the basicity of slag gradually increasing due to the composition of inclusions

being consistent with that of refining slag when the three phases of steel–slag–inclusion reached equilibrium.

3.6. Influence of Al_2O_3 Content and Basicity on the Viscosity and Structure of the Slag

Increasing the Al_2O_3 content and basicity in the refining slag had an obvious impact on the thermochemical and thermophysical properties of the slag, including their structure, viscosity and surface tension [31,32]. The effect of Al_2O_3 content and basicity on the viscosity of the slag at different temperatures was studied using a viscometer and the results are shown in Figure 12.

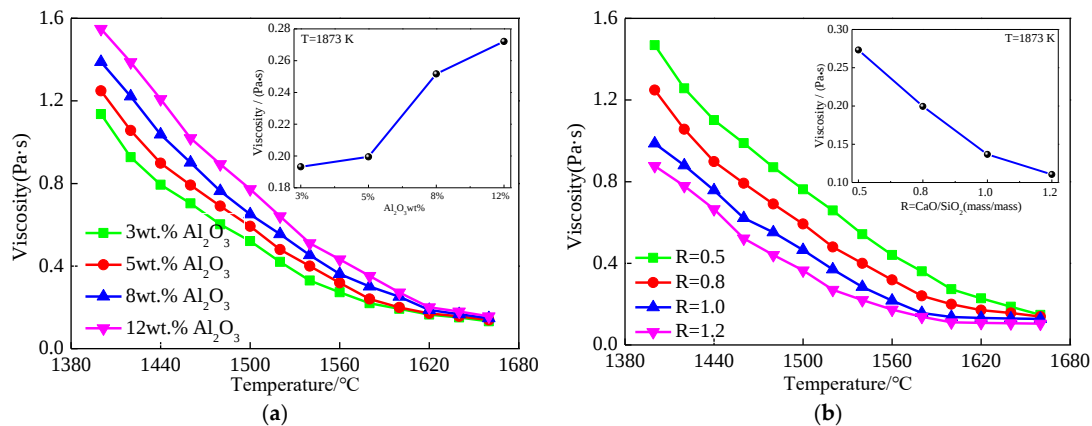


Figure 12. Effect of Al_2O_3 content and basicity in the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ slag on the viscosity of the slag at 1873 K. (a) Al_2O_3 content ranging from 3 wt.% to 12 wt.%; (b) basicity ranging from 0.5 to 1.2.

It was obvious that the viscosity of the slag increased gradually with the increase in the Al_2O_3 content. In contrast, the viscosity of the slag gradually decreased with the increase in basicity. In addition, the viscosity of the slag increased sharply as the temperature gently decreased. The change in slag viscosity was caused by the significant change in its microstructure.

The network structure of slag is shown in Figure 13. The viscosity of slag is often indirectly characterized by the degree of polymerization of the network structure, and the viscosity increases with the increase in the degree of polymerization.

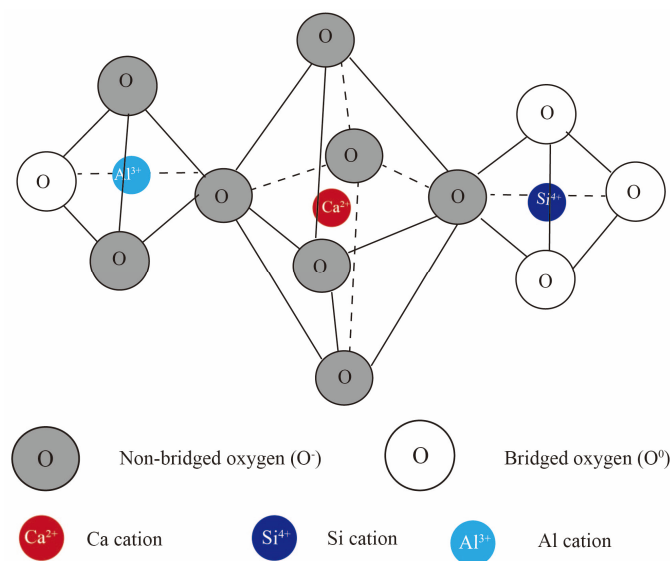


Figure 13. Schematic diagram of the molten slag structure.

In order to research the relationship between the structure and composition of molten slag, the molten slag quenched in water was further analyzed by using FTIR. Characteristic transmittance peaks in the FTIR spectra for silicate systems were observed in the wavenumber region between 1200 and 400 cm^{-1} [33]. In detail, the band group of Si-O bonds existed between 1030 and 750 cm^{-1} , which corresponds to NBO (non-bridging oxygen) of 1 to 4 [34]. The band group shown in the range of 750–630 cm^{-1} was related to the asymmetric stretching vibration of $[\text{AlO}_4]^{5-}$ tetrahedral units, and the trough near 500 cm^{-1} indicates Si-O-Al bending.

Figure 14 shows the effect of Al_2O_3 and basicity on the FTIR transmittance spectra of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-10 wt\% MgO}$ slag. As can be seen in Figure 14a, the transmittance trough for the $[\text{AlO}_4]^{5-}$ tetrahedral stretching for wavenumbers of 750–630 cm^{-1} became deeper and more pronounced with the increase in Al_2O_3 content. This suggested the occurrence of the polymerization of complex aluminate structures using the tetrahedral $[\text{AlO}_4]^{5-}$ structural units with higher Al_2O_3 . In addition, the Si-O-Al bending trough moved to higher wavenumbers, which suggested that the distance between Si/Al and O became shorter, i.e., the network structure was polymerized, as proposed by Badger's rule [35]. Moreover, the trough of the $[\text{SiO}_4]^{4-}$ tetrahedral band group experienced only a small change, which means that, in this experiment, Al_2O_3 content had little effect on the $[\text{SiO}_4]^{4-}$ tetrahedral structure. This showed that the amount of complex silicate structures increased. These results correlated well with the viscosity measurements.

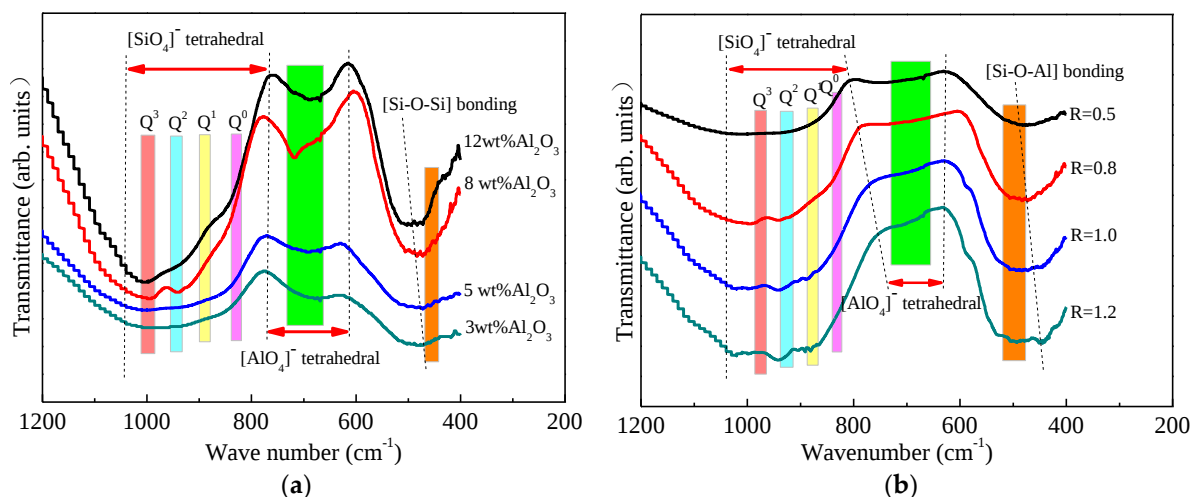


Figure 14. Effect of Al_2O_3 and basicity on the FTIR transmittance spectra of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-10 wt\% MgO}$ slag (a) at a fixed Al_2O_3 content and (b) at different basicities.

As can be seen from Figure 14b, the lower limit of the $[\text{SiO}_4]^{4-}$ tetrahedral bands at about 1030–750 cm^{-1} shifted to a lower wavenumber from about 790 to 750 cm^{-1} with an increase in the basicity of the slag from 0.5 to 1.2. Furthermore, the broadening of the width of the $[\text{SiO}_4]^{4-}$ tetrahedral bands suggested an increase in distance between the Si and O. This shows that the silicate network structures in the slag melt were depolymerized with an increase in the basicity of the slag. In addition, the trough of the $[\text{AlO}_4]^{5-}$ tetrahedral bands at about 750–630 cm^{-1} dampened with increasing basicity and almost disappeared at the basicity of 1.2 [36,37]. This indicated that the aluminate network structures in the slag melt were also depolymerized with increasing basicity. It seems reasonable to consider that the band groups observed at about 500 cm^{-1} were the Si-O-Al bending vibrations. It can be concluded that further depolymerization of a complex silicate and aluminate network structure occurred at a higher basicity. These results correlated well with the viscosity measurements.

3.7. Removal of Inclusions via the Adsorption of Refining Slag

The physical properties of slag can significantly affect its adsorption and removal of inclusions. The melting point of slag decreased with the increase in Al_2O_3 content, and the fluidity increased, which increased the adsorption capacity of slag to inclusions. In contrast, the viscosity of slag increased with the increase in Al_2O_3 content, which made it more difficult for inclusions to pass through the steel–slag interface. Therefore, the comprehensive effect caused the number of inclusions in the steel gradually decrease before it increased. In addition, the gradual increase in slag viscosity reduced the situation where it was entrapped in molten steel and became foreign inclusions, and thus, the proportion of large-sized inclusions in steel continued to decrease [38–40].

When the viscosity of slag decreased with the increase in slag basicity, it makes it easier for refining slag to be entrapped in molten steel and become foreign inclusions [38–40]. In addition, the fluidity will weaken sharply due to the melting point of slag increasing with the increase in CaO content in slag, resulting in a decrease in its adsorption capacity for inclusions [41]. Therefore, the comprehensive effect is that the percentage of the number of large inclusions in steel increased with the increase in slag basicity.

4. Conclusions

The effects of Al_2O_3 and basicity in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-10 wt.\% MgO}$ system LF refining slag on inclusions removal in 55SiCr spring steel were investigated at 1873 K. The results can be summarized as follows:

- (1) With the Al_2O_3 content increasing from 3 wt.% to 12 wt.%, the number percentage of inclusions with a diameter larger than 5 μm decreased sharply. Furthermore, the quality density of inclusions gradually increased simultaneously.
- (2) In contrast, the opposite pattern was found as the basicity increased from 0.5 to 1.2.
- (3) There were four kinds of typical inclusions in all steel samples, namely, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnS}$, MnS , and SiO_2 . In addition, most of the compound oxide inclusions, especially for $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ inclusions, were concentrated in the low-melting-point region.
- (4) The viscosity of the molten slag gradually increased with the content of Al_2O_3 increasing, which increased the degree of polymerization of the slag network structure, especially the $[\text{AlO}_4]^{5-}$ and $[\text{Si-O-Si}]$ structures. In contrast, the viscosity of molten slag experienced the opposite pattern with the basicity of molten slag increasing. This was due to the fact that Ca^{2+} can significantly reduce the degree of polymerization of a slag network structure, especially the percentages of $[\text{SiO}_4]^{4-}$, $[\text{AlO}_4]^{5-}$ and $[\text{Si-O-Si}]$ network structures.

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