Relationships between sulfur distribution ratio of molten slag and metal and that of tellurium

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Abstract: Molten slag treatment is essential for special steels in the modern steelmaking process. When molten slag is added to molten steel, several chemical reactions between the molten slag and steel take place. One of the main purposes of secondary refining is to control the components of molten steel and this also requires the composition of molten slag to be well controlled. The distribution ratio of molten slag and metal is the index related to the refining and is applied to evaluate the refining ability of the molten slag.

Sulfur is one of the chalcogens which are in group 16 of the periodic table. Since the qualities of steel are strongly affected by sulfur, clarifying the sulfur distribution ratio is important. It is known that sulfur distribution ratio is affected by the basicity of the molten slag and partial pressure of oxygen in the molten steel. Tellurium is also a chalcogen and its thermochemical properties are similar to sulfur but are not so well-known. In this study the tellurium distribution ratio of the molten slag and metal was experimentally estimated and the relationships between sulfur distribution ratio and that of tellurium were clarified.

Experiments were conducted with CaO-SiO_2-Al_2O_3-MgO and CaO-SiO_2-MnO-MgO slags. By using the experimental results, tellurium distribution ratio was estimated by means of the sulfur distribution ratio. The relationship between optical basicity and sulfide capacity had already been reported so that sulfur distribution ratio could be calculated with the molten steel and slag components and temperature. Calculated and observed tellurium distribution ratios were compared and they were in good agreement with each other regardless of slag components and temperature.

Keywords: Distribution ratio, Tellurium, Chalcogen, Optical basicity

1. Introduction

Molten slag treatment is essential for special steels in the modern steelmaking process so characteristics of the molten slag have been reported by many researchers. When molten slag is added to molten steel, several chemical reactions between the molten slag and steel would take place. Each reaction at high temperature is complex and thermodynamics and kinetic models are used to control the composition of the molten steel. The distribution ratio of the molten slag and metal is the index related to the refining. Sulfide, phosphate and nitride capacities in various slag systems are reported [1] and these are used to evaluate their distribution ratio.

Sulfur is one of the chalcogens which are in group 16 of periodic table. The chalcogens are considered as surface-active elements, and for this reason sulfur is added to free-cutting steel to improve its machinability. On the other hand, sulfur is removed from bearing steel because the sulfur degrades the rolling contact fatigue life. Since the qualities of steel are strongly affected by the sulfur, it is important to clarify the sulfur distribution ratio. It is known that the sulfur distribution ratio is affected by the basicity of the molten slag and partial pressure of oxygen in the molten steel. Tellurium is also a chalcogen and its thermochemical properties are similar to sulfur. It is said that tellurium can improve the removal of alumina cluster from molten steel [2] and improve machinability of steel. Tellurium is a common minor component of sulfide ore in copper refining so that various thermodynamic data related to tellurium and copper have been reported [3][4]. However, only a few thermodynamic data related to tellurium and steel have been reported [5][6] so that their thermochemical properties in steel refining are not so well-known.

Thus, sulfur and tellurium distribution ratio of molten slag and metal were experimentally estimated. The experiments were conducted with CaO-SiO_2-Al_2O_3-MgO and CaO-SiO_2-MnO-MgO slags. From the experimental results, tellurium distribution was estimated by means of the sulfur distribution ratio. Optical basicity [7] was used to estimate sulfide capacity. Relationships between the sulfur distribution ratio of molten slag and metal and that of tellurium were summarized as an empirical formula in this paper.

2. Experiment

Tellurium added steel experiments under CaO-SiO_2-Al_2O_3-MgO and CaO-SiO_2-MnO-MgO slags were conducted with the same apparatus. Experimental apparatus is shown in Figure 1 and the conditions are shown in Table 1. Molten steel and slag were held in the magnesia crucible and heated by the carbon heater. Premixed flux was added after the steel melted as a synthetic slag. Slag compositions were adjusted as an experimental parameter. Metal and slag compositions are shown in Table 2 and Table 3 respectively. Both metal and slag were stirred by the input of argon gas from the bottom of the crucible. Tellurium was added to the molten steel after the slag had completely melted. The added amount of tellurium was controlled for each experiment. The molten steel and the slag were kept for at least 20 minutes, after which both molten steel and slag samples were taken simultaneously with the steel sampler. Molten steel temperature was measured with the probe at regular intervals in the experiment.

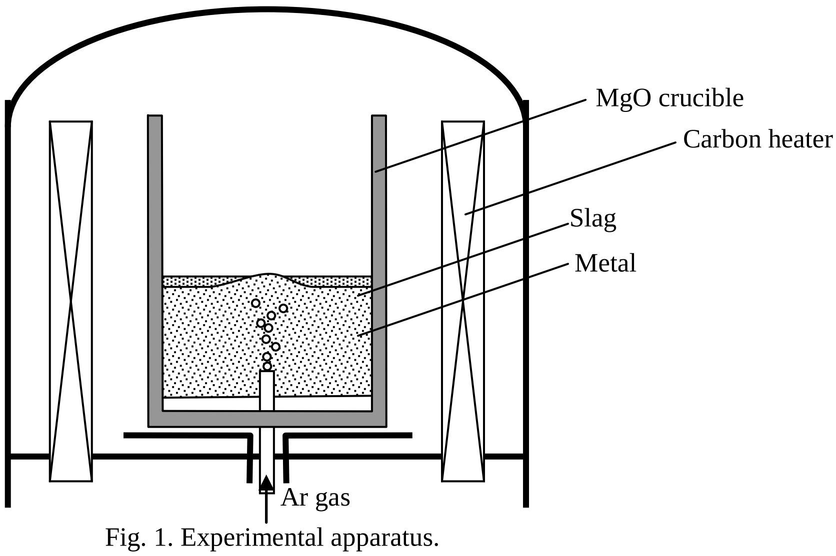

Fig. 1. Experimental apparatus.

Table 1. Experimental condition.

Item	Condition
Temperature	1773, 1823, 1873 (K)
Amount of metal /slag	10.0 / 0.3 (kg)
Stirring	Ar, 101.3 (kPa)
Atmosphere	Ar, 5.0×10^{-6} (m^3/s)

Table 2. Metal compositions (mass %).

C	Si	Mn	S	Te	Fe
0.01~0.95	0.01~0.2	0.4~1.5	0.005~0.5	0.003~0.05	Bulk

Table 3. Slag compositions (mass %).

CaO	SiO_2	Al_2O_3	MnO	MgO
15~45	5~40	5~45	2~35	5~15

3. Results

3.1 Relationships between CaO/SiO_2 ratio and L_{Te} and L_S

Relationships between basicity of slag (CaO/SiO_2 ratio) and distribution of tellurium (L_{Te}) are shown in Figure 2 and relationships between basicity of slag and distribution of sulfur (L_S) are shown in Figure 3. Linear relationships were found in both figures so that the similarity of the thermochemical properties of tellurium and sulfur was experimentally confirmed. However, the individual distributions of tellurium and sulfur against the basicity of slag are dispersed so that it is difficult to describe each distribution with only basicity of slag.

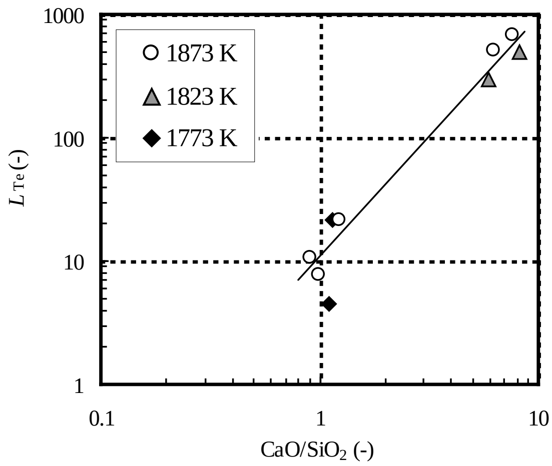

Fig. 2 Relationship between CaO/SiO_2 ratio and distribution of tellurium.

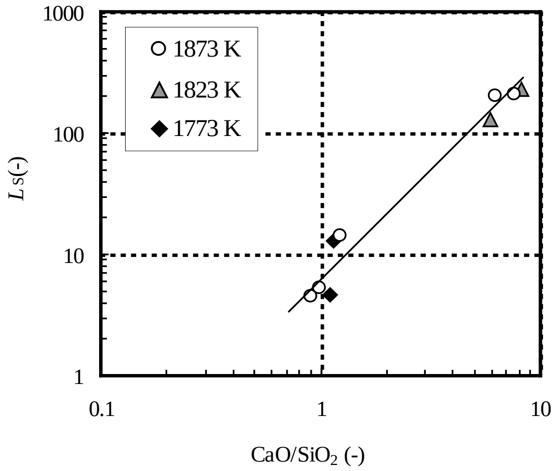

Fig. 3 Relationship between CaO/SiO_2 ratio and distribution of sulfur.

3.2 Relationships between L_S and L_{Te}

Relationships between L_S and L_{Te} are shown in Figure 4. A linear relationship was found regardless of steel grade, components of slag and temperature. From the experimental results, their relationship was formulated with Eq. (1). By using this equation, L_{Te} can be estimated directly if L_S is known.

$L_{Te}=2.19L_S$ ......(1)

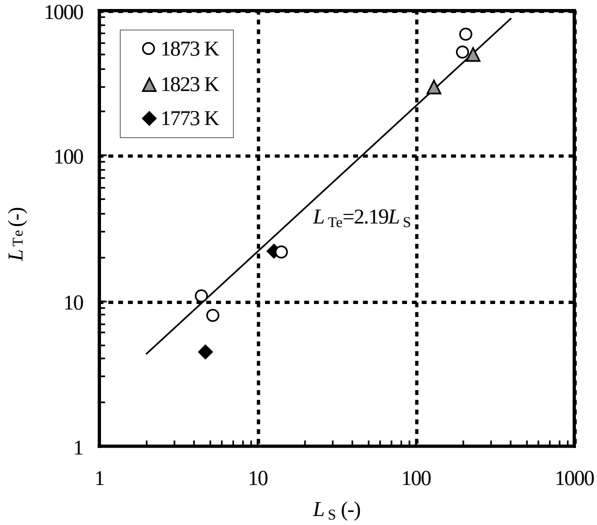

Fig. 4. Relationship between L_S and L_{Te}.

4. Discussion

4.1 Estimation of L_S with optical basicity

Sulfide capacity ($C_{S^{2-}}$) is one of the indexes which show the ability of desulfurization so that the sulfur distribution can be estimated immediately with Eq. (2). Here, a_O is activity of oxygen, f_S is activity coefficient of sulfur and T is temperature of metal.

$$\log L_S = \log C_{S^{2-}} - \log a_O + \log f_S - 465/T + 1.174 \quad \text{......(2)}$$

The estimation method of sulfide capacity by means of optical basicity [7] from the slag compositions and temperature was applied in this study. The relationship between sulfide capacity and optical basicity as a function of temperature was shown with Eq. (3) [8]. Here, Λ is optical basicity of slag and can be calculated with the components of slag through Eq. (4), Eq. (5) and Table 4 [8]. Sulfur was regarded as SO_3 in the slag and tellurium in the slag was not considered because the amount of tellurium in the slag was negligible in this study.

$$\log C_{S^{2-}} = (22690 - 54640\Lambda)/T + 43.6\Lambda - 25.2 \quad \text{......(3)}$$

$$\Lambda = X_A \Lambda_A + X_B \Lambda_B + \cdots \quad \text{......(4)}$$

$$X = \frac{\text{mole fraction of component} \times \text{number of oxygen atoms in oxide molecule}}{\Sigma\ \text{mole fraction of component} \times \text{number of oxygen atoms in oxide molecule}} \quad \text{......(5)}$$

Table 5. Theoretical optical basicity index. [8]

Oxide	CaO	SiO_2	Al_2O_3	MnO	MgO	FeO	SO_3
Λ_{Th}	1.0	0.48	0.61	1.21	0.78	1.03	0.33

Eq. (3) was adjusted as Eq. (6) in this study, to make the relationships show a good agreement with each other. Relationships between optical basicity and sulfide capacity calculated with experimental results and Eq. (6) are shown in Figure 5. They are in good agreement with each other.

$$\log C_{S^{2-}} = (22690 - 54640\Lambda)/T + 43.6\Lambda - 24.92 \quad \text{......(6)}$$

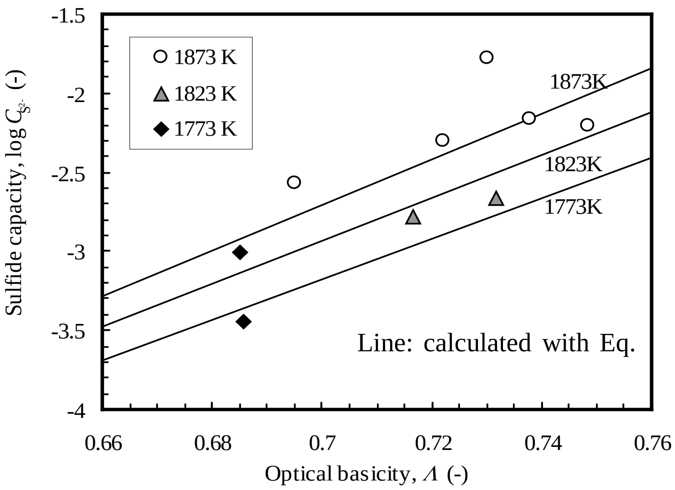

Fig. 5. Relationships between optical basicity and sulfide capacity calculated with Eq. (6).

4.2 Estimation of L_{Te} by means of L_S

L_{Te} was calculated with calculated L_S and Eq. (1). Comparison between calculated and observed L_{Te} is shown in Figure 6. They were in good agreement with each other regardless of steel grade, components of slag and temperature. The similarity of thermochemical properties of sulfur and tellurium was confirmed too because L_{Te} could be described as a function of L_S.

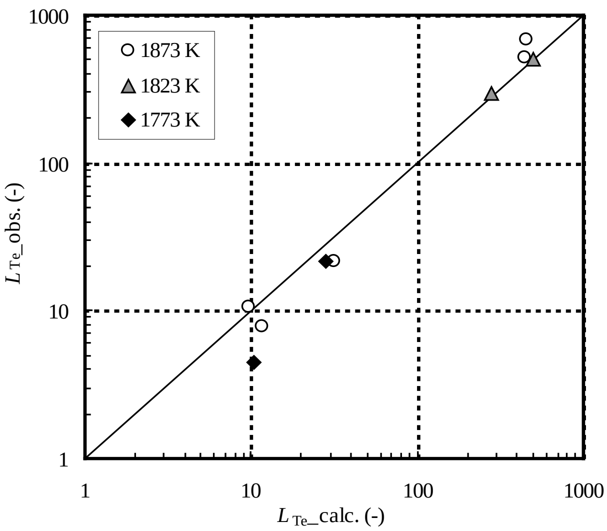

Fig. 6. Comparison between calculated and observed distribution of tellurium.

5. Conclusion

Tellurium added experiments using CaO-SiO_2-Al_2O_3-MgO and CaO-SiO_2-MnO-MgO slags were conducted at 1773, 1823 and 1873 K in magnesia crucible. From the experiments, sulfur and tellurium distribution ratio of molten slag and metal were experimentally estimated. The conclusions are summarized as follows.

1. The similarity of thermochemical properties of tellurium and sulfur was experimentally confirmed.
2. A linear relationship between the distribution ratio of sulfur and that of tellurium was found and their relationship was

formulated as $L_{Te}=2.19L_S$.

3. The distribution ratio of tellurium was estimated by means of the distribution ratio of sulfur which can be calculated as a function of the slag components and temperature using the optical basicity.

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