Thermodynamics of Sulfur in Carbon Saturated Liquid Ferro-alloys Containing Ni, Mo and V at 1 873 K

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The spent catalysts discarded from the petroleum refinery operations contain a substantial amount of valued metals such as Ni, Mo and V together with high sulfur content. Recently, the smelting reduction process of this resource using the carbothermic reaction is being developed and commercialized to recover these metals in the form of carbon saturated ferro-alloys containing Ni, Mo and V. Sulfur can be picked up into alloy melts from the sulfur bearing spent catalysts during the smelting process. Therefore, thermodynamics of sulfur in these alloy melts is very important for producing low sulfur ferro-alloys. In the present study, thermodynamic interactions between those alloying elements and sulfur in liquid iron was studied using the slag/metal equilibration technique at 1 873 K. The equilibrium sulfur distribution was measured between a slag with a known sulfide capacity and carbon saturated liquid Fe–V–Ni–Mo alloys of various compositions. The carbon solubility in liquid alloy was significantly changed with alloy composition. The specific effects of V, Ni and Mo on sulfur was determined by considering the effect of carbon on sulfur using Wagner’s formalism as the first- and second-order interaction parameters as well as the second-order cross-product terms.

KEY WORDS: sulfur; vanadium; nickel; molybdenum; ferro-alloy; spent catalysts.

1. Introduction

Solid spent catalysts from the hydrotreating units of petroleum refining industries are alumina based material and contain metallic constituents of Ni, Mo and V up to 30 mass% in the form of oxides and sulfides with high sulfur content up to 15 mass%. These spent catalysts could be used as a cheap source for valuable metals. Several industrial scale wet processes such as roasting with soda salts, acid leaching and ammonia neutralization have been developed for the recovery of these metals.1,2) However, the roasting process for sulfur removal by oxidation from the catalysts and the leaching processes produce unattractive by-products such as toxic gases, waste water containing strong acids, bases and chlorine etc. which require a high level of environmental precautions and costs. Therefore, recently the pyro-metallurgical process such as an electric arc furnace smelting reduction of spent catalysts have been developed because of its superiority in environmental issues and cost-effectiveness. Alumina in the catalysts can be fluxed with lime to form liquid slags and metallic oxides and sulfides can be recovered in the form of ferro-alloys by the carbothermic reaction. The slag can be used as cement or landfills, and the ferro-alloys can be used extensively in the steel industry.

In this process, one of the main issues is how to keep the sulfur in the slag as much as possible and obtain low sulfur ferro-alloys during the smelting reduction. Therefore, thermodynamic information of sulfur in carbon saturated ferro-alloys of high Ni, Mo and V contents is very important.

In the present study, the sulfur distribution ratio between a CaO–Al2O3 slag of known sulfide capacity and carbon saturated Fe–V, Fe–Ni, Fe–Mo, Fe–V–Ni, Fe–Mo–Ni and Fe–V–Ni–Mo alloy melts was measured at 1 873 K. The carbon solubility in liquid alloy was also determined as a function of alloy composition. Using the Wagner’s interaction parameter formalism (WIPF), the specific effects of V, Ni and Mo on sulfur was determined as the first- and second-order interaction parameters as well as the second-order cross-product terms of two different alloying elements. Using thermodynamic parameters determined in the present study, the sulfur distribution between a smelting slag and ferro-alloy melt of various compositions can be predicted to find out the optimum operational conditions such as slag composition and tolerable sulfur content in spent catalysts for producing low sulfur ferro-alloys.

2. Experimental

The slag-metal equilibration experiments were carried out to measure the sulfur distribution ratio between a CaO–Al2O3 slag and carbon saturated liquid iron alloy melts containing V, Ni and Mo using an electric resistance furnace.
heated by super kanthal (MoSi₂) with an alumina reaction tube (OD: 70 mm, ID: 63 mm, H: 1 100 mm) at 1 873 K as shown in Fig. 1. The reaction temperature was measured by a Pt/Pt-13%Rh thermocouple protected with an alumina tube at the bottom of the crucible, and it was controlled within ±1 K using a PID controller. The temperature reading of the thermocouple was corrected by measuring the temperature inside the crucible using a separate thermocouple prior to experiments.

Two slag compositions of CaO–Al₂O₃ (C/A = 40/60 and 50/50 in mass%) slags containing various sulfur content up to CaS saturation was prepared by melting the reagent grade CaO, Al₂O₃ and CaS in a graphite crucible using a high frequency induction furnace. It was cast onto a steel plate, crushed into powder, and stored in a desiccator until use. The master alloys of Fe-30mass%V-2mass%C-S, Fe-30mass%Mo-2mass%C-S and Fe-40%Ni-2mass%C-S were prepared by melting high purity electrolytic iron, metallic vanadium (99.9% purity), metallic molybdenum (99.95% purity), metallic nickel (99.99% purity), FeS (99.99% purity) and high purity graphite powder in a high purity alumina crucible in an Ar-10%H₂ atmosphere using a high frequency induction furnace. Desired portions of master alloys were charged to make an aimed melt composition for each experiment. Two grams of slag containing 0 to 0.1 mass%S and six grams of alloys containing 0 to 0.1 mass%S were placed in the hole of a graphite crucible. The graphite crucible was tied up by Mo wire and placed in the hot zone of the furnace for 10 hours. The initial sulfur contents in the crucible was measured with an accuracy of ±1 mass ppm using the standard sample of steel containing 7±1 mass ppm sulfur.

3. Results and Discussion

3.1. Thermodynamic Considerations

The sulfur distribution ratio between a slag and liquid iron alloys at equilibrium is defined as

\[ L_S = \frac{[\%S]}{[\%S]} = \frac{([\%S] + [\%C] + [\%V] + [\%M])}{([\%S] + [\%C] + [\%V] + [\%M])} \tag{1} \]

where \([\%S]\) and \([\%S]\) are the equilibrium sulfur content in mass% in slag and metal, respectively, and the sulfur distribution ratio depends on the oxygen partial pressure and the thermodynamic properties of sulfur in slag and metal. The desulfurizing power of a slag can be normalized by the sulfide capacity defined by:

\[ C_S = \frac{([\%S])}{([\%S])} \tag{2} \]

where \(P_{O_2}\) is the oxygen partial pressure at the slag-metal interface, and \(P_{S_2}\) is the partial pressure of sulfur gas in equilibrium with sulfur in liquid iron which can be calculated from the thermochemical data for sulfur in the liquid iron.

\[ \frac{1}{2} S_2(g) = S \tag{3} \]

\[ \Delta G_i = -135 060 + 23.437 [J/mo] \tag{4} \]

\[ K_i = \frac{f_S}{P_{S_2}} \tag{4} \]

where \(f_S\) is the Henrian activity coefficient of sulfur in 1 mass% standard state in liquid iron.

Using Wagner’s formalism,7) the activity coefficient of sulfur in Fe–C–V–Ni–Mo–S alloy melt can be expressed as the following relation using the interaction parameters:

\[ \log f_S = \epsilon_S^I [\%S] + \epsilon_S^I [\%C] + \epsilon_S^C [\%C]^2 \]

\[ + \sum_{i,j} \left( \epsilon_{ij}^I [\%i] + \epsilon_{ij}^C [\%i] [\%j] \right) + \sum_{i,j,k} \epsilon_{ijk}^C [\%i] [\%j] [\%k] \tag{5} \]

where \(\epsilon_S^I\) is the first-order self interaction parameter of sulfur in liquid iron, \(\epsilon_S^I\) and \(\epsilon_C\) are the first- and second-order interaction parameters of elements on sulfur in liquid iron, respectively, and \(\epsilon_{ij}^C\) is the second-order cross-product parameter on sulfur in liquid iron which indicates the simultaneous effect of two different alloying elements (i and j) on the activity coefficient of sulfur in liquid iron.
Ishii and Fuwa\(^9\) determined the value of \(e^S_{\Delta} \) as \(-120/T + 0.018\) in Fe–S melt using the gas-metal equilibration technique at 1 823–2 023 K. Ban-ya and Chipman determined \(e^S_{\Delta} \) and \(r^C_{\Delta} \) values at 1 823–1 923 K in Fe–C–S alloys containing carbon from 0.44 mass% to 5.6 mass% (carbon saturation at 1 923 K) as 0.114 and 0.0058, respectively, using the gas-metal equilibration technique.\(^9\) Their data are the recommended values of the Japan Society for Promotion of Science (JSPS).\(^10\)

Therefore, the sulfide capacity of a slag, \(C^s\), can be obtained from the experimentally measured sulfur distribution between a slag and Fe-C saturated-S melt under a controlled oxygen partial pressure. Conversely, for a given slag composition with a known sulfide capacity, the values of \(f^S\) in Fe-C saturated-S melts (i.e., V, Ni and Mo) can be obtained from the \(L_S\) values measured for these alloy melts.

\[
\log C^s = \log L_S + \frac{1}{2} \log P_O + \log K_1 - \log f^S \quad \text{...... (6)}
\]

where the partial pressure of oxygen, \(P_O\), in equilibrium with carbon \((\alpha_C=1)\) and CO at 1 atm can be obtained from Eq. (7).

\[
C(g) + \frac{1}{2} O_2(g) = CO(g) \\
\Delta G^\circ_T = -114 391 - 85.777 T [J/mol] \quad \text{...... (7)}
\]

### 3.2. Sulfide Capacity of CaO–Al\(_2\)O\(_3\) Slag

The equilibrium sulfur distribution, \(L_S\), between the CaO–Al\(_2\)O\(_3\) slags and Fe-C saturated-S melt was measured at 1 873 K as summarized in Table 1. The \(L_S\) values were obtained by approaching the sulfur equilibrium by transfer of sulfur from slag to metal and metal to slag, and they agree well with each other. Therefore, the sulfide capacity of a slag can be calculated from Eqs. (2) through (7) assuming that the C–CO reaction \((\alpha_C=1, P_{CO}=1\ \text{atm})\) controls the oxygen partial pressure in the system. The \(f^S\) value in Fe-C saturated-S melt at 1 873 K can be calculated by Eq. (5) using the recommended values of \(e^S_{\Delta} , e^C_{\Delta} \) and \(r^C_{\Delta} \) in JSPS\(^10\) as discussed in the preceding section.

In the present study, sulfur content in slag was varied from 0.275 mass% up to CaS saturation values of 1.50 and 2.01 mass% for two different slag compositions as shown in Table 1. The CaS solubility in liquid CaO–Al\(_2\)O\(_3\) slags was separately measured by contacting sintered CaS pellets with liquid slags in a graphite crucible as shown in Fig. 2.

Figure 3 shows the log\(C^s\) values of CaO–Al\(_2\)O\(_3\) slags determined in the present study together with the data reported by other workers as a function of slag composition in CaO–Al\(_2\)O\(_3\) system at 1 873 K. Several authors determined the \(C^s\) values for CaO–Al\(_2\)O\(_3\) slag system by different experimental techniques.\(^11,12\) Banya et al.\(^11\) determined the sulfide capacity of CaO–Al\(_2\)O\(_3\) slag by the gas-slag equilibration technique using a CO–CO\(_2–SO_2–Ar\) gas mixture under the oxygen partial pressures controlled by CO–CO\(_2\) gas mixture at 1 873 K. They kept sulfur content in slag below 0.8 mass% in order to avoid CaS formation which could significantly affect the sulfide capacity of the slag. Ozturk and Turkdogan\(^12\) determined the sulfide capacity of CaS saturated CaO–Al\(_2\)O\(_3\) slag from the equilibrium sulfur distribution between Fe–S–Al–O melts and the slag in contact with pure solid CaS under Ar atmosphere at 1 873 K, assuming that the oxygen partial pressure was controlled by Al–O deoxidation equilibrium in liquid iron.

As shown in Fig. 3, the \(C^s\) value increased linearly with CaO content in slag, and the dissolved sulfur content in slag up to CaS saturation did not affect the sulfide capacity of the slag. The \(C^s\) values determined by the slag/metal equilibration method using Fe-C saturated-S melt in the present study are in excellent agreement with those data determined by different experimental techniques.\(^11,12\) This also confirms that thermodynamics of sulfur in Fe-C saturated-S melt used in the present study is valid.\(^10\)

### Table 1. Experimental \(L_S\) data for CaO–Al\(_2\)O\(_3\) slags and Fe-C saturated-S alloys at 1 873 K.

| Slag composition | Melt composition (mass%) | \(L_S\) | \(\log L_S\) |
|------------------|--------------------------|--------|------------|
| CaO–Al\(_2\)O\(_3\) | [C] 0.40 [S] 0.0006 [S] 0.275 | 458    | 2.66       |
| 40%CaO–60%Al\(_2\)O\(_3\) | [C] 0.40 [S] 0.0006 [S] 0.304 | 507    | 2.71       |
| 50%CaO–50%Al\(_2\)O\(_3\) | [C] 0.40 [S] 0.0031 [S] 1.50 \(^\dagger\) | 484    | 2.68       |

\(^\dagger\): CaS saturation
### 3.3. Thermodynamics of Sulfur in Fe-C<sub>sat</sub>-Ni-Mo-V Melts

Using the sulfide capacity of 40%CaO-60%Al<sub>2</sub>O<sub>3</sub> slag determined in the preceding section, the effect of V, Ni and Mo on sulfur in Fe-C<sub>sat</sub>-i-S (i = V, Ni, Mo) melts can be determined from the sulfur distribution ratios between the slag and those alloy melts under CO atmosphere at 1 873 K.

The experimental results are summarized in Table 2, and the \( L_S \) values are plotted as functions of V, Ni and Mo content in the melt in Fig. 4. Some experiments were carried out using a 40%CaO-60%Al<sub>2</sub>O<sub>3</sub> slag saturated with solid CaS. In this case, the sulfur content in slag was assumed to be 1.50 mass% as determined in the preceding section. The \( L_S \) values increased linearly with increasing Mo and V in the melt, but it decreased with Ni addition. The V, Ni and Mo contents in slag were negligible, therefore the effect of their oxides on sulfide capacity was ignored under the present experimental condition.

The addition of V, Ni or Mo in liquid iron significantly affects the carbon solubility and carbon has a large effect on sulfur in the melt as discussed in the preceding section. Figure 5 shows the variations of carbon solubility in alloy melts as a function of alloy content. Vanadium and molybdenum increase the carbon solubility significantly while nickel decreases it. The solid lines are the calculated carbon solubility values using the parameters determined in the author’s recent study on carbon solubility in Fe–V–Ni–Mo melts.\(^1\) Therefore, using the relation of Eqs. (5) and (6), the specific effect of an alloying element on sulfur in liquid iron can be obtained from the \( L_S \) values measured for Fe-C<sub>sat</sub>-i-S (i = V, Ni, Mo) melts with a 40%CaO-60%Al<sub>2</sub>O<sub>3</sub> slag of the known sulfide capacity value determined in the preceding section.

Combining Eqs. (5) and (6)

\[
\log L_S = \log L_{s} + 1/2 \log P_{O_2} + \log K_1 - \log C_S \quad \ldots \quad (8)
\]

where \( f_S^i \) is the interaction coefficient of V, Ni and Mo on sulfur in liquid iron.

Table 2. Experimental \( L_S \) data for a 40%CaO-60%Al<sub>2</sub>O<sub>3</sub> slag and Fe-C<sub>sat</sub>-i-S alloys at 1 873 K.

| System (Fe-C<sub>sat</sub>-i) | Melt composition (mass%) | \( L_S \) | \( \log L_S \) |
|---------------------------|--------------------------|----------|----------------|
| Fe-C<sub>sat</sub>V       |                          |          |                |
| 9.50                      | 6.61                     | 0.0028   | 1.50\(^1\)     | 536 2.73        |
| 11.3                      | 6.84                     | 0.0026   | 1.50\(^1\)     | 577 2.76        |
| 19.6                      | 7.89                     | 0.0024   | 1.50\(^1\)     | 625 2.80        |
| 25.4                      | 8.63                     | 0.0022   | 1.50\(^1\)     | 682 2.83        |
| 29.0                      | 9.09                     | 0.0020   | 1.50\(^1\)     | 750 2.88        |
| Fe-C<sub>sat</sub>Ni      |                          |          |                |
| 8.91                      | 4.98                     | 0.0008   | 0.348          | 435 2.64        |
| 13.2                      | 4.77                     | 0.0008   | 0.305          | 381 2.58        |
| 13.9                      | 4.74                     | 0.0006   | 0.236          | 393 2.59        |
| 17.4                      | 4.57                     | 0.0008   | 0.275          | 344 2.54        |
| 24.1                      | 4.25                     | 0.0007   | 0.214          | 306 2.49        |
| 24.2                      | 4.24                     | 0.0005   | 0.151          | 302 2.48        |
| 26.4                      | 4.14                     | 0.0010   | 0.301          | 301 2.48        |
| 36.5                      | 3.65                     | 0.0015   | 0.377          | 251 2.40        |
| 16.1                      | 4.64                     | 0.0041   | 1.50\(^1\)     | 366 2.56        |
| 21.3                      | 4.38                     | 0.0043   | 1.50\(^1\)     | 349 2.54        |
| Fe-C<sub>sat</sub>Mo      |                          |          |                |
| 4.76                      | 5.46                     | 0.0006   | 0.338          | 563 2.75        |
| 4.91                      | 5.49                     | 0.0006   | 0.349          | 582 2.77        |
| 8.32                      | 5.54                     | 0.0006   | 0.342          | 570 2.76        |
| 9.19                      | 5.56                     | 0.0005   | 0.315          | 630 2.80        |
| 15.0                      | 5.65                     | 0.0005   | 0.33           | 660 2.82        |
| 15.6                      | 5.66                     | 0.0005   | 0.337          | 674 2.83        |
| 17.9                      | 5.70                     | 0.0004   | 0.305          | 763 2.88        |
| 20.4                      | 5.74                     | 0.0004   | 0.321          | 803 2.91        |
| 24.2                      | 5.80                     | 0.0004   | 0.333          | 833 2.92        |
| 24.2                      | 5.80                     | 0.0004   | 0.324          | 810 2.91        |

\(^1\): CaS saturation

Fig. 4. Sulfur distribution between a 40%CaO-60%Al<sub>2</sub>O<sub>3</sub> slag and Fe-C<sub>sat</sub>-i melts (i = V, Ni, Mo).

Fig. 5. Carbon solubility in Fe–V, Fe–Ni and Fe–Mo melts.
of vanadium in Fe-C sat -S melt apparently increased the \( L_S \) value, and one might expect that vanadium in the melt increase the activity coefficient of sulfur in the melt. However, when the effect of the carbon solubility increase with vanadium addition was considered, the specific effect of vanadium actually decreased the activity coefficient of sulfur in the melt. The first-order interaction parameter of vanadium on sulfur in Fe–V–S system, \( e_S^V \), can be determined as \(-0.019 \pm 0.001\) by the regression analysis of data, and there are no significant second-order effect of vanadium on sulfur up to 29 mass\% V. Banya and Chipman\(^3\) and Ishii et al.\(^4\) determined the effect of V on sulfur in liquid Fe–V–S alloy by the gas-metal equilibration technique using H\(_2–H_2S\) gas mixture, and reported the \( e_S^V \) values as \(-0.016\) and \(-0.019\) at 1 823 K, respectively. Examining their data up to 15 mass\% V and the data determined in the present study, the \( e_S^V \) value in liquid Fe–V–S alloy containing vanadium up to 30 mass\% can be determined as \(-0.019\) in the temperature range from 1 823 to 1 873 K.

Using the same method, the interaction coefficients of Ni and Mo on sulfur in liquid iron were determined from the \( L_S \) values for Fe-C sat -Ni and Fe-C sat -Mo alloy melts as shown in Figs. 7 and 8, respectively. The specific effect of nickel on sulfuration was negligible up to 37 mass\% Ni in Fe-C sat -Ni-S melt, and the value of \( e_S^Ni \) was determined as \(0 \pm 0.0003\) at 1 873 K. Banya and Chipman\(^5\) and Ishii et al.\(^6\) also determined the \( e_S^Ni \) values in Fe–Ni–S system by the gas-metal equilibration technique as \(-0.0009\) and 0, respectively, at 1 823 K. Examining the data up to 15 mass\% V and the data determined in the present study, the \( e_S^V \) value in liquid Fe–V–S alloy containing vanadium up to 30 mass\% can be determined as \(-0.019\) in the temperature range from 1 823 to 1 873 K.

Table 3. Experimental \( L_S \) data for a 40\%CaO-60\%Al\(_2\)O\(_3\) slag and Fe-C sat -V-Ni-Mo-S alloys at 1 873 K.

\[
\begin{array}{cccccc}
\text{System} & \text{Melt composition (mass\%)} & \text{[V]} & \text{[Ni]} & \text{[Mo]} & \text{[C]} & \text{[S]} \\
\text{(Fe-C sat -i-j-k)} & \text{Fe-C sat -V-Ni} & 8.37 & 9.18 & – & 6.03 & 0.0009 & 0.398 & 442 & 2.65 \\
& & 17.2 & 8.86 & – & 7.17 & 0.0008 & 0.379 & 474 & 2.68 \\
& & – & 4.50 & 17.3 & 5.47 & 0.0006 & 0.403 & 672 & 2.83 \\
& Fe-C sat -Mo-Ni & 4.40 & 18.5 & 5.50 & 0.0007 & 0.456 & 651 & 2.81 \\
& & 14.0 & 13.7 & 4.96 & 0.0008 & 0.394 & 493 & 2.69 \\
& Fe-C sat -V-Ni-Mo & 5.00 & 27.8 & 5.20 & 0.0013 & 0.440 & 338 & 2.53 \\
& & 4.70 & 27.3 & 4.90 & 0.0015 & 0.508 & 339 & 2.53 \\
& & 8.20 & 29.0 & 9.00 & 5.20 & 0.0013 & 0.489 & 376 & 2.58 \\
& & 10.1 & 27.1 & 10.2 & 5.55 & 0.0008 & 0.336 & 420 & 2.62 \\
\end{array}
\]
sulfur content in metal sample. This could cause some errors in determining sulfur content in metal samples. Therefore, nickel was added in all experiments since it decreased the \( L_S \) values as shown in Fig. 4.

Using the relations shown in Eqs. (5) and (6), the second-order cross-product parameters on sulfur in liquid iron, \( r_{ij}^S \), can be determined from the experimental results as shown in Fig. 9. For Fe–C sat–V–Ni and Fe–C sat–Mo–Ni melts, it was noted that the cross-product effect of pair alloying elements of V–Ni and Mo–Ni on sulfur was negligible, and therefore the values of \( r_{VN}^S \) and \( r_{NM}^S \) were all determined as 0 at 1 873 K. Then these values were used to determine the \( r_{VM}^S \) value as 0.0003 ± 0.00002 at 1 873 K from the sulfur distribution data for Fe–C sat–V–Ni–Mo melts as shown in Fig. 9(c).

Table 4 summarizes the interaction parameters determined in the present study as well as in other studies.\(^{3,4}\) Therefore, the sulfur distribution between a slag and multicomponent iron alloy melts of Fe–C sat–V–Ni–Mo can be predicted from the sulfide capacity of slag and the interaction parameters of alloying elements on sulfur determined in the present study. Combining Eqs. (5) and (6),

\[
\log L_S = \log C_S - \frac{1}{2} \log P_{O_2} - \log K_S + e_S^V [\% S] + e_S^C [\% C] + r_S^C [\% C]^2 + \sum_{ij \neq V-Ni, Mo} r_{ij}^S [\% i] [\% j] + \sum_{V-Ni, Mo} r_{ij}^S [\% i] [\% j] + \sum_{V-Ni, Mo} r_{ij}^S [\% i] [\% j]
\]

.......................................... (9)

**Table 4. Interaction parameters of V, Ni and Mo on S in liquid iron alloys.**

| Interaction parameters | Value | Temperature (K) | Conc. Range [mass%] | Ref. |
|------------------------|-------|-----------------|----------------------|------|
| \( e_S^V \) V \( : 29 \) | \(-0.019 ± 0.001\) | 1 873 | V \( : 29 \) | Present |
| \( e_S^V \) V \( : 17 \) | \(-0.016\) | 1 823 | V \( : 17 \) | 2 |
| \( e_S^V \) V \( : 11 \) | \(-0.019\) | 1 823 | V \( : 11 \) | 3 |
| \( e_S^Ni \) Ni \( : 37 \) | \(-0.00006\) | 1 823 | Ni \( : 37 \) | Present |
| \( e_S^Ni \) Ni \( : 50 \) | \(0\) | 1 823 | Ni \( : 50 \) | 2 |
| \( e_S^Ni \) Ni \( : 15 \) | \(0\) | 1 823 | Ni \( : 15 \) | 3 |
| \( e_S^Mo \) Mo \( : 25 \) | \(0.0004 ± 0.0004\) | 1 873 | Mo \( : 25 \) | Present |
| \( e_S^Mo \) Mo \( : 40 \) | \(0.0027\) | 1 823 | Mo \( : 40 \) | 2 |
| \( e_S^Mo \) Mo \( : 20 \) | \(0.0064\) | 1 823 | Mo \( : 20 \) | 3 |
| \( r_S^V \) V \( : 29 \) | \(0\) | 1 873 | V \( : 29 \) | Present |
| \( r_S^Ni \) Ni \( : 37 \) | \(0\) | 1 873 | Ni \( : 37 \) | Present |
| \( r_S^Mo \) Mo \( : 25 \) | \(0\) | 1 873 | Mo \( : 25 \) | Present |
| \( r_{VN}^S \) V \( : 18 \) Ni \( : 29 \) | \(0.0003\) | 1 873 | V \( : 18 \) Ni \( : 29 \) | Present |
| \( r_{NM}^S \) Ni \( : 29 \) Mo \( : 19 \) | \(0.0003\) | 1 873 | Ni \( : 29 \) Mo \( : 19 \) | Present |

**Table 5. A typical composition of spent petroleum catalyst.**

| V | Ni | Mo | Al₂O₃ | S |
|---|----|----|-------|---|
| 15 | 5  | 3  | 50    | < 15 |

![Fig. 9](image_url)  
Relation of Eq. (5) to determine the value of (a) \( r_{VN}^S \), (b) \( r_{NM}^S \) and (c) \( r_{VM}^S \) in liquid iron.

![Fig. 10](image_url)  
Variation of final sulfur content in Fe-25%V-8%Ni-5%Mo-8%C melt vs. initial (%S) in spent catalyst for different slag compositions at 1 873 K.
Using thermodynamic parameters determined in the present study, a simple material balance calculation can be made to predict the sulfur content in a ferro-alloy melt produced by the smelting reduction of spent petroleum catalysts. A typical composition of spent catalyst is shown in Table 5. Iron and carbon sources and lime can be added to produce a ferro-alloy of Fe-25%V-8%Ni-5%Mo-8%C and CaO-Al₂O₃ slags of various compositions (C/A = 35/65 ~ 50/50). Figure 10 shows the variation of final sulfur content in a ferro-alloy as a function of initial sulfur content in the spent catalyst for different slag compositions. Therefore, the optimum operational parameters such as slag/metal ratio, slag composition and a tolerable sulfur content in spent catalysts can be decided to produce low sulfur ferro-alloys by the smelting reduction process.

4. Conclusions

The interaction parameters of alloying elements on sulfur in liquid Fe-Cₐₚₜ-V-Ni-Mo alloys have been determined from the equilibrium sulfur distribution between a CaO–Al₂O₃ slag and liquid iron alloys of carbon saturated Fe, Fe–V, Fe–Ni, Fe–Mo, Fe–V–Ni, Fe–Mo–Ni and Fe–V–Ni–Mo melts under CO atmosphere at 1 873 K. These parameters could be used to predict the sulfur distribution between a slag and ferro-alloys produced by the smelting reduction process of spent catalysts. The main finding of this study can be summarized as follows.

(1) The first and second-order interaction parameters of vanadium, nickel and molybdenum on sulfur in liquid Fe–V–S, Fe–Ni–S and Fe–Mo–S melts at 1 873 K can be expressed as:

\[ e^V_s = -0.019, r^V_s = 0 \quad (V \leq 29\%) \]
\[ e^N_s = 0, r^N_s = 0 \quad (Ni \leq 37\%) \]
\[ e^Mo_s = 0.0064, r^Mo_s = 0 \quad (Mo \leq 25\%) \]

(2) The second-order cross-product parameters on sulfur in liquid Fe–V–Ni–Mo–S melts at 1 873 K can be expressed as:

\[ r^{V,N}_s = 0 \quad (V \leq 18\%, \ Ni \leq 29\%) \]
\[ r^{V,Mo}_s = 0.0003 \quad (V \leq 18\%, \ Mo \leq 19\%) \]
\[ r^{N,Mo}_s = 0 \quad (Ni \leq 29\%, \ Mo \leq 9\%) \]

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