Solubility Products of VS and NbS in Iron Alloys

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Solubility of sulfur in Fe–V and Fe–Nb alloys was experimentally determined using a diffusion couple technique. Solubility product of VS and NbS in ferrite (α) and austenite (γ) phases were determined as log(mass%V)(mass%S)α = 4.76 − 10 1000/T, log(mass%V)(mass%S)γ = 4.90 − 11 000/T and log(mass%Nb)(mass%S)γ = 4.70 − 10 5000/T in the temperature range from 1523 to 1573 K. A thermodynamic analysis was also carried out to evaluate the formation energy of VS and NbS. The estimated formation energy of VS and NbS are ΔGVSfus = −263 100 + 61.0T (J/mol) and ΔGNbSfus = −260 800 + 68.4T (J/mol), respectively.

KEY WORDS: microalloying steels; solubility of sulfur; niobium sulfide; vanadium sulfide; thermodynamic analysis.

1. Introduction

It is well known that non-metallic inclusions such as oxide, sulfide, carbide and nitride in steels have significant effects on their material properties. During the course of the last decade, the utilization of the inclusions for the control of microstructure have been a subject of considerable interest for improving the mechanical properties of steels.1,2) The precise control of precipitation and dissolution of them is one of the most important factors for controlling the material properties. Phase diagrams are basic information to understand the precipitation and dissolution. In particular, the solubility limit curve in iron corner is very important, which is generally described as solubility product. Information on the solubility product of sulfide in iron alloys is limited to several systems such as MnS,3–5) TiS,6,7) CrS,8,9) although those of carbides and nitrides are well established.10) Experimental solubility products of sulfide in steels is key data to evaluate the thermodynamic properties for database of sulfide in steels.10)

Nb and V are one of the most important microalloying elements in steels to improve the material properties. These elements have a strong chemical affinity for sulfur as well as carbon and nitrogen in iron alloys. Carbon and nitrogen form NbC, NbN, VC and VN with NaCl structure and the solubility product of them were well established.11–14) In the case of sulfur, NbS and VS with the NiAs structure are formed in steels,15) which are also effective to control of the properties of steels.16) However, information on solubility data of sulfur in Fe–V and Fe– Nb alloys is very limited. The solubility limit of sulfur in Fe–10mass%V alloy at 1 273 K was only reported by Josey and Floridis,17) and that of the Fe–Nb alloys could not be found.

The purpose of this study is to examine the solubility limit of sulfur in the solid Fe–V and Fe–Nb alloys in low alloying content region by obtaining iso-activity lines for sulfur through the use of diffusion couple technique. In addition, a thermodynamic analysis on the experimental data has been conducted to estimate the formation energy of VS and NbS.

2. Experimental Procedures

2.1. Materials

High purity Fe (>99.99%), Nb (>99.9%), V (>99.7%) and FeS (>99.9%) were used to prepare samples. At first, the pure metals were melted by an arc-melting furnace to make a button. Then, alloys with various compositions were prepared by a levitation melting with induction furnace under Ar gas to avoid a contamination of impurity from a crucible. Melts of alloys were poured into a copper mold to obtain cylindrical ingots with 15.4 mm in diameter. Typical examples of oxygen, nitrogen and carbon in selected alloy specimens are shown in Table 1.

2.2. Diffusion Couples

Disks of 15.4 mm diameter and 2.3 mm thickness were machined from the ingots and four disks with different composition were pressed by a fastener as shown in Fig. 1. Diffusion couples were prepared by annealing at 1 173 K for 1 h under vacuum (1.5 · 10−8 Pa) with titanium chips to avoid oxidation.

Obtained diffusion couples were annealed in the range from 1 523 to 1 573 K for long time to obtain the equal ac-
tivity state for sulfur throughout the diffusion couple under high purity Ar gas (>99.999%). After the annealing, the diffusion couples were quenched into water. The annealed diffusion couples were then sliced into each disk and cut into small pieces for analysis of niobium, vanadium and sulfur content. The chemical composition for each diffusion couple specimen is shown in Table 2. Further details of the diffusion couple technique can be found elsewhere.14,18)

3. Experimental Results

Figure 2 shows typical experimental results obtained for the iso-activity lines of sulfur in each diffusion couple, where the data on the diffusion couples of No. 1, No. 3 and No. 6 in Table 2 are plotted. The matrix phase of diffusion couple shown in Fig. 2(a) is considered as the ferrite (α) phase at annealing condition, while those in Figs. 2(b) and 2(c) are considered as the austenite (γ) phase from the Fe–M (M: V, Nb) binary alloy phase diagrams.19) The slope of the iso-activity lines is quite different in low and high concentration region. The sulfur content in the disks with high V and Nb content proportionally increases with increasing the V and Nb content. These facts suggest that the sulfide might be precipitated in the disks with high alloying elements. FeS could be dissolved in VS and form solid solution (V, Fe)S.15) It is however considered that FeS content in the precipitated sulfide might be negligible small, because the slope of the iso-activity line for sulfur in the α+ VS two-phase region is found to be equal to the molar weight ratio, i.e. \( W_S/W_{V} = 32.065/50.9415 = 0.6294 \), which means that the precipitated sulfide phase is near the stoichiometric VS phase. Therefore, the precipitated sulfide is assumed as the stoichiometric VS and the slope of iso-activity line is drawn as 0.6294 in the two-phase region, as shown in Figs. 2(a) and 2(b).

The activity of sulfur \((a_S)\) in the α and γ single-phase region can be described by the Wagner’s interaction parameters \(e_S^S\) and \(e_S^V\) as follows

\[
\ln a_S = \ln x_S + \ln \gamma_S^\alpha + e_S^S x_S + e_S^V x_V \quad \text{.........(1)}
\]

| Specimens | mass%M | mass%S | mass%C | mass%Mn | mass%O |
|-----------|--------|--------|--------|---------|--------|
| A         | 0.18(Nb)| 0.0049 | 0.012  | 0.0008  | 0.0102 |
| B         | 0.37(Nb)| 0.0097 | 0.032  | 0.0009  | 0.0088 |
| C         | 0.011(V)| 0.0156 | 0.017  | 0.0010  | 0.0133 |

Table 2. Chemical composition of diffusion couples and solubility limits determined from the iso-activity lines.
where, $x_S$ and $x_V$ are the mole fraction of S and V, respectively. $g_S$ is the activity coefficient of sulfur in dilute solutions. The slope of the iso-activity line in the $\alpha$ and $\gamma$ phase is obtained by differentiation of Eq. (1) as follows.

\[
\frac{\partial x_S}{\partial x_V} = - \frac{\varepsilon_S^\alpha x_S}{1 + \varepsilon_S^\gamma x_S}
\]  

Experimental information on the $\varepsilon_S^\alpha$ and $\varepsilon_S^\gamma$ in the temperature range of this work has not been clarified, but Ban-ya et al. reported them at 1873 K in liquid phase as $\varepsilon_S^\alpha = -3.30$ and $\varepsilon_S^\gamma = -3.32$. The values of $\varepsilon_V^\alpha$ and $\varepsilon_V^\gamma$ in the $\alpha$ and $\gamma$ phases are expected as similar value with those of liquid, which suggest that the slope of the iso-activity-lines in the $\alpha$ and $\gamma$ phases calculated from Eq. (2) might be negligible small when the sulfur content is $x_S \ll 1$. Therefore, the slope of activity lines in the $\alpha$ and $\gamma$ single-phase region is assumed as zero, hence, the solubility limit of S in the $\alpha$ and $\gamma$ single-phase region can be determined as the break-points of the iso-activity lines in the diffusion couples as shown in Figs. 2(a) and 2(b). The same assumptions to the Fe–V–S diffusion couples are also applied to the analysis of the experimental data of the Fe–Nb–S diffusion couple. The precipitated sulfide is assumed as the stoichiometric NbS although solid solution of (Nb, Fe)S has been reported and the slope of iso-activity line is drawn as 0.3451 in the two-phase region as shown in Fig. 2(c). The analyzed data of the solubility of sulfur in the Fe–V and Fe–Nb alloys are listed in Table 2 and are plotted in the form of the solubility product as shown in Fig. 3. The solubility product of mono-sulfide can be generally approximated by

\[
\log (\text{mass}\%M)(\text{mass}\%S) = A + B/T,
\]

where $M$ is the constant. The solubility products of VS in the $\alpha$ and $\gamma$ phases and NbS in the $\gamma$ phase are evaluated from the experimental data as follow.

\[
\log (\text{mass}\%V)(\text{mass}\%S)_{\alpha} = 4.76 - \frac{10100}{T} \quad \ldots (3)
\]

\[
\log (\text{mass}\%V)(\text{mass}\%S)_{\gamma} = 4.90 - \frac{11000}{T} \quad \ldots (4)
\]

\[
\log (\text{mass}\%Nb)(\text{mass}\%S)_{\gamma} = 4.70 - \frac{10500}{T} \quad \ldots (5)
\]

The solubility product of VS in the $\alpha$ phase is larger than that in the $\gamma$ phase. This tendency is similar to those of MnS$^{15}$ and CrS$^{19}$ in iron alloys. According to the result by Josey and Florids, the solubility of sulfur in the Fe–10mass%V $\alpha$ phase alloy was 5 · 10$^{-4}$mass% S at 1273 K. The solubility product calculated from their result is larger than that of calculated value from Eq. (3). V composition range in their results quite larger than that of the present study. In addition, their analytical value of sulfur may have large experimental error, because their result is near to the composition limit of the analysis technique. An experimental error of the temperature dependence of the present study may be large also, because the experimental temperature range is narrow. These may be reasons of the difference of the solubility product of VS at 1273 K between present result and Josey and Florids.$^{17}$

4. Thermodynamic Analysis

The formation energy of VS and NbS are estimated from the solubility product. Those data have not also been reported yet. The Gibbs energies of the $\alpha$ and $\gamma$ phases are described by the two-sublattice model, where the substitutional Fe, V and Nb atoms occupy the first sublattice and the S and vacancies (denoted by $V_a$) occupy the second sublattice. The Gibbs energies, $G$ of $\alpha$ and $\gamma$ phases for (Fe, $M_a$,S, $V_a$) per mole are expressed as follows.
where $\phi$ denotes the $\alpha$ and $\gamma$ phases and $y_i$ represents the fraction of elements $i$ on each sublattice and related to the mole fractions $x_i$ as follows.

$$y_M = x_M(1-x_M) \quad \text{and} \quad y_S = (a/c)x_S/(1-x_M)
$$

The coefficients $a$ and $c$ in the formulate denote the number of sites for each sublattice, which are given as $a=1$ and $c=3$ for the $\gamma$ phase and $a=1$ and $c=1$ for the $\alpha$ phase, $\Delta yM$ is the Gibbs energy when the first sublattice is filled with $M$ atoms and the second with $X$ atoms. $M$ denotes V or Nb and $X$ denotes S or $\alpha$. In the subscripts of the interaction parameters $\lambda$, the components on the different sublattices are separated by a colon and in the same sublattice by a comma. The chemical potentials of $M$ and $S$ are derived from Eq. (6) as follow, considering $y_M$, $y_S < 1$

$$\mu_M^{\phi} = \Delta yM + aRT \ln y_M + L_{Fe,M}^{\phi}$$

$$\mu_S^{\phi} = \Delta yM - \Delta yS + cRT \ln y_S + L_{Fe,S}^{\phi}
$$

Since VS and NbS can be assumed to be a stoichiometric compound, the solubility product of the monosulfide in the $\alpha$ and $\gamma$ phase can be derived from the equilibrium condition as follows.

$$G^{\phi}_{M} = y_M y_S \Delta yM + y_M y_S \Delta yS + y_M y_S \phi$$

$\phi$ denotes the formation energy of VS and NbS from the solubility product.

$$G^{\phi}_{Fe} = y_M y_S \phi$$

$$G^{\phi}_{Fe,S} = y_M y_S \phi$$

$$G^{\phi}_{M} = y_M y_S \phi$$

where $\phi$ represents the Gibbs energy of VS and NbS.

Substituting Eq. (8) in Eq. (9) yields the following equation.

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

where $\Delta yM$ represents the Gibbs energy of $S_2$ gas phase. $RT \ln(y_M y_S)$ in Eq. (10) can be approximated as follows.

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$\Delta yM$ is the formation energy of VS and NbS as shown in Eq. (11) and (11) as shown in Fig. 4. The formation energy of VS and NbS is calculated from Eqs. (10) and (11) listed in Table 3 and the present experimental data, the formation energy of VS and NbS is calculated from Eqs. (10) and (11) as shown in Fig. 4. The formation energy of VS and NbS is evaluated as follows.

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM = \Delta yS$$

$$\Delta yM$$

These values are between those of MnS and CrS, which agree with the sulfide formation tendency.

4. Conclusions

(1) Solubility limits of sulfur in the $\alpha$ and $\gamma$ phases of the Fe–V alloys, and that in the $\gamma$ phase of the Fe–Nb alloys were measured by the diffusion couple techniques in the temperature range from 1.523 to 1.573 K. The solubility products of VS and NbS were evaluated as log(mass%V)(mass%S) = 4.76 – 10 100/T, log(mass%V)(mass%S) = 4.90 – 10 000/T and log(mass%Nb)(mass%S) = 4.70 – 10 500/T from the experimental results.

(2) A thermodynamic analysis was carried out to evaluate the formation energy of VS and NbS from the solubility

| Phase | Parameter | Value (J/mol) | Reference |
|-------|-----------|---------------|-----------|
| $\gamma$ | $\Delta G^{\phi}_{Fe} - \Delta G^{\phi}_{Fe,S}$ | +13500+1.7T | 22) |
| | $\Delta G^{\phi}_{M} - \Delta G^{\phi}_{Fe,M}$ | +7500+1.7T | 22) |
| | $\Delta G^{\phi}_{Fe,S} - \Delta G^{\phi}_{Fe,M} \cdot \frac{1}{2} \frac{\Delta G^{\phi}_{Fe,S}}{\Delta G^{\phi}_{Fe,M}}$ | -47500+247T | 23) |
| | $\mu_{Fe,S}^{\phi} y_{Fe,S} y_{Fe,M}$ | -15291+1.438T | 24) |
| | $\mu_{Fe,M}^{\phi} y_{Fe,M} y_{Fe,S}$ | -26087+11T | 25) |

Table 3. Thermodynamic parameters.
products, which yields the following equations.

\[ \Delta G_{VS}^{\mathrm{solid}} = -263 \, 100 + 61.0T \, (J/mol) \]
\[ \Delta G_{NbS}^{\mathrm{solid}} = -260 \, 800 + 68.4T \, (J/mol) \]

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