Abstract: The mechanism governing the deoxidation of vanadium metal is regarded as fundamental knowledge; however, it has not been elucidated in existing literature. In this paper, the thermodynamic data of V-H-O systems were summarized, and the Gibbs free energies of the main compounds were calculated. Consequently, the deoxidation limits of different reductants in a V-O system were evaluated, namely: Si, Al, and Mg. It was observed that Si cannot remove an O content of less than 7.27 wt% from V. However, Al was the stronger reducing agent; it could remove O contents of up to 0.01 and 0.1 wt% at 800 and 1050 °C, respectively. Nevertheless, Mg exhibited the best reducing properties as it could remove less than 0.01 wt% of O at 1100 °C. The addition of H$_2$ renders the V-O solid solution unstable to a certain extent, thereby indicating that H$_2$ facilitates deoxygenation. Furthermore, the results obtained by analyzing the equilibrium conditions were in accordance with the results of the deoxidation limit in the V-O system. In other words, this study demonstrates that the oxygen in vanadium can be effectively controlled by changing the reductant dosage and temperature.

Key words: V-H-O solid solution; generating Gibbs free energy; deoxidation limit; Equilibrium phase

1. Introduction

Vanadium is widely distributed in the crust with a total content of 160 ppm [1] and is generally associated with other metal elements in the ore [2-4]. As a valuable metal, vanadium and its compounds are widely used in the steel, chemical, vanadium battery, aerospace, and nuclear power industries because of their excellent material performance [5-9]. At present, metal vanadium or V-bearing alloy was prepared using aluminum with an aluminothermic reduction process at high temperature due to its high melting point, which necessitates a significant amount of energy for the heating and holding process [1, 10-14]. Moreover, the addition of CaO flux not only removes a lot of heat, but also

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leads to a large amount of vanadium loss [15]. Therefore, a cleaner and more efficient preparation of metal vanadium is urgently required to supersede the traditional process.

The root cause for the high cost of vanadium production is its strong affinity with oxygen. According to the Ellingham diagram [16], VO is more stable than the majority of the metal oxides, except for the oxides of active metals such as Ca, Mg, and Al. In addition, a V-O solid solution is formed easily because oxygen is soluble in vanadium [17-19]; further, the deoxidation limit in the V-O solid solution depends on the oxygen activity and temperature [20, 21]. Thus, the thermodynamic data of the V-O system plays a guiding role in the preparation of vanadium metal. Numerous studies on V-O systems are available; however, the useful thermodynamic data are extremely scattered to apply directly in the actual process. This study collects and summarizes the data in the V-O system by simultaneously calculating the Gibbs free energy of the V-O solid solution and the deoxidation limit of different reductants used in the metallothermic reduction process (such as Si, Mg, and Al). Moreover, the data in the V-H and V-H-O systems were determined using the same approach.

2. Analysis method

2.1 Sieverts law

The gas dissolution up to terminal solubility can be assumed by the Sieverts’ law [22-26]. Therefore, the corresponding equilibrium \(1/2X_2(g) = X_{\text{diss}} \) (X=H or O) yields the following mass action law:

\[
C_X = K_X \cdot P_X^{0.5} \quad (X = \text{H or O})
\]

where \(C_X\) stands for the terminal solubility of hydrogen or oxygen in the metal, \(P_X\) is the equilibrium hydrogen or oxygen pressure, and \(K_X\) is the Sieverts’ constant. Wang et al.[26] and Lupis [27] elucidated that the appropriate concentration unit is the gas-to-metal atomic ratio. Accordingly, this study prefers the gas-to-metal atomic ratio as the appropriate concentration unit.

2.2 Integral constraint

The integral Gibbs energy of the VO\(_C\) oxide formed follows Eq. (2)

\[
V + X\text{O}_2 /2 = VO_C
\]

which is related to the relative partial molar free energies of oxygen \([\Delta G(\text{O}_2) = RT \ln p]\) over the entire O/V range

\[
\Delta G^\circ_i(\text{VO}_C) = \frac{RT}{2} \int_0^{C} \ln p dC
\]

where \(p(\text{atm})\) is the equilibrium oxygen pressure of the oxide, \(R\) is the gas constant, and \(C\) is the oxygen-to-metal atomic ratio. The derivation process is detailed in the Supporting Information. In this system, \(p\) is a function of \(C\) and \(T\). Pure vanadium is used as the standard state for the integral Gibbs energy of formation, and 1 atm of \(\text{O}_2\) is the reference standard state of the relative partial molar energies in Eq. (3). Similar calculations can also be applied to V-H and V-H-O systems.

3. Results and discussion

The thermodynamic data for V-O solid solutions with various oxygen contents were summarized by Kim [28] in previous studies. However, the thermodynamic data for V-H-O is incomplete. A thermodynamic model of V-H-O was created to determine
the oxygen potential in this study.

Research on the oxygen potential of the Ti-H-O solid solution was carried out by Zhang et al. [29]; the results of their study are suitable for the V-H-O system as well. We assume that solid solutions of V-H-O were formed via two routes, as shown in Eqs. (4–5), where $\Delta G_1$ and $\Delta G_3$ are the Gibbs free energies of the formation of VH and VO, respectively. The values of $\Delta G_2$ and $\Delta G_4$ represent the energy changes that occur during the oxygenation of VH and hydrogenation of VO, respectively. The oxygen potential of VH$_x$O$_y$ can be acquired from $\Delta G_2$. According to Hess’s law [30], the total Gibbs energy change is invariant in any path when starting and ending with the same materials, that is, $\Delta G_1 + \Delta G_2 = \Delta G_3 + \Delta G_4$. Therefore, it is necessary to obtain the values of $\Delta G_1$, $\Delta G_3$, and $\Delta G_4$.

The relationships between equilibrium pressure ($p$), temperature ($T$), and composition ($C$) for the binary systems of V-H and V-O and the ternary V-H-O system, can be found in the $p$-$C$-$T$ diagrams as reported in the literature [28, 31, 32]. According to the $p$-$C$-$T$ data, the Gibbs energy of the unknown species can be calculated by numerically integrating Eq. (3) or its other forms. Since there is no data in the V-H-O ternary phase diagram and the corresponding VH$_x$ and VO$_y$ are both located in the $\alpha$ phase with low hydrogen or oxygen content ($x \leq 0.2$ and $y \leq 0.044$) at 600–800°C [33, 34], the V-H-O solid solution is considered to be in the $\alpha$ phase.

$$V + \frac{x}{2} H_2 \xrightarrow{\Delta G} VH_x, VH_x + \frac{y}{2} O_2 \xrightarrow{\Delta G} VH_xO_y$$ (4)

$$V + \frac{y}{2} O_2 \xrightarrow{\Delta G} VO_y, VO_y + \frac{x}{2} H_2 \xrightarrow{\Delta G} VH_xO_y$$ (5)

3.1 V-O binary system ($\Delta G_3$)

The $p$-$C$-$T$ data of the V-O solid solution was summarized by Kim [23] and contains the thermodynamic data of the oxygen-to-vanadium atomic ratio from 0 to 1. The $p$-$C$-$T$ diagram is shown in Fig. 1, and the relationships are listed in the following equations via numerical establishment; where $p$ (atm) represents the equilibrium oxygen pressure of the V-O solid solution, $y$ is the oxygen-to-vanadium atomic ratio, and $C_{\alpha/(\alpha+\beta)}$ is the phase boundary composition between $\alpha$ and $\alpha+\beta$.

$$\ln p_\alpha = 20.48 + 2 \ln \frac{y}{C_{\alpha/(\alpha+\beta)}} - \frac{1.62 \times 10^4}{T}$$ (6)

$$\ln p_{\alpha+\beta} = 20.48 - \frac{1.62 \times 10^4}{T}$$ (7)

$$\ln p_b = 9.32 + 46.08y + 2 \ln \frac{y}{3-y} - \frac{1.06 \times 10^4}{T}$$ (8)

$$\ln p_{\beta+\gamma} = 21.88 - \frac{1.15 \times 10^4}{T}$$ (9)

$$\ln p_{\gamma+\delta} = 21.96 + 81.15y + 2 \ln \frac{y}{3-y} - \frac{1.18 \times 10^4}{T}$$ (10)

$$\ln p_{\gamma+\delta} = 22.46 - \frac{1.17 \times 10^4}{T}$$ (11)

$$\ln p_{\beta+\delta} = 21.99 - \frac{1.17 \times 10^4}{T}$$ (12)
Based on Eqs. (3, 6–13), the Gibbs energy of formation of the oxide VO$_y$ ($\Delta G_3$) at various oxygen contents and temperatures is calculated and plotted in Fig. 2, and the oxygen potential of the metallic oxide and V-O solid solution are shown in Fig. 3. The oxygen potential increases with increasing temperature, indicating that VO$_y$ becomes relatively unstable at higher temperatures. When O is dissolved in the V lattice, V-O is more stable than SiO$_2$, Al$_2$O$_3$, or MgO, depending on the O content and temperature. In other words, thermodynamically pure Si, Al, and Mg can remove the O in V to a known limit. For instance, compared with V$_4$O, SiO$_2$ is less stable; therefore, Si cannot remove an O content of less than 7.27 wt% from V. Further, Al is a strong reductant that can remove up to 0.01 and 0.1 wt% of O from V at 800 and 1050 °C. However, Mg is the stronger reductant, and its deoxidation limit can be less than 0.01 wt% at 1100 °C.

The relationships between the Gibbs free energy of the formation of VO$_y$ and the temperature are listed in Table 1.

\[
\ln \rho_\delta = -11.74 + 53.05y + 2\ln \left( \frac{y}{3-y} \right) \frac{11.36 \times 10^4}{T} \tag{13}
\]
Fig. 2 The Gibbs energy of formation of the oxide VO\(_y\) (\(\Delta G_3\)) with various temperature and oxygen contents.

![Graph showing the Gibbs energy of formation of VO\(_y\) with various temperature and oxygen contents.](image)

Table 1 the Gibbs free energy of formation of the representative V-O solid solutions

|         | \(\Delta G_3\), kJ/mole | 600°C  | 700°C  | 800°C  |
|---------|--------------------------|--------|--------|--------|
| VO\(_{0.04}\) (1.36 wt%) | -18.431 | -18.111 | -17.804 |
| VO\(_{0.01}\) (0.96 wt%) | -13.065 | -12.848 | -12.641 |
| VO\(_{0.02}\) (0.65 wt%) | -8.910  | -8.769  | -8.636  |
| VO\(_{0.01}\) (0.31 wt%) | -4.297  | -4.236  | -4.179  |

3.2 V-H binary system (\(\Delta G_1\)) and V-H-O ternary system (\(\Delta G_4\))
The \( p\text{-}C\text{-}T \) data of the V-H and V-H-O solid solutions are available in literature. The data for hydrogen solubility in pure vanadium and V-O solid solution followed the Sieverts’ law, as shown in Equation (1). The temperature dependence of the Sieverts constant \( K_H \) is represented by

\[
\ln K_H = A + \frac{B}{T}
\]  

(14)

where \( T(K) \) is the temperature, and \( A \) and \( B \) are constants. The values of \( A \) and \( B \) with various oxygen contents at 600–800 °C were measured by Yamanaka et al. [26–27], and the relationship of \( \ln p_{\text{H}_2} \) (atm) with \( x \) (H/V atomic ratio) and \( T \) is listed in the following equations:

\[
\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.3 - 3910 / T), \ y(O/V) = 0
\]

(15)

\[
\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.2 - 3770 / T), \ y(O/V) = 0.010
\]

(16)

\[
\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.3 - 3840 / T), \ y(O/V) = 0.021
\]

(17)

\[
\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.4 - 3890 / T), \ y(O/V) = 0.031
\]

(18)

\[
\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.8 - 4240 / T), \ y(O/V) = 0.044
\]

(19)

The Gibbs energies of formation of the \( \text{VH}_x \) (\( \Delta G_1 \)) and \( \text{VH}_x\text{O}_y \) (\( \Delta G_4 \)) are related to the relative partial molar free energies of hydrogen integrated over the entire hydrogen-to-vanadium atomic ratio by Eqs. (20–21). The derivation process is detailed in the Supporting Information. One atm of \( \text{H}_2 \) is the reference standard state of the relative partial molar energies. The results are plotted in Fig. 4. Using Eqs. (16–22), the Gibbs energies of the formation of \( \text{VH}_x \) (\( \Delta G_1 \)) and \( \text{VH}_x\text{O}_y \) (\( \Delta G_4 \)) are calculated and listed in Table 2.

\[
\Delta G_f (\text{VH}_x) = \frac{RT}{2} \int_0^x \ln p \, dx
\]

(20)

\[
\Delta G_f (\text{VH}_x\text{O}_y) = \frac{RT}{2} \int_0^x \ln p \, dx
\]

(21)

Fig. 4 The Gibbs energy of formation of the \( \text{VH}_x \) (\( \Delta G_1 \)) and \( \text{VH}_x\text{O}_y \) (\( \Delta G_4 \)) with various
temperature and oxygen contents

Table 2 the Gibbs free energy of formation of the representative V-H and V-H-O solid solutions

| Phase         | $x$  | $\Delta G$, kJ/mole |
|---------------|------|---------------------|
|               |      | 600 °C  | 700 °C  | 800 °C  |
| VH$_x$        | 0.05 | -0.413  | -0.274  | -0.135  |
|               | 0.10 | -0.323  | 0.013   | 0.348   |
|               | 0.20 | 0.361   | 1.147   | 1.933   |
|               | 0.05 | -0.391  | -0.256  | -0.121  |
| VH$_x$O$_{0.010}$ | 0.10 | -0.279  | 0.048   | 0.375   |
|               | 0.20 | 0.449   | 1.218   | 1.988   |
|               | 0.05 | -0.384  | -0.245  | -0.106  |
| VH$_x$O$_{0.021}$ | 0.10 | -0.264  | 0.071   | 0.406   |
|               | 0.20 | 0.477   | 1.264   | 2.050   |
|               | 0.05 | -0.368  | -0.225  | -0.082  |
| VH$_x$O$_{0.031}$ | 0.10 | -0.233  | 0.110   | 0.454   |
|               | 0.20 | 0.540   | 1.342   | 2.145   |
|               | 0.05 | -0.369  | -0.209  | -0.049  |
| VH$_x$O$_{0.044}$ | 0.10 | -0.234  | 0.143   | 0.520   |
|               | 0.20 | 0.538   | 1.407   | 2.277   |

3.3 The Gibbs energy change of oxygenation of VH$_x$ ($\Delta G_2$) and the oxygen potential of VH$_x$O$_y$

The above section discusses the determination of $\Delta G_1$, $\Delta G_3$, and $\Delta G_4$ per mole of V. Therefore, the value of $\Delta G_2$ can be calculated by deducting the sum of $\Delta G_3$ and $\Delta G_4$ from $\Delta G_1$ and the oxygen potential of VH$_x$O$_y$ under the basis that 1 mole of O$_2$ can be acquired by dividing $\Delta G_2$ by $y/2$. The results are listed in Table 3, and the corresponding relationship of $x$ and the oxygen potential of VH$_x$O$_y$ is shown in Fig. 5. Owing to the contrasting oxygen potentials of the V-O and V-H-O systems, the addition of H$_2$ renders the V-O solid solution unstable to a certain extent, indicating that the deoxygenation is easier with H$_2$. Moreover, the dehydrogenation of VH$_x$ or VH$_x$O$_y$ occurs easily because the values of $\Delta G_1$ and $\Delta G_4$ are highly positive, implying that hydrogen pollution of the product is nonexistent at the end of the reaction.
Fig. 5: the oxygen potential of MgO, Al₂O₃, V-O and V-H-O solid solution with x:
(a) 700 °C; (b) 800 °C

Table 3: the calculated values of $\Delta G_2$ and oxygen potential in VHₓOᵧ at 700 °C

| y  | x  | $\Delta G_3$ | $\Delta G_1$ | $\Delta G_4$ | $\Delta G_2$ | Oxygen potential | H mass content in VHₓOᵧ wt% | O mass content in VHₓOᵧ wt% |
|----|----|--------------|--------------|--------------|--------------|------------------|----------------------------|-----------------------------|
| 0.010 | 0.05 | -4.236 | -0.274 | -0.256 | -4.218 | -843.6 | 0.098 | 0.312 |
| 0.010 | 0.10 | -4.236 | 0.013 | 0.048 | -4.201 | -840.2 | 0.195 | 0.312 |
| 0.010 | 0.20 | -4.236 | 1.147 | 1.218 | -4.165 | -833.0 | 0.389 | 0.312 |
| 0.021 | 0.05 | -8.769 | -0.274 | -0.256 | -8.751 | -833.4 | 0.097 | 0.654 |
| 0.021 | 0.10 | -8.769 | 0.013 | 0.048 | -8.734 | -831.8 | 0.194 | 0.653 |
| 0.021 | 0.20 | -8.769 | 1.147 | 1.218 | -8.698 | -828.4 | 0.388 | 0.652 |
| 0.031 | 0.05 | -12.848 | -0.274 | -0.245 | -12.819 | -827.0 | 0.097 | 0.962 |
| 0.031 | 0.10 | -12.848 | 0.013 | 0.071 | -12.790 | -825.2 | 0.194 | 0.961 |
| 0.031 | 0.20 | -12.848 | 1.147 | 1.264 | -12.731 | -821.4 | 0.387 | 0.959 |
| 0.044 | 0.05 | -18.111 | -0.274 | -0.225 | -18.046 | -820.3 | 0.097 | 1.360 |
| 0.044 | 0.10 | -18.111 | 0.013 | 0.110 | -17.981 | -817.3 | 0.193 | 1.359 |
| 0.044 | 0.20 | -18.111 | 1.147 | 1.342 | -17.851 | -811.4 | 0.385 | 1.356 |

### 3.4 Equilibrium phase in magnesiothermic and aluminothermic reduction of vanadium oxide

As analyzed in Section 3.1, the oxygen potential of the V-O solid solution with various oxygen contents and temperatures was calculated, and the oxygen potential of representative V-O is listed in Table 4. According to the data in Table 4, an in-house
compound database has been established to assist in calculating the equilibrium phase in magnesiothermic and aluminothermic reduction processes. Since the input upper limit of atoms is 255 in the Compound module, only the V-O solid solution with oxygen content exceeding 0.12% was entered into the database.

FactSage was used to calculate the equilibrium phases for the roasted products by minimizing the Gibbs free energy under isothermal and isobaric conditions. The data for the V-O solid solution were provided by the compound database, and other required data for computation were provided by the FactPS database of the program. The calculations were performed on a mixture of 1 mole of V₂O₃ with variable amounts of Mg or Al at 800 and 1200 °C under an inert atmosphere at a pressure of 1 atm. The results of their equilibrium are presented in Fig. 6. With an increase in Mg, V₂O₃ is gradually reduced into the lower valent phase; when the Mg amount reaches 3 mole, V₂O₃ is completely reduced to V at 800 and 1200 °C. The reduction process using Al is similar to that of Mg in the early and intermediate stages; however, V₂O₃ could be reduced to V₂₅₅O(s) by Al at 1200 °C, even though the Al amount is in excess. Generally, the analysis of equilibrium amounts is in accordance with that of the deoxidation limit in the V-O system, thereby implying that the oxygen in vanadium can be controlled effectively by changing the reductant dosage and temperature.

Table 4 the Gibbs free energy of formation of VOₓ with temperature (based on formation of 1 mole VOₓ)

| V-O solid solution | ΔG°(VOₓ)/KJ·mole⁻¹ = a + b(T/K) + c(T/K)ln(T/K) + σ/KJ·mole⁻¹ | a  | b   | c   | σ   |
|--------------------|---------------------------------------------------------------|----|-----|-----|-----|
| V₂O (13.56 wt%)    | -412.2852                                                     | 0.0819 | 0.0195 | ±0.3833 |
| V₄O (7.27 wt%)     | -433.6947                                                     | 0.0027 | 0.0070 | ±0.2209 |
| V₆O (3.37 wt%)     | -466.9019                                                     | 0.0531 | 0.0018 | ±0.5393 |
| V₂₀O (1.5 wt%)     | -518.6935                                                     | 0.3808 | 0.0392 | ±0.2400 |
| V₃₁O (1 wt%)       | -518.6935                                                     | 0.3771 | 0.0392 | ±0.2836 |
| V₆₂O (0.5 wt%)     | -518.6935                                                     | 0.3714 | 0.0392 | ±0.2350 |
| V₅₅O (0.2 wt%)     | -518.6935                                                     | 0.3636 | 0.0392 | ±0.2933 |
| V₅₅O (0.12 wt%)    | -518.6935                                                     | 0.3596 | 0.0392 | ±0.2682 |
| V₃₁₃O (0.1 wt%)    | -518.6935                                                     | 0.3579 | -0.0392 | ±0.1623 |
| V₆₂₇O (0.05 wt%)   | -518.6935                                                     | 0.3521 | -0.0392 | ±0.1623 |
| V₁₅₆₈O (0.02 wt%)  | -518.6935                                                     | 0.3445 | -0.0392 | ±0.1623 |
| V₃₁₆₇O (0.01 wt%)  | -518.6935                                                     | 0.3387 | -0.0392 | ±0.1623 |
Fig. 6 Equilibrium amounts of species in roasted products as a function of temperature and Mg or Al amount: (a) Mg addition at 800 °C; (b) Mg addition at 1200 °C; (c) Al addition at 800 °C; (d) Al addition at 1200 °C.

In conclusion, the behavior of dissolved oxygen and hydrogen in pure vanadium has been investigated, which provides a theoretical basis for the removal of oxygen in vanadium. By calculating the oxygen potential of V-O solid solution, the deoxidation limit in vanadium with different reductant can be obtained, for which the varied purity vanadium and its alloy could be prepared by choosing appropriate reductant under the consideration of cost and reducibility. Specifically, Mg is the optimum reductant for prepared high purity vanadium and its alloy due to its price (almost half as less as Ca under the same molar) and excellent reducibility; As an important component of V-Al alloy, Al can be used to prepare V-Al alloy or vanadium with low requirement of impurity content attributed to its lower cost and reducibility. Moreover, it provides a theoretical basis for the preparation of high purity vanadium or its alloys with a hydrogen assisted thermal reduction process via investigating the effect of dissolved hydrogen on oxygen potential of V-O solid solution.

4. Conclusions

The Gibbs free energies of V-O, V-H, and V-H-O systems were calculated by determining their data in this paper. The main conclusions are as follows:

1. The calculation results show that Si can only remove O from V, if the O content is greater than 7.27 wt%. Further, Al is the stronger reductant, and the O in V cannot be removed if the O content is below 0.01 and 0.1 wt% at 800 and 1050 °C, respectively. Nevertheless, Mg is the best reductant, and its deoxidation limit can be less than 0.01 wt% at 1100 °C.

2. Because the oxygen potentials of V-O and V-H-O systems are significantly different, the addition of H₂ renders the V-O solid solution unstable to a certain extent;
this result indicates that deoxygenation is easier with H$_2$.

(3) The results obtained via the analysis of the equilibrium conditions agree with the results of the deoxidation limit in the V-O system, implying that the oxygen in vanadium can be controlled effectively by changing the reductant dosage and temperature.

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References
[1] R.R. Moskalyk, A.M. Alfantazi, Miner. Eng., 16(9) (2003) 793-805.
[2] E. Janssens, S.M. Lang, M. Brummer, A. Niedziela, G. Santambrogio, K.R. Asmis, J. Sauer, Phys Chem Chem Phys, 14(41) (2012) 14344-53.
[3] S. Liu, S. Shen, K. Chou, J. MIN. METALL. B, 54(2) (2018) 153-159.
[4] H. Peng, J. Environ. Chem, Eng., 7(5) (2019) 103313.
[5] W. Shuai, Y.F. Guo, F.Q. Zheng, C. Feng, L.Z. Yang, T. Jiang, G.Z. Qui, Trans. Nonferrous Met. Soc. China, 30(6) (2020) 1687-1696.
[6] M. Lübke, N. Ding, M.J. Powell, D.J.L. Brett, P.R. Shearing, Z. Liu, J.A. Darr, Electrochem. Commun., 64 (2016) 56-60.
[7] V.Y. Zadorozhnyy, S.N. Klyamkin, M.Y. Zadorozhnyy, O.V. Bermocheva, S.D. Kaloshkin, J. Alloys Compd., 586 (2014) S56-S60.
[8] Z. Wei, D. Liu, C. Hsu, F. Liu, Electrochem. Commun., 45 (2014) 79-82.
[9] M.N. Le, M.S. Lee, J. MIN. METALL. B, 56(1) (2020) 127-133.
[10] G. Pottlacher, T. Hüpf, B. Wilsman, C. Cagran, Thermochim. Acta, 461(1) (2007) 88-95.
[11] R. Venugopalan, D. Sathiyanamoorthy, J. Mater. Process. Technol., 176(1-3) (2006) 133-139.
[12] S. Baoping, X. Jilai, T. Jun, L. Youjun, W. Ruobin, Chin. J. Rare Met., 30 (2006) S1.
[13] Y. Xu, H. Jiao, M. Wang, S. Jiao, J. Alloys Compd., 779 (2019) 22-29.
[14] A.K. Suri, C.K. Gupta, A. Tekin, Miner. Process. Extr. Metall. Rev., 22(1) (2001) 139-163.
[15] M. Lindvall, J. Gran, D. Sichen, Calphad, 47 (2014) 50-55.
[16] H.J.T. Ellingham, J. Soc. Chem. Ind., 63(5) (1944) 125–160.
[17] D.L. Smith, J. Less-Common Met., 31(3) (1973) 345-358.
[18] Dale, E., Smith, Metall. Mater. Trans. B, 2(2) (1971) 579-583.
[19] J.Stringer, J. Less-Common Met., 8(1) (1965) 1-14.
[20] E., Fromm, and, R., Kirchheim, J. Less-Common Met., 26(3) (1972) 403-406.
[21] N.P. Allen, O. Kubaschewski, O.V. Goldbeck, J. Electrochem. Soc., 98(11) (1951) 417-424.
[22] W.E. Wang, D.R. Olander, J. Am. Ceram. Soc., 76(5) (1993) 1242-1248.
[23] D.R. Olander, J. Electrochem. Soc., 131(9) (1984) 2161-2169.
[24] W.E. Wang, J. Alloys Compd., 233(1-2) (1996) 89-95.
[25] W.E. Wang, D.R. Olander, J. Alloys Compd., 224(1) (1995) 153-158.
[26] W.E. Wang, J. Alloys Compd., 238(1-2) (1996) 6-12.
[27] C.H.P. Lupis, Elsevier, New York, 1983.
[28] Y.S. Kim, J. Alloys Compd., 312(1-2) (2000) 86-93.
[29] Y. Zhang, Z.Z. Fang, P. Sun, T. Zhang, Z. Huang, J. Am. Chem. Soc., 138(22) (2016) 6916-6919.
[30] F. Brescia, J. Arents, H. Meislich, A. Turk, E. Weiner, Fundam. Chem. Lab. Stud.,  (1975) 157-163.
[31] S. Yamanaka, Y. Kashiwara, H. Sugiyama, M. Katsura, J. Nucl. Mater., 247 (1997) 244–248.
[32] S. Yamanaka, Y. Kashiwara, M. Miyake, J. Alloys Compd., 231(1-2) (1995) 730-734.
[33] Z. Cao, S. Li, W. Xie, G. Du, Z. Qiao, Calphad, 51 (2015) 241-251.
[34] Shusuke, Ukita, Hiroshi, Ohtani, Mitsuhiro, Hasebe, Mater. Trans., 49(11) (2008) 2528-2533.