

THERMODYNAMIC BEHAVIOR OF DISSOLVED OXYGEN AND HYDROGEN IN PURE VANADIUM

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Abstract

The mechanism governing de-oxidation 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 de-oxidation limits of different reductants in a V-O system were evaluated, namely: Si, Al, and Mg. It was observed that Si could not 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 H₂ rendered the V-O solid solution unstable to a certain extent, thereby indicating that H₂ facilitated de-oxygenation. Furthermore, the results obtained by analyzing the equilibrium conditions were in accordance with the results of the de-oxidation limit in the V-O system. In other words, this study demonstrated that oxygen in vanadium can be effectively controlled by changing the reductant dosage and temperature.

Keywords: V-H-O solid solution; Generating Gibbs free energy; De-oxidation 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 is 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 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 de-oxidation 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 de-oxidation limit of different reductants used in the metallurgical

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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:

$$C_X = K_X \cdot P_{X_2}^{0.5} \quad (X = H \text{ or } O) \quad (1)$$

where C_X stands for the terminal solubility of hydrogen or oxygen in the metal, P_{X_2} 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)



which is related to the relative partial molar free energies of oxygen $[\Delta G(O_2) = RT \ln p]$ over the entire O/V range

$$\Delta G_f^\circ(VO_C) = \frac{RT}{2} \int_{p_0}^C \ln p dC' \quad (3)$$

where p (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 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.

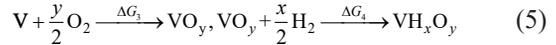
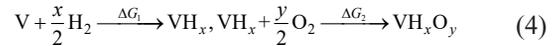
3. Results and discussion

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. It is assumed that solid solutions of V-H-O were formed via two routes, as shown in Eqs. (4–5), where ΔG_1 and ΔG_3 are the Gibbs free energies of the formation of VH_x and VO_y , respectively. The values of ΔG_2 and ΔG_4 represent the energy changes that occur during the oxygenation of VH_x and hydrogenation of VO_y , respectively. The oxygen potential of VH_xO_y can be acquired from ΔG_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 ΔG_1 , ΔG_3 , and ΔG_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 α 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 α phase.



3.1. V-O binary system (ΔG_j)

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 α and $\alpha+\beta$.

$$\ln p_\alpha = 20.48 + 2 \ln \frac{y}{C_{\alpha/(\alpha+\beta)}} - \frac{11.62 \times 10^4}{T} \quad (6)$$

$$\ln p_{\alpha+\beta} = 20.48 - \frac{11.62 \times 10^4}{T} \quad (7)$$

$$\ln p_\beta = 9.32 + 46.08y + 2 \ln \frac{y}{3-y} - \frac{10.06 \times 10^4}{T} \quad (8)$$

$$\ln p_{\beta+\gamma} = 21.88 - \frac{10.15 \times 10^4}{T} \quad (9)$$



$$\ln p_\gamma = 21.96 + 8.15y + 2 \ln \frac{y}{3-y} - \frac{11.18 \times 10^4}{T} \quad (10)$$

$$\ln p_{\gamma+\delta} = 22.46 - \frac{10.17 \times 10^4}{T} \quad (11)$$

$$\ln p_{\beta+\delta} = 21.99 - \frac{10.17 \times 10^4}{T} \quad (12)$$

$$\ln p_\delta = -11.74 + 53.05y + 2 \ln \frac{y}{3-y} - \frac{11.36 \times 10^4}{T} \quad (13)$$

Based on Eqs. (3, 6–13), the Gibbs energy of formation of the oxide VO_y (ΔG_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_2O_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_4O , 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 de-oxidation 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.

3.2. V-H binary system (ΔG_1) and V-H-O ternary system (ΔG_2)

The p - C - T data of the V-H and V-H-O solid solutions are available in literature. The data for

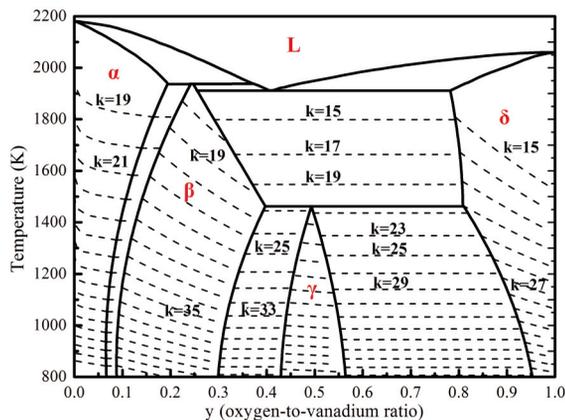


Figure 1. Phase diagram of the V–O system. Oxygen pressure isobars are indicated by the index k in $p = 10^{-k}$ atm [23]

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

$$\ln K_H = A + \frac{B}{T} \quad (14)$$

where $T(K)$ is the temperature, and A and B are

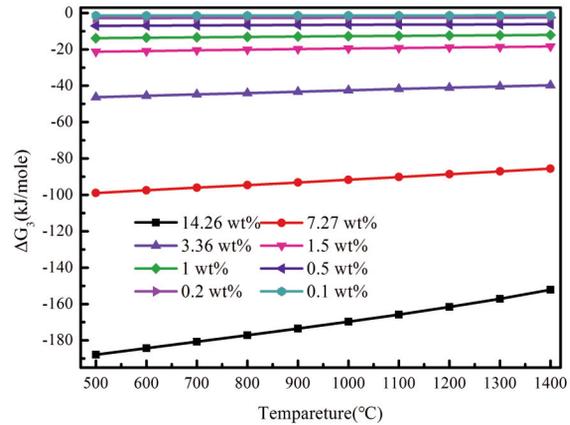


Figure 2. The Gibbs energy of formation of the oxide VO_y (ΔG_3) with various temperature and oxygen contents

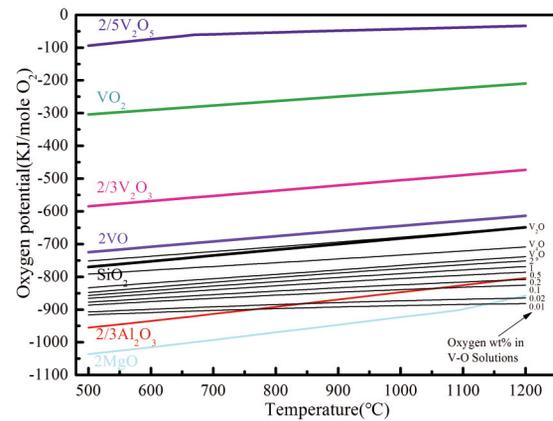


Figure 3. The oxygen potential of MgO , Al_2O_3 , SiO_2 , V_2O_5 , V_2O_3 , VO and V-O solid solution with temperature

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

ΔG_3 , kJ/mole	600°C	700°C	800°C
$VO_{0.044}$ (1.36 wt%)	-18.431	-18.111	-17.804
$VO_{0.031}$ (0.96 wt%)	-13.065	-12.848	-12.641
$VO_{0.021}$ (0.65 wt%)	-8.910	-8.769	-8.636
$VO_{0.010}$ (0.31 wt%)	-4.297	-4.236	-4.179



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:

$$\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.3 - 3910/T), y(\text{O/V}) = 0 \quad (15)$$

$$\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.2 - 3770/T), y(\text{O/V}) = 0.010 \quad (16)$$

$$\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.3 - 3840/T), y(\text{O/V}) = 0.021 \quad (17)$$

$$\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.4 - 3890/T), y(\text{O/V}) = 0.031 \quad (18)$$

$$\ln p_{\text{H}_2} = 2\ln x + 2 \times (7.8 - 4240/T), y(\text{O/V}) = 0.044 \quad (19)$$

The Gibbs energies of formation of the VH_x (ΔG_1) and VH_xO_y (ΔG_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 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 VH_x (ΔG_1) and VH_xO_y (ΔG_4) are calculated and listed in Table 2.

$$\Delta G_f^0(\text{VH}_x) = \frac{RT}{2} \int_0^x \ln p dx' \quad (20)$$

$$\Delta G_f^0(\text{VH}_x\text{O}_y) = \frac{RT}{2} \int_0^x \ln p dx' \quad (21)$$

3.3. The Gibbs energy change of oxygenation of VH_x (ΔG_2) and the oxygen potential of VH_xO_y

The above section discusses the determination of ΔG_1 , ΔG_3 , and ΔG_4 per mole of V. Therefore, the value of ΔG_2 can be calculated by deducting the sum of ΔG_3 and ΔG_4 from ΔG_1 and the oxygen potential of VH_xO_y under the basis that 1 mole of O_2 can be acquired by

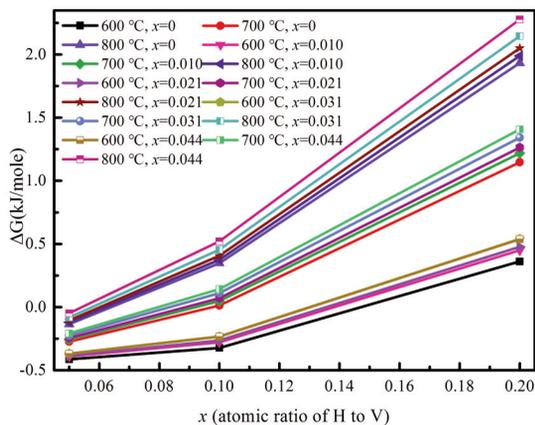


Figure 4. The Gibbs energy of formation of the VH_x (ΔG_1) and VH_xO_y (ΔG_4) with various temperature and oxygen contents

dividing ΔG_2 by $y/2$. The results are listed in Table 3, and the corresponding relationship of x and the oxygen potential of VH_xO_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 de-oxygenation is easier with H_2 . Moreover, the dehydrogenation of VH_x or VH_xO_y occurs easily because the values of ΔG_1 and ΔG_4 are highly positive, implying that hydrogen pollution of the product is nonexistent at the end of the reaction.

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

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

Phase	x	ΔG , 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
$\text{VH}_x\text{O}_{0.010}$	0.05	-0.391	-0.256	-0.121
	0.10	-0.279	0.048	0.375
	0.20	0.449	1.218	1.988
$\text{VH}_x\text{O}_{0.021}$	0.05	-0.384	-0.245	-0.106
	0.10	-0.264	0.071	0.406
	0.20	0.477	1.264	2.050
$\text{VH}_x\text{O}_{0.031}$	0.05	-0.368	-0.225	-0.082
	0.10	-0.233	0.110	0.454
	0.20	0.540	1.342	2.145
$\text{VH}_x\text{O}_{0.044}$	0.05	-0.369	-0.209	-0.049
	0.10	-0.234	0.143	0.520
	0.20	0.538	1.407	2.277

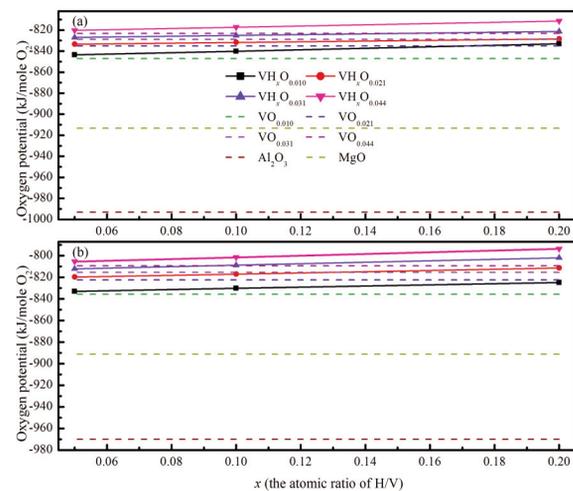


Figure 5. The oxygen potential of MgO , Al_2O_3 , V-O and V-H-O solid solution with x : (a) 700 °C; (b) 800 °C



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 V_2O_3 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, V_2O_3 is gradually reduced into the lower valent phase; when the Mg amount reaches 3 mole, V_2O_3 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, V_2O_3 could be reduced to $V_{255}O(s)$ 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 de-oxidation limit in the V-O system, thereby implying that the oxygen in vanadium can be controlled effectively by changing the reductant dosage and temperature.

In conclusion, the behavior of dissolved oxygen and hydrogen in pure vanadium was investigated, which provided a theoretical basis for the removal of oxygen in vanadium. By calculating the oxygen potential of V-O solid solution, the de-oxidation limit

in vanadium with different reductant could 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 was the optimum reductant for prepared high purity vanadium and its alloy due to its price (almost half as less as Ca under

Table 4. The Gibbs free energy of formation of VO_x with temperature (based on formation of 1 mole VO_x)

V-O solid solution	$\Delta G^0 f(VO_x)/KJ \cdot mole^{-1} = a + b(T/K) + c(T/K)\ln(T/K) + \sigma/KJ \cdot mole^{-1}$			
	a	b	c	σ
V_2O (13.56 wt%)	-4.122.852	0.0819	0.0195	± 0.3833
V_4O (7.27 wt%)	-4.336.947	0.0027	0.0070	± 0.2209
V_9O (3.37 wt%)	-4.669.019	0.0531	0.0018	± 0.5393
$V_{20}O$ (1.5 wt%)	-5.186.935	0.3808	0.0392	± 0.2400
$V_{31}O$ (1 wt%)	-5.186.935	0.3771	0.0392	± 0.2836
$V_{62}O$ (0.5 wt%)	-5.186.935	0.3714	0.0392	± 0.2350
$V_{157}O$ (0.2 wt%)	-5.186.935	0.3636	0.0392	± 0.2933
$V_{255}O$ (0.12 wt%)	-5.186.935	0.3596	0.0392	± 0.2682
$V_{313}O$ (0.1 wt%)	-5.186.935	0.3579	-0.0392	± 0.1623
$V_{627}O$ (0.05 wt%)	-5.186.935	0.3521	-0.0392	± 0.1623
$V_{1568}O$ (0.02 wt%)	-5.186.935	0.3445	-0.0392	± 0.1623
$V_{3167}O$ (0.01 wt%)	-5.186.935	0.3387	-0.0392	± 0.1623

Table 3. The calculated values of ΔG_2 and oxygen potential in VH_xO_y at 700 °C

y	x	ΔG_3	ΔG_1	ΔG_4	ΔG_2	Oxygen potential, KJ/mole O_2	H mass content in VH_xO_y , wt%	O mass content in VH_xO_y , 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



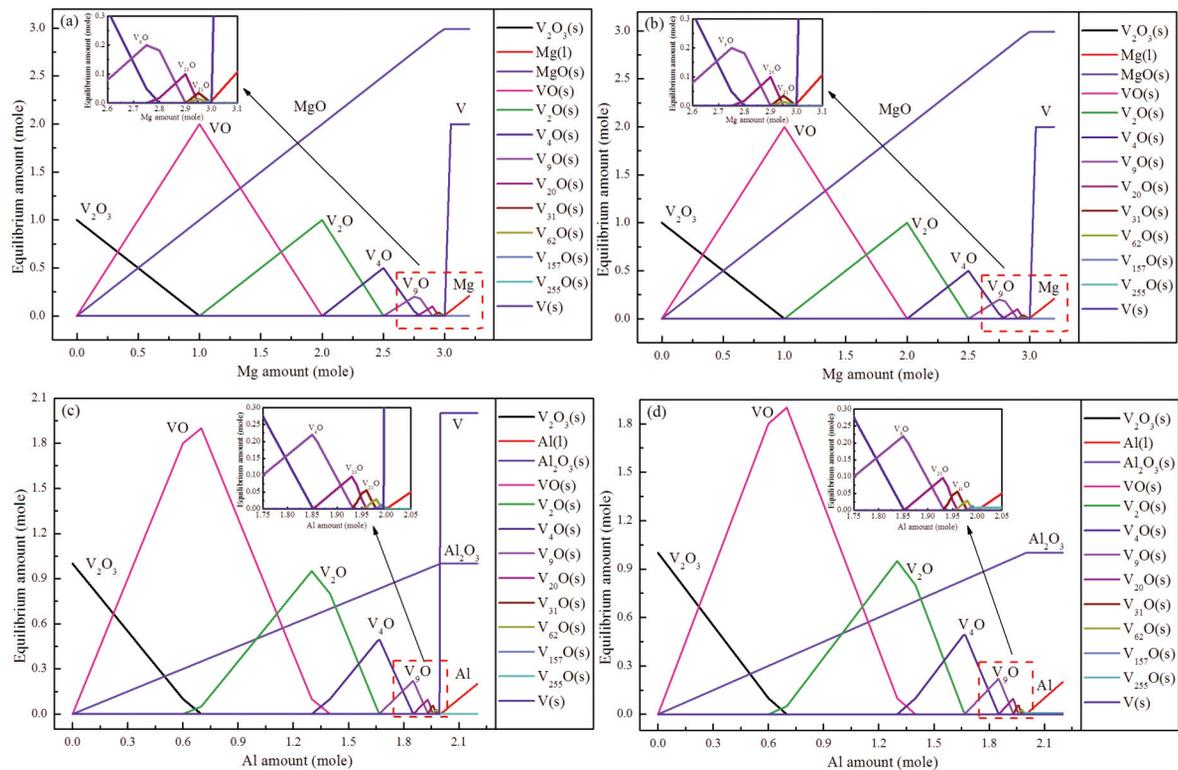


Figure 6. Equilibrium amounts of species in roasted products as a function of temperature and Mg or Al amount: (a) Mg addition at 800 °C; (b) Mg addition at 1200 °C; (c) Al addition at 800 °C; (d) Al addition at 1200 °C

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 provided 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 showed that Si could only remove O from V, if the O content was greater than 7.27 wt%. Further, Al was the strongest reductant, and O in V could not be removed if the O content was below 0.01 and 0.1 wt% at 800 and 1050 °C, respectively. Nevertheless, Mg was the best reductant, and its de-oxidation limit was less than 0.01 wt% at 1100 °C.

(2) Because the oxygen potentials of V-O and V-H-O systems were significantly different, the addition of H₂ rendered the V-O solid solution unstable to a certain extent; this result indicated that de-oxygenation was easier with H₂.

(3) The results obtained via the analysis of the

equilibrium conditions agreed with the results of the de-oxidation limit in the V-O system, implying that the oxygen in vanadium could be controlled effectively by changing the reductant dosage and temperature.

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TERMODINAMIČKO PONAŠANJE RASTVORENOG KISEONIKA I VODONIKA U ČISTOM VANADIJUMU

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Apstrakt

Mehanizam koji upravlja postupkom dezoksidacije metala vanadijuma smatra se osnovnim znanjem, ali taj mehanizam nije potpuno objašnjen u postojećoj literaturi. U ovom radu su sumirani termodinamički podaci o V-H-O sistemu i izračunate je Gibsova slobodna energija za glavna jedinjenja. Takođe su procenjene granice dezoksidacije različitih reducenata u V-O sistemu, kao što su Si, Al i Mg. Uočeno je da Si ne može da ukloni sadržaj O manji od 7,27 wt% iz V. Međutim, Al se pokazao kao jači redukcionni agens, odnosno, uklonio je sadržaj O do 0,01 i 0,1 wt% na 800 i 1050 °C. Ipak, Mg je pokazao najbolja redukciona svojstva zato što je uklonio manje od 0,01 wt% O na 1100 °C. Dodavanje H₂ je dovelo do nestabilnosti čvrstog V-O rastvora u određenoj meri, što dokazuje da je H₂ olakšao dezoksidaciju. Povrh toga, rezultati dobijeni analizom ravnotežnih uslova su bili u skladu sa rezultatima dobijenim za granice deoksidacije u V-O sistemu. Drugim rečima, ovo istraživanje je pokazalo da se sadržaj kiseonika u vanadijumu može kontrolisati promenom količine reducenta i temperature.

Ključne reči: V-H-O čvrsti rastvor; Gibsova slobodna energija; Granica dezoksidacije; Ravnotežna faza

