Investigation of the conditions required for the formation of V(C,N) during carburization of vanadium or carbothermal reduction of V_2O_5 under nitrogen

Hanjung Kwon[a,b], Ahram Moon[a,b], Wonbaek Kim[a], Jiwoong Kim[a,b,*]

[a] Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Yuseong-gu, Daejeon 305-350, South Korea
[b] Korea University of Science and Technology, Gajeong-ro, Yuseong-gu, Daejeon 305-350, South Korea

ARTICLE INFO

ABSTRACT

Phase stability diagrams of V–C–N and V–O–C–N systems were constructed as a function of carbon activity, nitrogen partial pressure, oxygen partial pressure, and solution formation characteristics to determine the conditions for the formation of V(C,N) via the carburization of vanadium or carbothermal reduction of V_2O_5 under nitrogen. The diagram showed that only V, V_2C, and V(C,N) phases would be stable in the V–C–N system. From the diagram, it was also observed that only V(C,N) exists after the carburization of vanadium under nitrogen atmosphere more than 10^{-5} atm. The diagram of V–O–C–N system suggests that V_2O_5 can be reduced to V(C,N) without forming VO, owing to the high stability of the V(C,N) phase. Using these stability diagrams, the conditions for preparing V(C,N) from vanadium or V_2O_5 were deduced and the validity of the diagrams was verified using the experimental results.

1. Introduction

Transition metal carbonitride has unique chemical and physical properties, such as a high melting point, superior hardness, excellent thermal/chemical stability, catalytic properties, and good metallic electrical conductivity [1–8]. Among transition metal carbonitrides, vanadium carbonitride (V(C,N)) is used as an additive in WC–Co cutting tools because V(C,N) prohibits the grain growth of WC effectively (through the interruption of coalescence between WC grains) [3–5]. V (C,N) also has the virtue of catalytic properties. V(C,N) proved to be an active catalyst of ammonia decomposition and hydrotreating of distillate fuels [6,7]. It was observed that the onset potential of oxygen reduction under the catalysis of V(C,N) is only 23 mV lower than that of Pt/C catalyst and V(C,N) has the potential to become a low–cost and high–performance catalyst for fuel cells [8].

V(C,N) is traditionally prepared via the reaction of vanadium with carbon or carbothermal reduction of vanadium oxide under nitrogen atmosphere at high temperature [2,9]. In the process of formation of V (C,N), the conditions that should be optimized are carbon content in the starting materials and partial pressure of nitrogen/oxygen during heat treatment. If the carbon content exceeds the adequate amount, free carbon exists in V(C,N). Conversely, if the carbon content is not sufficient to remove the oxygen in the starting materials or the partial

pressure of oxygen is high, the oxygen content of V(C,N) becomes high. Further, the ratio of carbon and nitrogen varies according to the carbon content and partial pressure of nitrogen during heat treatment; consequently, the properties of V(C,N) differ according to the carbon content and partial pressure of nitrogen.

Thus, it is important to determine the optimum conditions (carbon content and partial pressure of nitrogen/oxygen) for the formation of V (C,N) with low content of free carbon and oxygen or the optimization of the properties of V(C,N). Nevertheless, there are few studies on the conditions for the formation of V(C,N) via the carburization of vanadium or the carbothermal reduction of vanadium oxide in nitrogen. In 1964, Brauer and Schnell reported a phase diagram of the V–VC–VN system at 1100–1400 °C [10]. In their study, they determined that a V (C,N) phase with a B1 (NaCl–like) structure exists in the V–VC–VN system. In 1982, Pompe studied the limit of the value of x for the one–phase carbonitride region of $V(C_xN_y)$ using thermogravimetric equilibrium measurements [11]. In 1998, Gusev calculated the equilibrium nitrogen partial pressure of V(C,N) with respect to the composition of V(C,N) and temperature [12]. However, in these studies, the stable domains of V(C,N) were defined by two dependent variables, i.e., the composition of $V(C_xN_y)$ and nitrogen partial pressure. Therefore, the stable domains should be modified by the introduction of independent variables (carbon content and partial pressure of nitrogen/

oxygen) to determine the optimum conditions for the formation of V(C,N).

In this study, the stable domains for V(C,N) during the carburization of vanadium or the carbothermal reduction of V_2O_5 under nitrogen were defined by the independent variables (carbon content and partial pressure of nitrogen/oxygen). First, the standard Gibbs free energies of formation of stoichiometric V(C,N) phases with various C:N ratios were determined using ab initio simulations. Phase stability diagrams of V–C–N system and V–C–O–N system were subsequently constructed with respect to the carbon activity, a_C, nitrogen partial pressure, p_{N_2}, and oxygen partial pressure, p_{O_2}. Based on the obtained stability diagrams, the proper conditions for the formation of stoichiometric V(C,N) during the carburization of vanadium or the carbothermal reduction of V_2O_5 under nitrogen were investigated.

2. Calculation method

The Vienna ab initio simulation package (VASP) with plane–wave basis sets was used to calculate the standard Gibbs free energies of formation of V(C,N) solid solutions [13–16]. Exchange–correlation effects were considered in both the framework of the local density approximation (LDA) [17] and the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) parameterization [18]. However, we employed the results from GGA–PBE because GGA–PBE yielded more accurate calculation results than LDA, closely to the experimental results. Moreover, the standard Gibbs free energies of formation of various transition metal carbonitrides were obtained using the GGA–PBE exchange–correlation function [19–22]. In order to obtain the proper solid–solution models with randomly distributed C and V atoms in the sub–lattice of B1–structured V(C,N), special quasi–random structure (SQS) models were used [23]. SQS models with 32 and 16 atoms were constructed for the $V(C_{0.75}N_{0.25})$ and $V(C_{0.5}N_{0.5})$ solid solutions, respectively. Fig. 1 shows the SQS structures with 32 and 16 atoms. The apparent crystal structure in these cases is monoclinic with P2/m (32 atoms) and Pm (16 atoms) space groups. Although their apparent crystal structure differs from the practical B1 structure of V(C,N), these models successfully yield not only the thermodynamic properties but also the elastic and electronic properties of B1–structured transition metal oxycarbides and carbonitrides [19,23,24]. In order to obtain the optimized structures, integration in the Brillouin zone was performed using $13 \times 13 \times 13$ k–points for the unit cell models (8 atoms) of VC and VN with the B1 (NaCl) structure and $7 \times 5 \times 3$ and $5 \times 11 \times 5$ k–points for the SQS models (32 and 16 atoms, respectively). In order to improve the accuracy of the calculations, we employed a high energy cutoff of 500 eV and a precise energy convergence of 0.005 eV/Å. The tetrahedron method with Bloch correction was used for the energy calculations. In order to obtain the equilibrium volume at different temperatures and compositions, the total electronic energy and phonon vibrational effects were calculated at 13 vol points for each composition. The Birch–Murnaghan equation of state with five parameters (BM5 EOS) was utilized to fit the calculated E–V curves [22].

The phonon vibrational effects of the thermodynamic properties of V(C,N) were evaluated using PHONOPY, which provides a VASP interface [24]. In order to calculate the force constant using density functional perturbation theory [17,25], integration in the Brillouin zone was performed using $17 \times 17 \times 17$ k–points for the models with eight atoms of pure substances (VC and VN), and $9 \times 7 \times 5$ and $7 \times 13 \times 7$ k–points were used for the 32– and 16–atom solid–solution SQS models. An energy cutoff of 600 eV was used, and Gaussian smearing was employed for the force calculations. After obtaining the phonon density of states, we calculated the ZPE (Zero–Point Energy) and Helmholtz free energy. These are expressed as

$$E_{ZPE}(V) + F_{ph}(V, T) = \sum_i \left[\frac{1}{2}\hbar\omega_i + k_B T ln\left(1 - e^{-\frac{\hbar\omega_i}{k_B T}}\right) \right], \quad (1)$$

where k_B is the Boltzmann constant and ω_i is the phonon frequency. We do not consider the pressure effects. Thus, the Helmholtz free energy can represent the Gibbs free energies of formation of V(C,N) solid solutions [26]. The ideal configurational entropies were added to the total energies of the intermediated compositions. The effects of anharmonic vibrational and electronic excitation on the thermodynamic properties are not dealt with in the present study. This is a possible error source in the Gibbs free energies of formation, particularly in the high--temperature range; however, we assumed herein that this can be ignored in the general heat treatment temperature range (approximately 1500 K).

3. Experimental procedure

V/C and V_2O_5/C mixtures were heat–treated in vacuum or nitrogen atmosphere to evaluate the validity of the constructed phase stability diagrams. The mixtures were prepared by mixing vanadium (Sigma–Aldrich, 325 mesh, $\geq$ 99.5%) or vanadium oxide (Alfa Aesar, 325 mesh, 99.2%) powders with graphite powder (Alfa Aesar, 325 mesh, 99.8%) (mole fractions of carbon in the mixtures are 10^{-5}, 10^{-4}, 10^{-3}, 10^{-1}, and 0.5) using horizontal ball milling. Tungsten carbide balls were mixed with V/C or V_2O_5/C at a ball–to–powder weight ratio of 20:1. The milling was performed at a speed of 200 rpm for 20 h in ethanol. The mixtures were heat–treated at 1227 °C for 5 h in vacuum or nitrogen atmosphere (0.0136 and 1 atm) for carburization and carbothermal reduction. The phases in the heat–treated powder were analyzed using X–ray diffraction (XRD) analysis (SmartLab, Rigaku, Japan). Monochromatized Cu Kα radiation (λ = 1.5418 Å) was employed during the analysis, and Si was used as a standard to calibrate the diffractometer.

4. Results and discussion

4.1. Standard Gibbs free energies of formation of V(C,N)

Table 1 lists the standard Gibbs free energies of formation of V(C_xN_y) ($x + y = 1$, x = 0, 0.25, 0.5, 0.75, and 1) calculated at various
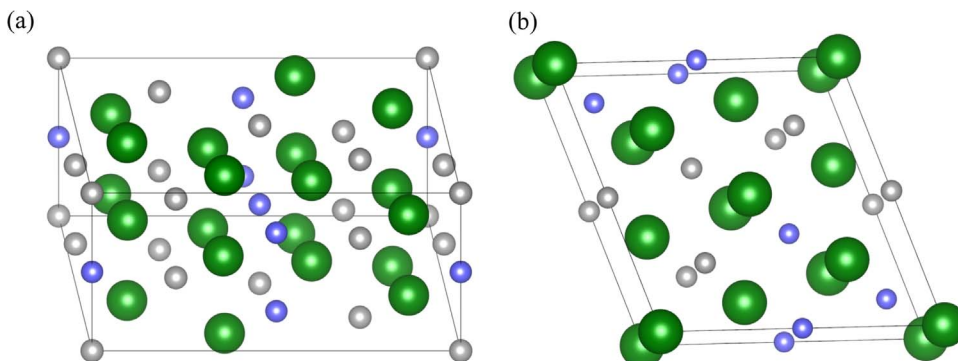
(a)

(b)

Fig. 1. SQS models of solid solutions of VCN: (a) V($C_{0.75}N_{0.25}$) with 32 atoms and (b) V($C_{0.5}N_{0.5}$) with 16 atoms. Green, grey, and purple spheres represent V, C, and N atoms, respectively.