Production of Metallic Vanadium by Preform Reduction Process

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A fundamental study was conducted on a new process for producing vanadium (V) metal by the preform reduction process (PRP) based on metallothermic reduction of vanadium pentoxide (V2O5). Feed preforms with good mechanical strength even at elevated temperatures were prepared by adding either CaO or MgO to V2O5 feed powder because V2O5 has a low melting point of 963 K; thus complex oxides (CaV4O9, Mg3(V2O5)7) with high melting point at more than 1273 K were obtained. Reduction experiments were conducted by using either Ca or Mg vapor at 1273 K for 6 h. V metal with a purity of more than 99% was successfully obtained when using Mg as a reductant. The feasibility of producing V metal by the PRP will be discussed on the basis of fundamental experiments. [doi:10.2320/matertrans.M2010027]

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1. Introduction

Vanadium (V) is a transition-metal element with an atomic number of 23. V metal is the 20th most abundant element among all elements in the earth’s crust. The abundance of V metal is 120 ppm in the earth’s crust, which is significantly larger than the well-used common metals such as nickel (Ni, 84 ppm, 23rd rank) and copper (Cu, 60 ppm, 26th rank). However, V metal belongs to a set of less common metals or “rare metals” since the production volume of V metal was only 58 kt in 2007 and is far smaller as compared to that of common metals. The small production volume of V metal is partly due to its low concentration in the ore and uneven distribution of its minerals. The principal V metal minerals such as titanomagnetite contain only 1–2 mass% of V2O5. The majority of the mineral resources are distributed in three countries: China, Russia, and South Africa.

V metal and its alloys are mainly used as additive elements (alloying elements) or as catalysts. In Japan, more than 85% of V metal is used as an additive in steel products for improving their tensile strength and heat resistance. Special steel containing V metal is applied in bridges, industrial tools, etc. In the field of chemical industries, V compounds are utilized as a desulfurization catalyst in sulfuric acid production processes. Furthermore, vanadium-titanium (V-Ti) alloys are now attracting considerable attention as new electrode materials in hydrogen storage batteries, because V has high hydrogen storage capacity at ambient temperature and moderate pressure. Considering the expanding market for hydrogen storage batteries, the demand for V-Ti alloys may be expected to increase in the future.

Currently, V feed for smelting V metal is produced in the form of its oxide (V2O5) as a byproduct of steel slag or as a residue of oil, and these V2O5 feeds are mostly used as a starting material for V products. V metal is commercially produced by the aluminothermic reduction (ATR) of V2O5. Although this process is simple and economical, the product is not a high-purity V metal; it is a vanadium-aluminum (V-Al) alloy containing 20% mass% of aluminum (Al). In order to produce high-purity V metal, multiple melting steps by using an electron beam melting process are necessary for removing the Al. For this reason, the ATR process is not a suitable production process of high-purity V metal. In the past, some researchers attempted to develop an alternative to the ATR process for producing V metal. Metallic V with more than 99% purity was first produced through electrochemical reduction by Marden and Rich. They used a mixture of V2O5, Ca and CaCl2 at 1173–1223 K. McKechenie and Seybolt proposed another reaction based on calciothermic reduction with a small amount of flux such as CaI2. Gregory researched calciothermic reduction of V2O5. In order to eliminate oxygen contamination, chloride metallurgy for producing high purity V metal was investigated by Campbell et al. Preparation of high-purity V by the Van Arkel-de Boer process (iodide disproportionation process) was studied by Carlson et al. However, an effective production process suitable for commercial mass production has not been established at this stage. Therefore, the development of a simple and efficient production process of high-purity V metal is strongly required. In the recent years, Suzuki et al. investigated electrochemical reduction of V2O5 or V2O3 in molten CaCl2 for producing high purity V metal and its alloys, as well as calciothermic reduction of V2O5 and TiO2 for producing V-Ti alloys. With these backgrounds, the present study aims to develop a new process for the effective production of V metal from its oxide by utilizing a simple metallothermic reduction.

2. Preform Reduction Process (PRP)

As an effective production process of high-purity V metal from V2O5, we selected the preform reduction process (PRP). Feed preforms are prepared by mixing a starting material oxide feed, flux, and binder solution. After drying, the preforms have sufficient mechanical strength to stand alone. By utilizing the features of the mechanical structure of the feed preforms, contamination from the reduction container can be prevented. In the PRP, the oxide in the preforms is directly reduced to metal by reductant vapor. After reduction, the produced metal is recovered by leaching. The advantages
of this process are its effective control of purity and morphology and its ability to flexibly scale the reduction process. Contamination into the product can be easily avoided because the feed material in the self-supporting preform does not have physical contact with the reaction container or the reductant. Highly flexible scalability is achieved as it is possible to simultaneously treat multiple pieces of preforms in a single reduction chamber. Furthermore, the amount of molten salt (or flux) used in this process is smaller than that used in other processes.

3. Thermodynamic Analysis

A reductant suitable for the PRP and the optimum reduction temperature were studied from the thermodynamic viewpoint. Calcium (Ca) or magnesium (Mg) was selected as a suitable reductant for the \( \text{V}_2\text{O}_5 \) reduction by considering the Gibbs energies for the formation of oxides shown in Fig. 1.\(^{24}\) For reducing \( \text{V}_2\text{O}_5 \) by the PRP, the reductant metal has to be supplied in a vapor form. The vapor pressure of some selected elements as a function of temperature is illustrated in Fig. 2.\(^{24}\) In order to have an efficient supply of a reducing agent in the gas phase, it is desirable that the vapor pressure of the reducing agent is higher than \(10^{-3} \text{ atm} \) at the reduction temperature.\(^{25}\) In this study, 1273 K was selected as the reduction temperature because their vapor pressures are higher than \(10^{-3} \text{ atm} \), which is high enough for sufficient gas supply of the reducing agents.

The melting point of \( \text{V}_2\text{O}_5 \) is 963 K, which is lower than the reduction temperature. This low melting point causes difficulty in the fabrication of a suitable feed preform for the PRP. The preforms fabricated only from \( \text{V}_2\text{O}_5 \) and a binder cannot retain their mechanical shapes at elevated temperatures.\(^{26,27}\) It is expected that Mg\(_2\)V\(_2\)O\(_7\) and Ca\(_2\)V\(_3\)O\(_8\) maintain enough mechanical strength even at the reduction temperature \( (T_{\text{red.}} = 1273 \text{ K}) \) because these compounds have high melting points.

4. Experimental

A flowchart of the production of V metal by the PRP employed in this study is shown in Fig. 4. The PRP of \( \text{V}_2\text{O}_5 \) using Ca or Mg vapor as a reductant consisted of four major steps: preform fabrication, calcination, reduction by reductant vapor, and sample recovery by acid leaching. Firstly, the feed preform was fabricated from a slurry made of \( \text{V}_2\text{O}_5 \) powder (99.9% purity), CaO or MgO powder as a flux, and a collodion solution (5 mass% nitrocellulose in ethanol and ether) as a binder. The experimental conditions for preparing the feed preform using the Ca or Mg vapor were determined. The viscosity of the slurry was controlled by varying the amount of the flux and binder. The cationic molar ratio, \( R_{\text{Cat.}}/V \), listed in Table 1 is defined as \( R_{\text{Cat.}}/V = N_{\text{Cat.}}/N_V \), where \( N_{\text{Cat.}} \) and \( N_V \) are the mole amounts of the cation in the flux and V, respectively. Plate-shaped preforms with a thickness of 3–10 mm were prepared by casting the obtained slurry into a stainless steel mold. Secondly, the cast preforms were heated and calcined in air for 2 h at calcined temperatures.
Figure 5(a) is a schematic illustration of the experimental apparatus used for the calcination step. In this calcination step, the binder and water in the feed preforms were removed, and an adequate amount of mechanical strength was further granted to the preforms. Then, the calcined preforms were installed in a reaction vessel and reduced by the Ca or Mg vapor in the reduction step. Figure 5(b) is a schematic illustration of the experimental apparatus used for producing V metal by the PRP. Four pieces of the calcined preforms (4–6 g each) containing vanadium oxides were placed in a thick-walled stainless steel vessel, and the reductant solid was placed at the bottom of the vessel. Two times excess stoichiometric amount of reductant (Ca or Mg) was used in the reduction experiment (see $R_{Ca/V}$ values in Table 2). The reductant solid was physically isolated from the feed preform, and the reductant vapor was supplied to the feed preform. Sponge titanium was also placed at the bottom of the vessel for gettering the nitrogen gas in the system. After being sealed by tungsten inert gas (TIG) welding, the flux, $V_2O_5$ and binder were introduced. The feed preform was then mixed and casted into a cylindrical shape. The calcination process was carried out at a temperature of 1173 K for 2 hours. The reduced preform was then leached with a mixture of 50% CH$_3$COOH aq., 20% HCl aq., and distilled water, isopropanol, and acetone. The waste solution was sent to the waste solution tank. The reduced solids were then vacuum dried at 873 K for 2 hours. The V metal powder was then obtained. Figure 4 Flowchart of the production of V metal by PRP in this study.
The obtained product in the preforms contribute to maintaining the shape of preforms, and MgO in the preforms demonstrated sufficient mechanical strength even at elevated temperatures. This is probably because MgO and MgO obtained preforms. Although the melting point of MgO is slightly lower than 1273 K (see Fig. 3), the preforms retained their original shapes since they lost their mechanical strengths due to the melting of V2O5. The preforms which retained their shapes were successfully produced in the calcination process by adjusting both the amount of flux and the calcination temperature. Figure 7 presents the appearance and X-ray diffraction patterns of the obtained samples after calcination experiment. As shown in Fig. 6(a), samples (Exp. A-1-Exp. A-4) did not sustain their original shapes, after the calcination process at a constant temperature of 1173 K for 2 h because of melting V2O5 in the feed preforms immediately after starting calcination procedure. Samples with a cationic molar ratio of \( R_{\text{Ca}/V} = 1.5 \) (Exp. A-6 and Exp. A-8) maintained their original shape (see Fig. 6(b)), after the calcination step at temperatures ranging from 873 K to 1173 K in 2 h. In contrast, other samples with \( R_{\text{Ca}/V} = 0.9 \) (Exp. A-5 and Exp. A-7) did not retain their original shapes since they lost their mechanical strengths due to the melting of V2O5. The preforms which retained their shapes were successfully produced in the calcination process by adjusting both the amount of flux and the calcination temperature. Figure 7 presents the appearance and X-ray diffraction patterns of the obtained samples after calcination experiment. The shape and color of the preform were retained after performing calcination at temperatures rising from 873 K to 1173 K in 2 h. By the reaction between V2O5 and the flux, Mg2V2O7 or CaV2O7 were formed in the obtained preforms. Although the melting point of Mg2V2O7 is slightly lower than 1273 K (see Fig. 3), the preforms demonstrated sufficient mechanical strength even at elevated temperatures. This is probably because MgO and Mg3V2O8 in the preforms contribute to maintaining the shape of preforms, and Mg2V2O7 is reduced to V metal or suboxides before melting the parts of preforms. The detail reason is under investigation.

Table 2 Experimental conditions for the reduction experiments, and representative analytical results of vanadium powder obtained after reduction.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Flux</th>
<th>Reductant</th>
<th>Cationic molar ratio, ( R_{\text{Ca}/V} )</th>
<th>Excess reductant ratio, ( R_{\text{R}/V} )</th>
<th>Reduction temperature, ( T_{\text{red}} )/K</th>
<th>Reduction time, ( t_{\text{red}} )/h</th>
<th>Mass of samples, ( w_{\text{i}} )/g</th>
<th>Composition of vanadium powder obtained after reduction, ( C_i )/mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-6-1</td>
<td>MgO</td>
<td>Mg</td>
<td>1.5</td>
<td>2.0</td>
<td>1273</td>
<td>6</td>
<td>3.937</td>
<td>99.7</td>
</tr>
<tr>
<td>A-6-2</td>
<td>MgO</td>
<td>Ca</td>
<td>1.5</td>
<td>2.0</td>
<td>1273</td>
<td>6</td>
<td>3.670</td>
<td>96.0</td>
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<tr>
<td>A-8-1</td>
<td>CaO</td>
<td>Mg</td>
<td>1.5</td>
<td>2.0</td>
<td>1273</td>
<td>6</td>
<td>3.474</td>
<td>2573</td>
</tr>
<tr>
<td>A-8-2</td>
<td>CaO</td>
<td>Ca</td>
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<td>2.0</td>
<td>1273</td>
<td>6</td>
<td>3.604</td>
<td>3976</td>
</tr>
</tbody>
</table>

*1\( R_{\text{Ca}/V} = \frac{x_\text{Ca}}{x_\text{V}} \), mole amounts of cations in flux, \( x_\text{V} \); mole amounts of vanadium

*2Excess reductant ratio: \( R_{\text{R}/V} = \frac{w_\text{R}}{w_\text{R,thc}} \), \( w_\text{R,thc} \): stoichiometic mass of reductant necessary for reduction.

*3Determined by XRF; value excludes carbon and gaseous elements.

Figure 5 Schematic illustration of the experimental setup for (a) the calcination experiment, (b) the reduction experiment.
5.2 Magnesiothermic reduction (Exp. A-6-1 and Exp. A-8-1, reductant: Mg)

Figure 8 illustrates the appearance and the representative XRD patterns of the samples with MgO flux obtained after each step in Exp. A-6-1, and the experimental conditions for reduction experiments are presented in Table 2. The color of the preform changed to a jet-black color after the PRP by Mg vapor at 1273 K for 6 h (Fig. 8(a)), and the shape of the preform was slightly deformed. However, it was easy to recover the preform from the reaction vessel because it was physically isolated from the vessel even after reduction. These results indicate that this PRP is suitable for avoiding contamination from the reaction vessel. During the leaching step in the acetic acid solution, the original shape of the preform was lost and a powder with a grayish black color was obtained without pulverizing the reduced preform (Fig. 8(b)). Figure 8(c) presents an XRD pattern of the preform after reduction at 1273 K for 6 h. All the complex oxides were reduced to V metal by the Mg vapor. The morphology of the sample was sponge like metal powder. A summary of the analytical results of the obtained V powder after reduction as well as of other samples is listed in Table 2. The XRF analysis revealed the purity of the obtained vanadium powder to be 99.7 mass% V, 0.2 mass% Mg, and 0.03 mass% Cr (Exp. A-6-1). In contrast, the preform with CaO flux (Exp. A-8-1) was not completely reduced to V metal. The XRD analysis revealed that the black powder obtained after leaching process consisted of V metal and CaV$_2$O$_4$. This is probably because the calcium complex
oxides (i.e. CaV\(_2\)O\(_4\)) formed in the preform are chemically stable and it becomes difficult to reduce by Mg vapor. The details are unclear at this stage.

5.3 Calciothermic reduction (Exp. A-6-2 and Exp. A-8-2, reductant: Ca)

Figure 9 presents the appearance and the representative XRD patterns of the samples obtained after each step in Exp. A-8-2 with CaO flux. When Ca was employed as the reductant, black solid in the form of flake was obtained after leaching. All of Ca\(_2\)V\(_2\)O\(_7\) was reduced to CaV\(_2\)O\(_4\) with the Ca vapor after reduction, that is, the oxidation state of V changed from +v to +iii. However, metallic V was not produced in the experimental conditions employed in this study. In the same way, V metal was not produced in Exp. A-6-2, in which MgO was used as a flux; rough black powder obtained after leaching was identified as Mg\(_3\)V\(_2\)O\(_8\) (i.e. Mg\(_3\)V\(_2\)O\(_8\)) by XRD analysis. The XRF analysis revealed the purity of the obtained powder in the Exp. A-8-2 and Exp. A-6-2 to be higher than 85 mass% V. It is assumed that a part of
the surface of the obtained powder was reduced to metallic V. At this stage, the reason for the unsuccessful results of calciothermic reduction is not clear. The difference between the results obtained using the Mg and Ca reductants are probably due to the difference in their vapor pressures. The vapor pressure of Mg (0.458 atm) is 26 times larger than that of Ca (0.018 atm) at 1273 K. In fact, the amount of Ca reductant remained in the crucible after the reduction was larger than that of Mg. From a thermodynamic view-point (see Fig. 1), Ca is a more favorable and strong reductant compared to Mg. Therefore, certain kinetic reasons may have hindered the calciothermic reduction of vanadium oxides under PRP employed in this study, e.g., the slow diffusion of Ca in the CaO byproduct formed at the surface of the reduction product, and/or formation of compounds acting as a kinetic barrier.

6. Conclusion

In order to develop a new reduction process for producing fine vanadium powder using the metallothermic reduction, the preform reduction process (PRP) has been applied. slurries obtained by mixing V$_2$O$_5$ powder, a flux (e.g. MgO, CaO) and a binder (e.g. collodion), were cast into molds and then dried to obtain the preforms. Before the reduction process, fabricated preforms with $R_{Ca}/V = 1.5$ were calcined by heating from 873 to 1173 K in 2 h in order to produce the preforms with good mechanical strength at elevated temperatures. The sintered solid preforms containing to complex oxides (Mg$_x$V$_y$O$_z$, Ca$_x$V$_y$O$_z$) were then reacted with Ca or Mg vapor at a constant temperature of 1273 K for 6 h. When Mg vapor was used as a reductant, pure vanadium powder of more than 99 mass% purity was obtained after leaching process. The PRP was thus demonstrated to be suitable for producing a fine, homogeneous metallic vanadium powder.

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