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<tr>
<td>Citation</td>
<td>Mineral Processing and Extractive Metallurgy, 117(2): 108-112</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2008</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/50036">http://hdl.handle.net/2115/50036</a></td>
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<td>MPEM117-2_108-112.pdf</td>
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DIRECT REDUCTION OF VANADIUM OXIDE IN MOLTEN CaCl₂

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Keywords: Calciothermic Reduction, Vanadium Oxide, Molten Salt Electrolysis, Deoxidation

Abstract

A combined process of electrolysis of CaO in the molten CaCl₂ and of calciothermic reduction, so-called OS process, was applied to prepare metallic vanadium directly from V₂O₃. The fine metallic powder containing 1860 mass ppm oxygen was obtained using 0.5mol%CaO-CaCl₂ melt for 10.8 ks at 1173 K. The oxygen level did not decrease further even when twice electricity was applied. Because the metallic vanadium could be electrochemically deoxidized to the level of 10 ppm oxygen from 1.48 %, the large amount of by-product, CaO, due to reduction and the large surface area of the fine particles are the reasons of high oxygen content in the reduced powder.

Introduction

Vanadium is one of the metals that can absorb and release a large amount of hydrogen at room temperature and at ambient pressure. Extremely high pure vanadium has been requested for this purpose. For example, vanadium containing oxygen less than 0.05 mass% is desired, because oxygen significantly damages the property for hydrogen storage [1]. It is reported that the pure vanadium with 200 mass ppm oxygen has four times better hydrogen absorbing capacity than that with 4000 ppm oxygen.

Metallic vanadium with 99% in purity was firstly produced by calciothermic reduction by Marden and Rich [2]. They reacted the mixture of V₂O₅, Ca and CaCl₂ at 1173-1223 K as,

\[ V₂O₅ + 5 \text{Ca} + 5 \text{CaCl}_₂ \rightarrow 2 \text{V} + 5 \text{CaO}.\text{CaCl}_₂. \]  (1)

CaCl₂ was reported as “a kind of the flux that does not concern directly with the reaction”. McKechnie and Seybolt [3] proposed another reaction with a small amount of I₂,

\[ V₂O₅ + 5 \text{Ca} \rightarrow 2 \text{V} + 5 \text{CaO} \]  (2)

I₂ reacts with Ca as

\[ 2 \text{Ca} + \text{I}_₂ \rightarrow 2 \text{CaI}. \]  (3)

It was reported that this exothermic reaction (3) enhanced the reaction (2), that “CaI” decreased the melting point by the reaction with the other nonmetallic elements, and that it removes the
impurities from the bulk. V powder was also produced by sealing $\text{V}_2\text{O}_3$, Ca and $\text{CaCl}_2$ in the vessel [4].

$$\text{V}_2\text{O}_3 + 3 \text{Ca} \rightarrow 2 \text{V} + 3 \text{CaO}$$  \hspace{1cm} (4)

However, the detailed roles of $\text{CaCl}_2$ and CaI were not well discussed. Because about 1.5 to 2 times larger amount of Ca than the theoretical value was needed, the calciothermic reduction was not taken as the practical procedure to form V.

At present, V metal for hydrogen storage was produced by combining the aluminothermic reduction and the successive electron-beam refining (EBR) in vacuum to eliminate the excess Al and the residual oxygen. Highly pure V becomes expensive partially because the EBR consumed a large amount of energy, time and labor.

The purpose of this study is to apply a so-called “OS process” for preparation of V metal. OS process consists of calciothermic reduction of the oxide to metal, dissolution of CaO into molten $\text{CaCl}_2$, and electrolysis. This simple process has been vigorously developed as the titanium production process [5-11]. The dissolution of CaO can enhance the reduction, and it is used for electrolysis to form Ca as reductant. Figure 1 shows the concept of OS process for V production. Here we will propose that it can form V metal directly from the oxides, as the alternative route of the current procedure.

![OS process for V production](image)

**OS process**

**Vanadium Oxide**

There exists many oxides in the binary V-O system, and various oxides are formed corresponding to the oxygen content [12]. The vanadium ore at ambient atmosphere mainly consists of the most stable V$_2$O$_5$, but many other suboxides such as V$_6$O$_{13}$ are mixed. It is well-known that these oxides can be easily reduced to pure $\text{V}_2\text{O}_3$ by hydrogen gas at a temperature as low as 773 K, where the impurity nitrogen can be removed. Therefore, $\text{V}_2\text{O}_3$ is selected as the starting solid oxide in this study. Note that its melting at 2230K is higher than the operation temperature of OS process (1000-1300 K), while $\text{V}_2\text{O}_5$ melts at 963 K.

**Why Calcium and CaCl$_2$?**

Mg, Li and the rare earth metals can be selected as the thermodynamically possible reductant of vanadium oxides in addition to Ca and Al. As mentioned above, Al is not suitable because Al is soluble in solid V to about 30 mass%, while Ca does not dissolve [12]. The reducing ability of
rare earth metals is superior to Ca thermodynamically, but they are too rare and expensive for the economic production of V. Therefore, Ca is expected as the practically strongest media both for reduction and deoxidation directly from the oxide. The calciothermic reduction in OS process is written as,

\[
V_2O_3 + 3 \text{Ca(in CaCl}_2) = V + 3 \text{CaO(in CaCl}_2) \tag{5}
\]

\[
O(\text{in V}) + \text{Ca(in CaCl}_2) = \text{CaO(in CaCl}_2) \tag{6}
\]

where \(O(\text{in V})\) indicates oxygen dissolved in metallic vanadium. The maximum solubility of oxygen in \(\alpha\)-V is 7 mass\% [12]. Ca dissolves a few mol\% in CaCl\(_2\) at 1100-1200 K [13-15], and it is supplied to the oxide. The calciothermic reduction normally forms solid CaO as the by-product, which covers the surface of the formed V particles and hinders from the successive reduction and deoxidation [16,17]. CaO can dissolve to about 20 mol\% at 1100-1200K [18], and the dissolution can physically eliminate the CaO layer. The lower thermochemical activity of CaO can promote both the reactions (5) and (6). Okabe \textit{et al}. succeeded to deoxidize thermochemically and electrochemically the plates and wires of various reactive metals in the molten CaCl\(_2\) [19-21].

**OS Process for V production**

It is favorable that Ca is recycled in a procedure of the calciothermic reduction. The authors propose to apply the in-situ molten salt electrolysis of CaO to recycle Ca from the by-product CaO of the reduction. As shown in Figure 1, calcium dissolving in the salt (will be expressed as Ca), is electrochemically formed in the close vicinity of cathode. When \(V_2O_3\) is injected in this area, the salt containing Ca with a high reducing ability can reduce \(V_2O_3\) to metallic V. The by-product CaO dissolves in CaCl\(_2\), and is decomposed by electrolysis. Oxygen ion is released as CO or CO\(_2\) gas from the carbon anode. The electrochemical reactions in the cell are written as,

\[
\text{Ca}^{2+} + 2 e = \text{Ca} \tag{7}
\]

\[
V_2O_3 + 3 \text{Ca} = V + 3 \text{CaO} \tag{8}
\]

\[
\text{CaO} = \text{Ca}^{2+} + 2 \text{O}^{2-} \tag{9}
\]

\[
\text{O}^{2-} + \text{C} = \text{CO} + 2 e \text{ or } 2 \text{O}^{2-} + \text{C} = \text{CO}_2 + 4 e \tag{10}
\]

The theoretical voltage for CaCl\(_2\) decomposition, \(E^0\), is 3.21 V at 1173 K, which is higher than those for CaO, \textit{i.e.}, 1.63 V for CO\(_2\) gas evolution and 1.54 V for CO gas evolution. Summarizing the above equations, the total reaction becomes carbon reduction.

\[
2 V_2O_3 + 3 \text{C} = 4 V + 3 \text{CO}_2 \tag{11}
\]

Total electricity is an index for Ca formation by electrolysis. Assuming that the whole amount of electrolyzed Ca is consumed for the reduction of \(V_2O_3\), the electricity needed for reduction is hereafter defined as the theoretical amount of electricity, \(Q_0\). Therefore, \(Q_0\) for 1 g \(V_2O_3\) is 3860 C, and it was used as a unit for the experiments.

**Deoxidation Limit**

Oxygen partial pressure \(P_{O_2}\) in equilibrium with Ca and CaO is written by standard free energy of formation of CaO, \(\Delta G^0_{\text{CaO}}\), as,

\[
P_{O_2} = ( a_{\text{Ca}} / a_{\text{CaO}} )^2 \exp( 2 \Delta G^0_{\text{CaO}} / RT ) \tag{7}
\]
Molar fraction of oxygen in solid V, $X_O$, is reported as [22],

$$\log_{10} [X_O] = \frac{1}{2} \log_{10} P_{O_2} - 7.73 + 22050 / T \ (873 < T < 1423, X_O < 0.03). \quad (8)$$

$a_{CaO}$, $a_{Ca}$, $R$, and $T$ are thermochemical activities of CaO and Ca, gas constant and temperature, respectively. Therefore, $X_O$ is determined by the activity ratio, $r (=a_{Ca}/a_{CaO})$, at a constant temperature. $a_{CaO}$ and $a_{Ca}$ are normally less than 1 in OS process[5-11]. Figure 2 shows the oxygen concentration evaluated as a function of temperature and the activity ratio, $r$. For example, the deoxidation limit is $4 \times 10^2$ mass ppb at $1173K$ and $r = 5$. Therefore, even if $a_{Ca}<1$, we can keep $a_{CaO}<<1$ to produce highly deoxidized V metal.

![Figure 2. Oxygen concentration in $\alpha$-V as a function of temperature.](image)

**Experimental**

Figure 3 shows the experimental arrangement for the simultaneous reactions, i.e., reduction and in situ electrolysis. A carbon rod (10mm in diameter, 250mm in length) and a pure Ti net (#100 mesh) were used for the anode and cathode materials, respectively. The Ti net was doubly wound like cylinder (8 mm I.D. and about 40 mm in length) and tightened by thin Ti wires. About 2 g $V_2O_5$ powder (>99 pct, primary particle size: <1 µm) was filled in this basket-type cathode. The cathode was connected with a Ti rod (10 mm O.D.) and lead to the power supply. It was reported that Ti was tight for OS process and does not react with Ca [7-9,23].

![Fig. 3 Experimental arrangement.](image)
818g of anhydrate CaCl₂ (>99 %) and 1.975g CaO (99 %, calcined at 1473 K in air) were filled in an yttria crucible (99.0 %, 100 mm O.D., 90 mm I.D. and 200 mm in depth) to be 0.5mol%CaO, and heated in vacuum at 623-773 K overnight. It was then melted in a purified Ar gas atmosphere. The depth of molten salt was about 60 mm. After pre-electrolysis for water elimination, the basket-type cathode was immersed in the salt (about 40-55 mm in depth), held at 1173±5 K in Ar gas. DC current was supplied under a constant voltage of 3.0 V [7]. The gas evolving was trapped in an aqueous solution containing Ca(OH)₂ to detect CO₂ gas. Because 818g of CaCl₂ was used, 5.63x10⁴ C is needed to saturate Ca in the molten salt. This electricity corresponds to 14.6 Q₀, when we assume that 1g of V₂O₃ is used. After electrolysis, the cathode was taken out of the melt and cooled down in Ar gas at the upper part of the furnace. The solidified salt in the basket-type cathode was leached in the flow of drinking water. The black V powder was subsequently rinsed with dilute HCl or acetic acid, distilled water and alcohol, in that order, and then dried in vacuum for analysis. The obtained powder was identified by X-ray diffraction (XRD) measurement. The oxygen concentration was analyzed by an inert gas fusion-infrared absorption method. The morphology and titanium concentration were analyzed using a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyzer.

Reduction from V₂O₃

Just after starting the electrolysis, a gas containing CO₂ was significantly evolved. A black substance started to cover the surface of the molten salt after 1.8 ks. This was identified as the mixture of carbon and CO₃ by XRD. A part of carbon was released from the anode surface, and another was due to reduction of CO/CO₂ gas by Ca, because the supplied electricity Q exceeded Q₀. The Ti basket became brittle and a part of it changed to TiC or a lower Ti oxide, identified by XRD. These phenomena were also reported previously [7,8].

Obtained powder

Table 1 shows the experimental conditions, the phase identification by XRD and the analyzed oxygen concentration (Figure 4). The recovered samples were gray powder of metallic V. Sample #1 contained a small amount of suboxide because the reduction time was short. When the time was too long (Sample #4), the powder was well sintered as a cylinder in the basket. Figure 5 shows the SEM images of the obtained powders. V particles were 0.5-a few μm in diameter, and sintered like a sponge as the time was longer.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conditions</th>
<th>Impurity concentration</th>
<th>Phase identification by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (ks)</td>
<td>Quantity of electricity (C)</td>
<td>Oxygen (mass ppm)</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>0</td>
<td>0</td>
<td>345700</td>
</tr>
<tr>
<td>#1</td>
<td>1.8</td>
<td>4108 (0.98Q₀)</td>
<td>30586</td>
</tr>
<tr>
<td>#2</td>
<td>3.6</td>
<td>5854 (1.37Q₀)</td>
<td>4995</td>
</tr>
<tr>
<td>#3</td>
<td>10.8</td>
<td>11216 (2.91Q₀)</td>
<td>1859</td>
</tr>
<tr>
<td>#4</td>
<td>21.6</td>
<td>24049 (5.92Q₀)</td>
<td>1974</td>
</tr>
</tbody>
</table>
Oxygen concentration

As shown in Figure 4, the oxygen concentration in the obtained V powder decreased when the reaction time became longer. It arrived at 1860 mass ppm oxygen after electrolysis for 10.8 ks. However, it did not reach the level of a few ppb as expected thermodynamically, and it increased slightly even when the sample #4 (21.6 ks) was exposed to an enough amount of electricity. This phenomenon was previously reported in calciothermic reduction of Nb and Ta oxides in the molten CaCl₂ [24].

The three possible reasons are the imperfect removal of CaO, the surface oxidation during handling, and the local equilibrium between Ca and CaO in the vicinity of cathode.

First, the existence of CaO in the rinsed powder was not found by XRD and EDX analysis, although the Ca concentration could not be analyzed wet-chemically.

Second, the fine V powder was reported as the sensitive against oxidation [25,26], it may be possible that the oxidation proceeded during leaching and handling in open air. As shown in Figure 5, the obtained powder had a very fine structure with open porosity and a large surface area.

Third, the thermochemical reasons are inspected. As discussed above, the activity ratio \( r = \frac{a_{\text{Ca}}}{a_{\text{CaO}}} \) is an index for oxygen concentration if thermodynamic equilibrium is established. If the oxygen concentration is 2000 mass ppm, \( r \) is evaluated as \( 9.37 \times 10^{-8} \) at 1173 K. In reduction of \( \text{V}_2\text{O}_3 \), a large amount of Ca is consumed just after immersing the oxide, and a large amount of CaO is formed. When 1g of \( \text{V}_2\text{O}_3 \) is reduced, it is evaluated that a volume of \( 4.46 \text{ cm}^3 \) in molten
CaCl$_2$ saturates with CaO. This volume (12mm in diameter, 40mm in height) is larger than the cathodic cylinder (8mm in diameter, 40mm in height). This means that the vicinity of cathode becomes CaO saturation during reduction process, and that the thermochemical activity of CaO remains high, if CaO dissolution does not proceed quickly [27]. Therefore, the ratio $r$ might be smaller than that expected. If V$_2$O$_5$ were applied as the alternative with V$_2$O$_3$, the oxygen content in the reduced powder would be higher.

**Contamination**

Titanium homogeneously dispersed as impurity in the powder, and its concentration increased as the reaction time was longer (Table 1). Because V and Ti are completely soluble, Ti diffused from the net into V particles. Some amount of Ti precipitated on the cathode (Sample #3) because Ti reference electrode was used to check the electrochemical potential. Because Ti can thermochemically reduce V$_2$O$_3$, Ti may contribute partially to decrease the oxygen concentration. Therefore, for example, a V net is needed to seek for high purity. In case of stainless steel net, the contamination of Fe, Ni and Cr was not detected. This is partially because the stainless steel does not reduce V$_2$O$_3$.

Carbon contamination was not clearly found. Because CO and CO$_2$ gas could be reduced to carbon by the excess calcium, the formed carbon polluted the metallic product [7,8].

**Deoxidation from V**

Deoxidation from the reduced powder may become realized by decreasing the chemical activity of CaO if we can remove CaO more efficiently after reduction. Assuming that CaO was once separated from the reduced powder in a wet-chemical process, and that the particle size were coarsened, the below-mentioned deoxidation using the similar experimental setup can be applied to match with the market demand. Okabe *et al.* reported that both the halide flux deoxidation and the electrochemical deoxidation were effective to obtain Ti and Y with the extra-low oxygen [19-21,28,29].

1g of a commercial V powder (<125μm) was naturally oxidized to 1.45 mass%, and filled in the Ti basket. Table 2 shows the experimental conditions and results. When the initial CaO content was high, the black substance containing carbon, CaCO$_3$ and Ca covered the melt surface. All the samples evolved hydrogen gas in leaching, and their oxygen concentrations were lower than the starting powder. They decreased to a level of 10 ppm, which was far lower than 500 mass ppm in the sample purified 3 times in EBM.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CaO content in CaCl$_2$ (mol%)</th>
<th>Time (ks)</th>
<th>Average current density (A/cm$^2$)</th>
<th>Quantity of electricity $Q$ (C)</th>
<th>$Q / Q_0$</th>
<th>Impurity concentration (mass ppm)</th>
<th>Oxygen</th>
<th>Nitrogen</th>
<th>Carbon</th>
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<tr>
<td>#V0</td>
<td>14500</td>
<td>0</td>
<td></td>
<td>2593</td>
<td>143</td>
<td></td>
<td>10</td>
<td>2314</td>
<td>118</td>
</tr>
<tr>
<td>#V1</td>
<td>0.5</td>
<td>32.4</td>
<td>0.0326</td>
<td>12483</td>
<td>54.9</td>
<td>10</td>
<td>2314</td>
<td>2743</td>
<td>2346</td>
</tr>
<tr>
<td>#V2</td>
<td>3</td>
<td>10.8</td>
<td>0.2263</td>
<td>28868</td>
<td>144.8</td>
<td>36</td>
<td>2743</td>
<td>2346</td>
<td></td>
</tr>
<tr>
<td>#V3</td>
<td>15</td>
<td>10.8</td>
<td>0.3786</td>
<td>48294</td>
<td>261.7</td>
<td>173</td>
<td>2920</td>
<td>682</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6 shows the relationship between the supplied electricity $Q$ and the oxygen concentration in V. The oxygen concentration did not depend on electricity and it decreased as the CaO concentration in the molten CaCl$_2$ was lower. When the CaO concentration was high, the activity of Ca became high, but that of CaO was also high. Therefore, the activity ratio $r$ did not decrease locally and the deoxidation (Eq.(6)) did not work efficiently. It may be effective to decrease the CaO concentration near the cathode.

Figure 7 shows the SEM image of the powder for deoxidation experiment. The primary particle size was about 10 times larger than that shown in Figure 5, and the surface area was about 100 times smaller. If the thickness of oxide film on the particle surface is the same, the analytical oxygen concentration of the reduced powder becomes about 100 times higher than that of the commercial powder deoxidized in the molten CaCl$_2$. Therefore, the contribution of the surface oxidation during handling is also large like the contribution of the high CaO concentration near the oxide.
Practical Model

Figure 8 shows a model for practical application. The oxygen ionic conductor, ZrO$_2$, seems attractive to suppress carbon contamination in OS process, because it can separate CO or CO$_2$ gas from the molten salt [30,31]. As shown in Fig. 8, these gases will be released outside of the ZrO$_2$ membrane, and the current efficiency will be improved. A continuous operation from V$_2$O$_3$ to metallic V powder is the first step, and the extracted powder will be sent to another vessel in order to keep CaO concentration low for deoxidation. The difference from FFC process [32-34] should be studied further, because it is also operated in the molten CaCl$_2$ for oxygen extraction.

![Figure 8. Future model for industrial application.](image)

Conclusion

This study proposes the application of OS process for production of high purity vanadium, and confirmed experimentally. The reduction of V$_2$O$_3$ was completed for 1.8 ks at 1173 K when 3.0 V was applied to the molten 0.5mol%CaO-CaCl$_2$. A fine powder with low oxygen content such as 1860 ppm was obtained for 10.8 ks. When the metallic powder with coarse gain containing 1.48mass% oxygen was immersed in the same experimental apparatus, the oxygen content decreased to 10 ppm. It is necessary to keep the CaO concentration low for better deoxidation.

Acknowledgement

The authors thank to Mr. K. Naito and M. Unesaki for their experimental assistance. This work was financially supported in part by Grants-in-Aid for Scientific Research under Contract No.14205109.

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