



Title	Direct reduction of vanadium oxide in molten CaCl ₂
Author(s)	Suzuki, Ryosuke O.; Ishikawa, Hiroyuki
Citation	Mineral Processing and Extractive Metallurgy, 117(2), 108-112 https://doi.org/10.1179/174328508X290894
Issue Date	2008
Doc URL	http://hdl.handle.net/2115/50036
Type	article (author version)
File Information	MPEM117-2_108-112.pdf



[Instructions for use](#)

DIRECT REDUCTION OF VANADIUM OXIDE IN MOLTEN CaCl_2

Ryosuke O. Suzuki¹ and Hiroyuki Ishikawa²

¹Department of Energy Science and Technology, Kyoto University;
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan,
Currently, Department of Material Science, Hokkaido Univ.,
N13W8 Kita-ku, Sapporo, Hokkaido 060-8628 Japan

²Undergraduate Student, Faculty of Engineering, Kyoto University;
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan,

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

Abstract

A combined process of electrolysis of CaO in the molten CaCl_2 and of calciothermic reduction, so-called OS process, was applied to prepare metallic vanadium directly from V_2O_3 . The fine metallic powder containing 1860 mass ppm oxygen was obtained using 0.5mol% CaO- CaCl_2 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 V_2O_5 , Ca and CaCl_2 at 1173-1223 K as,



CaCl_2 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 I_2 ,



I_2 reacts with Ca as



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 V_2O_3 , Ca and $CaCl_2$ in the vessel [4].



However, the detailed roles of $CaCl_2$ 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 $CaCl_2$, 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.

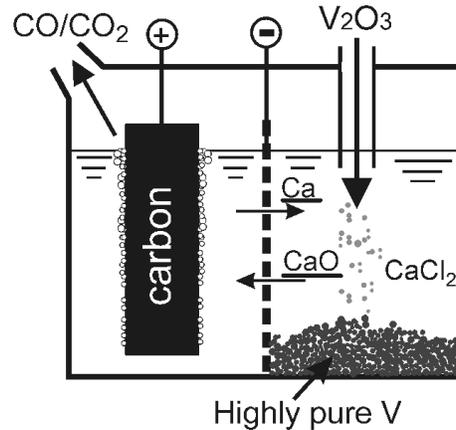


Figure 1. Concept of OS process for V production.

OS process

Vanadium Oxide

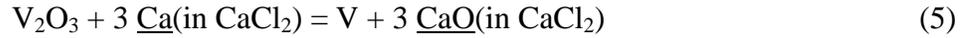
There exists many oxides in the binary V-O system, and various oxides are formed corresponding to the oxygen content [12]. The vanadium ore at ambient atmosphere mainly consists of the most stable V_2O_5 , but many other suboxides such as V_6O_{13} are mixed. It is well-known that these oxides can be easily reduced to pure V_2O_3 by hydrogen gas at a temperature as low as 773 K, where the impurity nitrogen can be removed. Therefore, V_2O_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 V_2O_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,



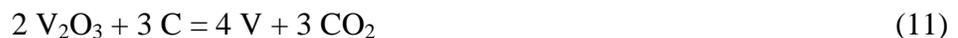
where $\underline{\text{O}}(\text{in V})$ indicates oxygen dissolved in metallic vanadium. The maximum solubility of oxygen in α -V is 7 mass% [12]. Ca dissolves a few mol% in CaCl_2 at 1100-1200 K [13-15], and it is supplied to the oxide. The calciothermic reduction normally forms solid CaO as the by-product, 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 *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 $\underline{\text{Ca}}$), is electrochemically formed in the close vicinity of cathode. When V_2O_3 is injected in this area, the salt containing $\underline{\text{Ca}}$ 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,



The theoretical voltage for CaCl_2 decomposition, E^0 , is 3.21 V at 1173 K, which is higher than those for CaO, *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.



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, ΔG^0_{CaO} , as,

$$P_{\text{O}_2} = (a_{\text{Ca}}/a_{\text{CaO}})^{-2} \exp(2 \Delta G^0_{\text{CaO}}/RT) \quad (7)$$

Molar fraction of oxygen in solid V, X_O , is reported as [22],

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

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 4×10^{-2} mass ppb at 1173K and $r = 5$. Therefore, even if $a_{Ca} < 1$, we can keep $a_{CaO} \ll 1$ to produce highly deoxidized V metal.

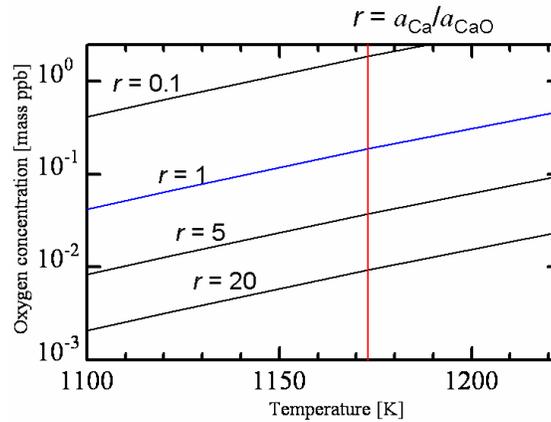


Figure 2. Oxygen concentration in α -V as a function of temperature.

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].

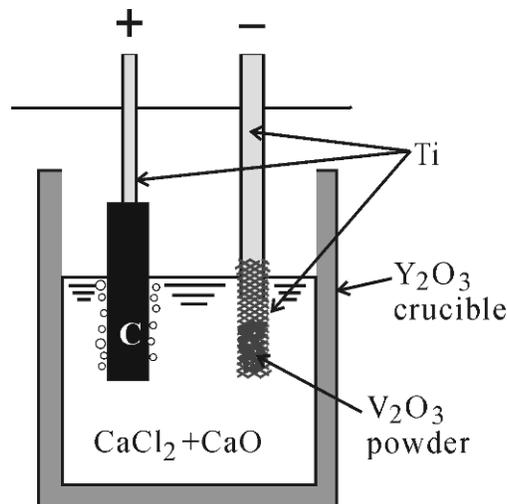


Fig. 3 Experimental arrangement.

818g of anhydrate CaCl_2 (>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 $\text{Ca}(\text{OH})_2$ to detect CO_2 gas. Because 818g of CaCl_2 was used, $5.63 \times 10^4 \text{C}$ is needed to saturate Ca in the molten salt. This electricity corresponds to $14.6 Q_0$, when we assume that 1g of V_2O_3 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 V_2O_3

Just after starting the electrolysis, a gas containing CO_2 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 CO_3 by XRD. A part of carbon was released from the anode surface, and another was due to reduction of CO/CO_2 gas by Ca, because the supplied electricity Q exceeded Q_0 . 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 1 Experimental conditions and results.

Sample No.	Conditions		Impurity concentration			Phase identification by XRD
	Time (ks)	Quantity of electricity (C)	Oxygen (mass ppm)	Carbon (mass ppm)	Titanium (mol %)	
V_2O_3	0	0	345700	118	NA	V_2O_3
[#1]	1.8	4108 (0.98 Q_0)	30586	1794	0.85	V, V_3O_5 , $\text{V}_{16}\text{O}_{37}$?
[#2]	3.6	5854 (1.37 Q_0)	4995	996	1.40	V
[#3]	10.8	11216 (2.91 Q_0)	1859	593	5.38	V
[#4]	21.6	24049 (5.92 Q_0)	1974	1154	1.66	V

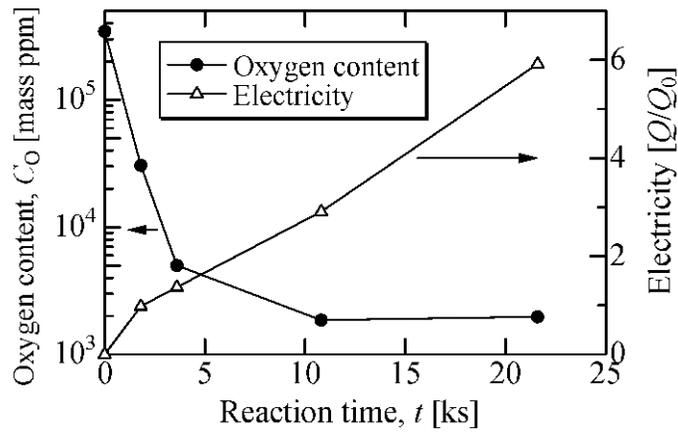


Figure 4. Oxygen concentration in the obtained powders.

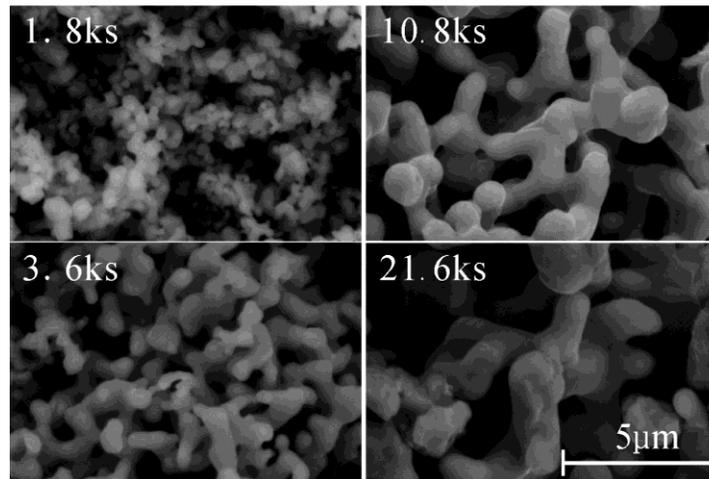


Figure 5. SEM images of the obtained V particles.

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 CaCl_2 [24].

The three possible reasons are the imperfect removal of CaO, the surface oxidation during handling, and the local equilibrium between $\underline{\text{Ca}}$ and $\underline{\text{CaO}}$ 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 $r (= a_{\text{Ca}} / a_{\text{CaO}})$ is an index for oxygen concentration if thermodynamic equilibrium is established. If the oxygen concentration is 2000 mass ppm, r is evaluated as 9.37×10^{-8} at 1173 K. In reduction of V_2O_3 , a large amount of $\underline{\text{Ca}}$ is consumed just after immersing the oxide, and a large amount of CaO is formed. When 1g of V_2O_3 is reduced, it is evaluated that a volume of 4.46 cm^3 in molten

CaCl₂ 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 V₂O₅ were applied as the alternative with V₂O₃, 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 V₂O₃, 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 V₂O₃.

Carbon contamination was not clearly found. Because CO and CO₂ 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, CaCO₃ 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 2 Experimental conditions and results.

Sample No.	CaO content in CaCl ₂ (mol%)	Time (ks)	Average current density (A / cm ²)	Quantity of electricity		Impurity concentration (mass ppm)		
				Q (C)	Q / Q_0	Oxygen	Nitrogen	Carbon
#V0		0				14500	2593	143
#V1	0.5	32.4	0.0326	12483	54.9	10	2314	118
#V2	3	10.8	0.2263	28868	144.8	36	2743	2346
#V3	15	10.8	0.3786	48294	261.7	173	2920	682

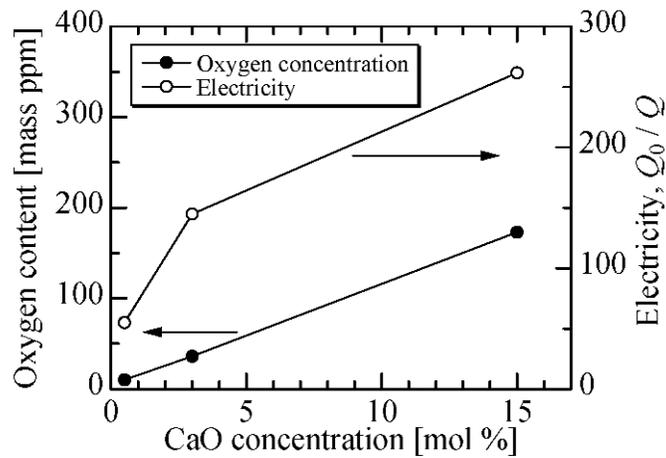


Figure 6. Oxygen concentration and charged electricity.

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.

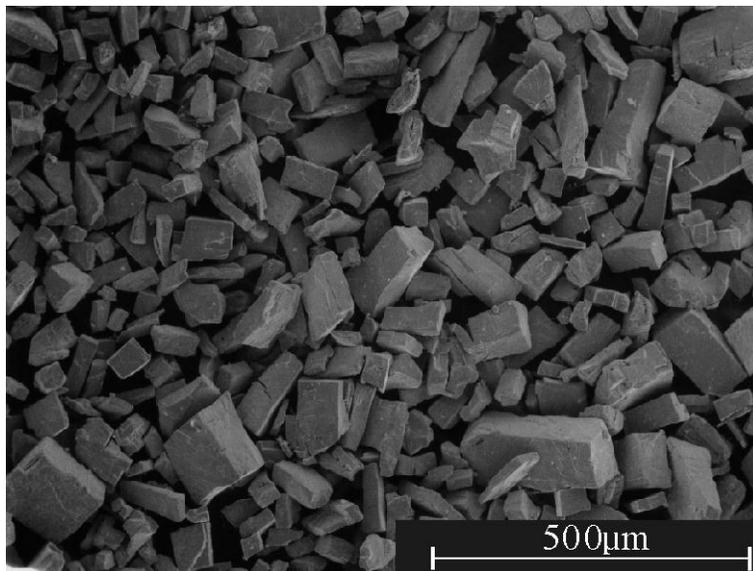


Figure 7. Starting powder for deoxidation.

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_2O_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.

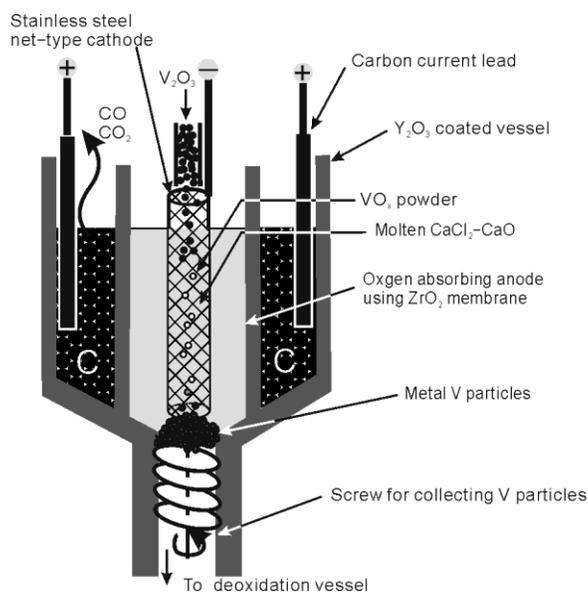


Figure 8. Future model for industrial application.

Conclusion

This study proposes the application of OS process for production of high purity vanadium, and confirmed experimentally. The reduction of V_2O_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 grain 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.

References

- [1] M. Tsukahara et al., "Influence of oxygen on hydrogen storage and electrode properties for micro-designed V-based battery alloys", *J. Alloys. Comp.*, 265(1998), 257-263.
- [2] J. W. Marden and M. N. Rich, *Ind. Eng. Chem.*, 19 (7) (1927), 786-788.
- [3] R. K. McKechnie and A. U. Seybolt, *J. Electrochem. Soc.*, 97 (10) (1950), 311-315.
- [4] C. Tyzach and P. G. England, *Extraction and Refining of the Rarer Metals*, (London, The Institution of Mining and Metallurgy, 1957), pp.175-195.

- [5] K. Ono and R. O. Suzuki, "Titanium Production From Oxide Using Reducible Molten Salt", *Materia Japan*, 41 (1) (2002), 28-31.
- [6] K. Ono and R. O. Suzuki, "A New Concept of Sponge Titanium Production by Calciothermic Reduction of Titanium Dioxide in Molten Calcium Chloride", *JOM Mem. J. Min. Met. Mater. Soc.*, 54 (2) (2002), 59-61.
- [7] R. O. Suzuki, K. Teranuma and K. Ono, "Calciothermic Reduction of Titanium Oxide and in-situ Electrolysis in Molten CaCl₂", *Metall. Mater. Trans. B* 34B (2003), 287-295.
- [8] R. O. Suzuki and S. Fukui, "Reduction of TiO₂ in the Molten CaCl₂ by Ca Deposited during CaO Electrolysis", *Mater. Trans.*, 45 (5) (2004), 1665-1671.
- [9] R. O. Suzuki, "Calciothermic Reduction of TiO₂ and in-situ Electrolysis of CaO in the Molten CaCl₂", *J. Phys. Chem. Solids*, 66 (2-4) (2004), 461-465.
- [10] R. O. Suzuki and K. Ono, "New Titanium Smelting Processes under Development", *Titanium Japan*, 50 (2) (2002), 105-108.
- [11] R. O. Suzuki, "OS Process - Thermo-Electro-chemical Reduction of TiO₂ in the Molten CaCl₂" *Ti-2003 Science and Technology*, Vol.1, ed.by G.Luetjering and J.Albrecht, (Weinheim, Germany: Wiley-VCH, 2004), 245-252.
- [12] J. F. Smith ed., *Phase Diagram of Binary Vanadium Alloys*, (Metals Park, OH: ASM International, 1989).
- [13] D. T. Peterson and J. A. Hinkelbein, "Equilibria in the Reaction of Barium with Calcium Chloride", *J. Phys. Chem.*, 63 (9) (1959), 1360-63.
- [14] R. A. Sharma, "Solubilities of Calcium in Liquid Calcium Chloride in Equilibrium with Calcium-copper Alloys", *J. Phys. Chem.*, 74 (22) (1970), 3896-3900.
- [15] V. Dosaj, Ch. Aksaranan and D. R. Morris, *J. Chem. Soc. Faraday Trans.*, 71 (1975), 1083-1098.
- [16] K. Ono, et al., "Production of Titanium Powders by the Calciothermic Reduction of TiO₂", *J. Iron & Steel Inst. Jpn.*, 76 (4) (1990), 568-575.
- [17] R. O. Suzuki, "Preparation of Intermetallic Compounds by the Calciothermic Reaction", *J. Adv. Sci.*, 1 (1) (1989), 69-73.
- [18] D. A. Wenz, I. Johnson and R. D. Wolson, "CaCl₂-rich region of the CaCl₂-CaF₂-CaO system", *J. Chem. Eng. Data*, 14 (2) (1969), 250-252.
- [19] T. H. Okabe, et al., "Production of Extra Low Oxygen Titanium by the Calcium-Halide Flux Deoxidation", *J. Iron & Steel Inst. Jpn.* 77 (1) (1991) 93-99.
- [20] T. H. Okabe, et al., *Metall. Trans. B*, 24B (1993), 449-456.
- [21] K. Hirota, et al., "Electrochemical deoxidation of RE-O (RE=Gd, Tb, Dy, Er) solid solutions", *J. Alloys Comp.*, 282 (1999), 101-108.
- [22] G. Hörz, et al., eds., "Physics Data, Gases and Carbon in Metals, Pt.VII: Group VA Metals(1), Vanadium", (Karlsruhe, Stuttgart, Germany, 1981).
- [23] R. O. Suzuki and S. Inoue, "Calciothermic Reduction of Titanium Oxide in Molten CaCl₂", *Metall. Mater. Trans. B*, 34B (3) (2003), 277-286.
- [24] M. Baba, Y. Ono, and R. O. Suzuki, "Tantalum and Niobium Powder Preparation from Their Oxides by Calciothermic Reduction in the Molten CaCl₂", *J. Phys. Chem. Solids*, 66 (2-4) (2004), 466-470.
- [25] R. R. Moskalyk and A. M. Alfantazi, "Processing of vanadium: a review", *Minerals Engineering*, 16 (9) (2003), 793-805.
- [26] H. Kaneko, *Rare Metals*, (Tokyo, Japan: Morikita-Press, 1990) 163-167
- [27] R. O. Suzuki and Y. Maki, "Dissolution Rate of CaO in Molten CaCl₂", *Met.Mater.Trans. B*, (2005) submitted.
- [28] T. H. Okabe, T. Oishi and K. Ono, "Preparation and characterization of extra-low-oxygen titanium", *J. Alloys. Comp.*, 184 (1) (1992), 43-56.
- [29] T. H. Okabe, et al., "Electrochemical deoxidation of yttrium-oxygen solid solutions", *J. Alloys. Comp.*, 237 (1-2) (1996), 150-154.

- [30] P. D. Ferro, et al., "Application of ceramic membrane in molten salt electrolysis of CaO-CaCl₂", *Waste Management*, 17 (7) (1997), 451-461.
- [31] P. D. Ferro, et al., *Trans. Indian Inst. Met.*, 51 (1998), 69-77.
- [32] G. Z. Chen, D. J. Fray, and T. W. Farthing, "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride", *Nature*, 407 (2000), 361-364.
- [33] G. Z. Chen, D. J. Fray, and T. W. Farthing, "Cathodic Deoxygenation of the Alpha Case on Titanium and Alloys in Molten Calcium Chloride", *Metall. Mater. Trans. B*, 32B (6) (2001), 1041-1052.
- [34] D. J. Fray, "Emerging Molten Salt Technologies for Metals Production", *JOM Mem. J. Min. Met. Mater. Soc.*, 53 (10) (2001), 26-31.