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Direct Reduction of Vanadium Oxide in Molten $CaCl_2$

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A process consisted of CaO electrolysis and calciothermic reduction in the molten $CaCl_2$ was applied to prepare metallic vanadium directly from V_2O_3. The fine metallic powder containing 1860 mass ppm oxygen was successfully obtained using 0.5mol%CaO-$CaCl_2$ melt for 10.8 ks at 1173 K. The oxygen level from the oxide fitted with the demand for hydrogen storage application, but it remained nearly constant even when twice the electricity was supplied. The commercial grade powder containing 1.48% oxygen was, however, well deoxidized to 10 ppm. The large amount of by-product, CaO, due to reduction and the large surface area of the fine particles are the possible reasons of high oxygen content in the reduced powder.

Introduction

Vanadium is one of a few elements that can absorb and/or release gaseous hydrogen at room temperature and at the ambient pressure. Its application as hydrogen storage material is, however, limited because the dissolved oxygen with a high concentration worsens the properties. For example, it was reported that pure vanadium containing 4000 mass ppm oxygen was about four times worse in hydrogen absorption capacity than that containing 360 ppm oxygen (1-3). Many alloys based on vanadium have been alternatively developed to minimize the oxygen contamination. The low oxygen concentration in these alloys is therefore essential to realize their good hydrogen storage properties.

In the industry, vanadium metal is produced starting from V_2O_5 by aluminothermic reduction, and the residual aluminum and oxygen in the obtained metal ingot are subsequently removed in vacuum as Al(gas) or AlO(gas) by melting the electron beam melting (EBM) (3-5). The alminothermic reduction often uses the Al scraps coming from the waste of Al cans, and it is industrially reasonable process due to exothermic reaction. However, the subsequent separations of residual Al and oxygen from V-Al alloy ingot costs much higher because of the huge energy consumption of EBM (4).

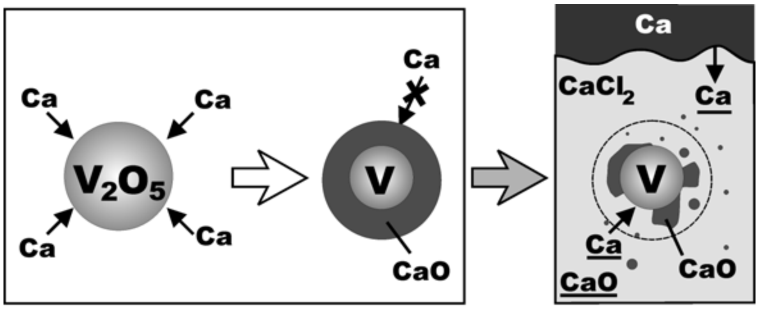
The electrolysis of VCl_2 in the molten LiCl-KCl bath has shown (6,7) that a high purity of V could be deposited on the cathode with a good efficiency. However, the anode containing 94%V was required. It is noted that the anode was formed through a long sequence of the carbothermic reduction of V_2O_5 and the subsequent nitridation and denitridation above 2000 K.

The authors report the calciothermic reduction directly from the oxide using the molten $CaCl_2$ and the CaO electrolysis. This process is called the OS process and it is applicable to Ti, Ta, Nb, Zr, Fe, Cr, etc (8-12). It is expected that this process can save the energy consumption because of direct reduction to oxygen free metal. It consists of two mechanisms in a single bath of $CaCl_2$ melt: the calciothermic reduction of the starting oxide and the electrolysis of the by-product CaO in the molten $CaCl_2$.

In 1927, Marden and Rich (13) firstly reported the calciothermic reduction (reaction using calcium as reductant) in vanadium production, and they reported that 99% pure metallic vanadium was successfully formed when using $CaCl_2$. They suggested that $CaCl_2.CaO$ was formed as,

$$V_2O_5 + Ca + CaCl_2 = V + CaCl_2.CaO \qquad [1]$$

They reported that $CaCl_2$ was a kind of non-reactive substance for the reduction. It is noted that the chemical formula of $CaCl_2.CaO$ is currently believed not to form (14-16). In our recent studies (8-12, 17-21), it is clarified that the molten $CaCl_2$ is a suitable media for the calciothermic reaction to dissolve Ca (as the reductant, see Fig.1(b)) and to remove CaO from the metallic oxides (see Fig.1(a)), because the molten $CaCl_2$ can coexist with metallic Ca as illustrated in Fig.1(b), and because it can dissolve a few mol%Ca and about 20 mol%CaO (14-16, 22-28).



(a) (b)

Figure 1. Calciothermic reduction (a) and reduction in the molten $CaCl_2$ (b).

The dissolution of CaO enhances the reaction as shown in Fig.1, and the dissolved CaO is recycled to metallic Ca when using the molten salt electrolysis simultaneously operating, as shown in Fig.2. This calciothermic reduction accompanying with molten salt electrolysis was successfully applied, for example, to produce Ti from TiO_2 (8-12).

The purpose of this work is to prepare pure V from its oxides using OS process for hydrogen storage application of vanadium. This fundamental study will be expanded to the direct alloy formation from the oxide mixture, for example, to form V-Ti-Cr hydrogen storage alloy powder directly from their oxides (18,19,29). Comparing with TiO_2, the raw oxide, V_2O_5, contains larger amount of oxygen per unit molar metal. Therefore, the larger amount of oxygen should be removed from this oxide to obtain a good quality of pure vanadium.

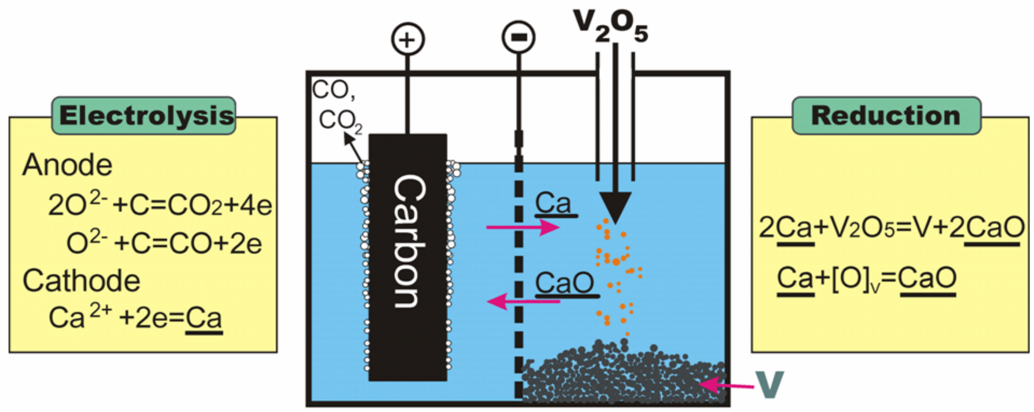


Figure 2. Concept of OS process (Mark 3) for V_2O_5 reduction in the molten $CaCl_2$.

The reactions in the bath are written as,

$$Ca^{2+} + 2\ e = \underline{Ca} \qquad [2]$$
$$V_2O_5 + 3\ \underline{Ca} = V + 3\ \underline{CaO} \qquad [3]$$
$$\underline{CaO} = Ca^{2+} + 2\ O^{2-} \qquad [4]$$
$$O^{2-} + C = CO + 2\ e \text{ or } 2\ O^{2-} + C = CO_2 + 4\ e \qquad [5]$$

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 and 1.54 V for CO_2 and CO gas evolution, respectively (8-12). As shown in Fig.3, even if we consider the decrease of thermochemical activity of CaO, a_{CaO}, due to dissolution in the molten $CaCl_2$, we can open the window for electrolysis of CaO above the theoretical decomposition voltage of CaO and below that of $CaCl_2$.

As shown in Fig.4, the most stable oxide, V_2O_5, melts below the melting temperature of $CaCl_2$. The liquid electrode was industrially used in the Al production, but it is different that the liquid oxide electrode changes to the metallic solid, while the Al liquid was kept during the whole electrolysis. The alternative oxide such as V_2O_3 was also tested. The

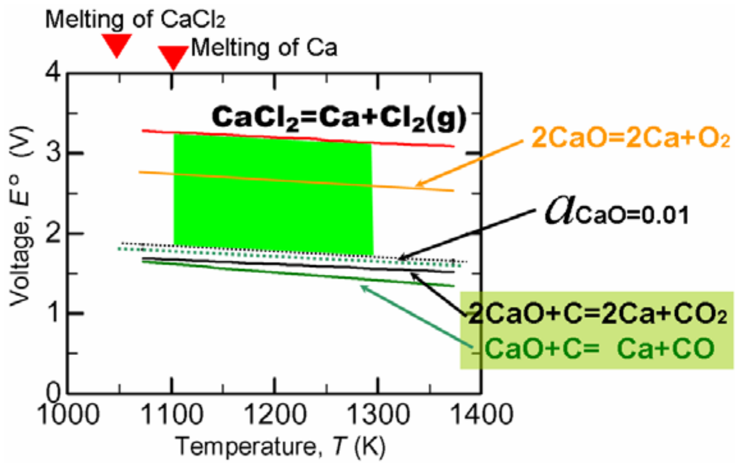


Figure 3. Theoretical decomposition voltage of CaO and $CaCl_2$. When carbon is used as anode, the voltage can be lowered by about 1.0 V (8-12).

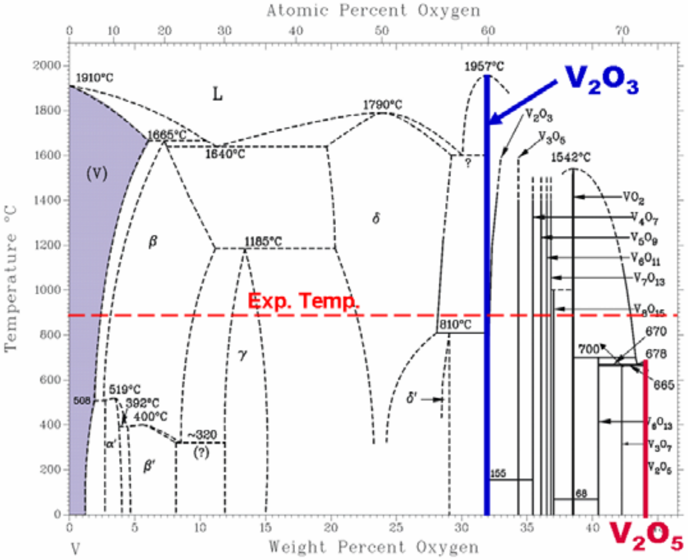


Figure 4. Phase diagram of the binary V-O system (30).

incongruent melting temperature of V_2O_3 is enough high, and V_2O_3 can be formed by hydrogen gas reduction at the lower temperatures from V_2O_5.

Reduction from V_2O_5

About 6 mol $CaCl_2$ was melted in the Y_2O_3 crucible (99%, 100 mm O.D. and 250 mm in length) with a small amount of CaO to be $CaCl_2$-0.5mol%CaO in Ar gas atmosphere. The anode and the basket-like cathode consisted of carbon bar (12 mm in diameter) and of Ti net (100 mesh), respectively. The voltage of 2.0-3.2 V was applied between these two electrodes for CaO decomposition at 1173 K. The oxide powder was continuously dropped from the top of stainless tube into the Ti cathode to be reduced by the dissolved Ca in the vicinity of the cathode.

After 10.8 ks at 1173 K, the electrodes were pulled up and cooled above the salt in Ar. The solidified salt with the cathode was removed by water, and the samples in the Ti basket cathode were rinsed by acetic acid aqueous solution, distilled water and alcohol in this order. They were dried and kept in vacuum before analysis.

As shown in Fig. 5, the samples obtained in the cathode was classified into two parts by the positions at the cathode; the black powder at the bottom part and the gray power at the upper part (partially in the stainless tube). The former was identified as pure V by X-ray diffraction (XRD) measurement. Oxygen analysis using LECO TC-500 analyzer showed that the black powder contained 0.43 mass% oxygen. However, the powder recovered from the upper part was identified as the mixture of V and CaV_2O_4 by XRD measurement, and it contained 7 mass% oxygen. It is certain that a part of oxide powder was melted inside the stainless tube to V_2O_5 liquid, and that it blocked the additional charge from the upper part. Some amount of the molten salt and the dissolved Ca leached into the piled oxide liquid, and the liquid vanadium oxide was reduced to metal or partially reduced to the complex oxide, CaV_2O_4, after reacting with the residual CaO. Note that CaV_2O_4 can be written as $CaO.V_2O_3$ in which the valence of V should be +3.

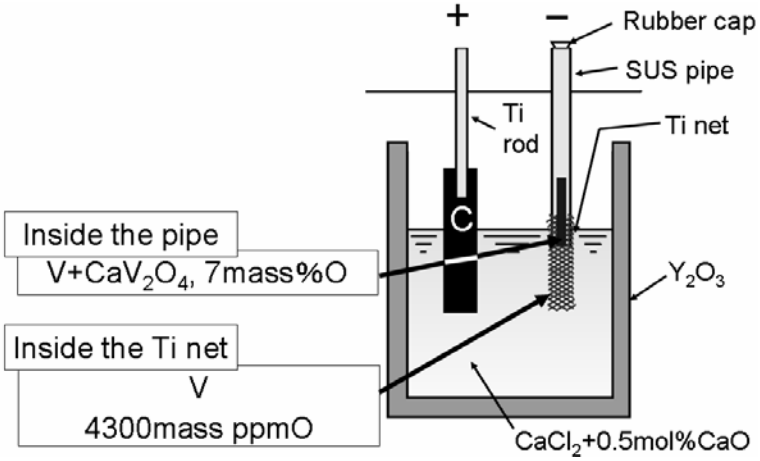
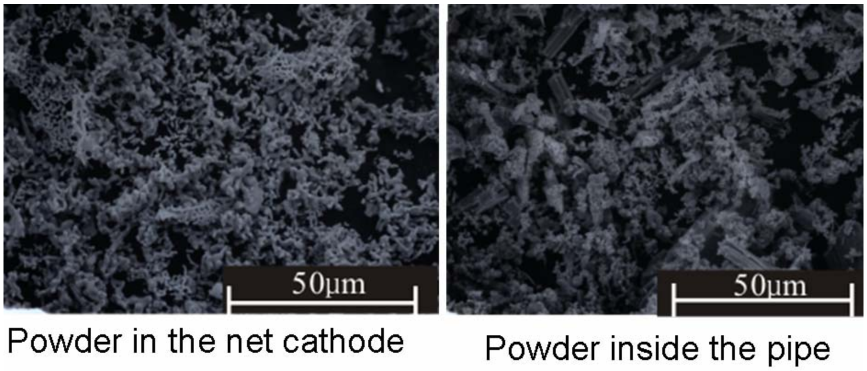


Figure 5. Schematic illustration of experimental arrangement when V_2O_5 was used.



Powder in the net cathode

Powder inside the pipe

Figure 6. SEM image of the powders obtained from V_2O_5.

Fig. 6 shows the scanning microscopic (SEM) image of these powders. The particle of V metals looks fine and round, while the intermediate oxide, CaV_2O_4, shows rectangular crystalline particles.

Reduction from V_2O_3

When V_2O_3 with the high melting point was used, the oxide powder was simply stacked in the Ti basket-type cathode, which was immersed into the molten salt, as shown in Fig. 7. The other experimental conditions were set as the same as the above-mentioned procedure.

The black powder was recovered from the cathode when the electrolysis was conducted for the time longer than one hour at 1173 K. XRD analysis identified that the whole powder was pure V. The produced V particles were spherical, about 1 μm in size, as shown in Fig. 8. The diameter of the particles grew larger as the time increased.

The residual oxygen was lower than 0.20% after 10.8 ks, as shown in Fig. 9. It is again noted that the oxide could be reduced within one hour to metallic V, but the residual oxygen decreased slowly to the lower level because of wide oxygen solubility in V, as shown in Fig. 4.

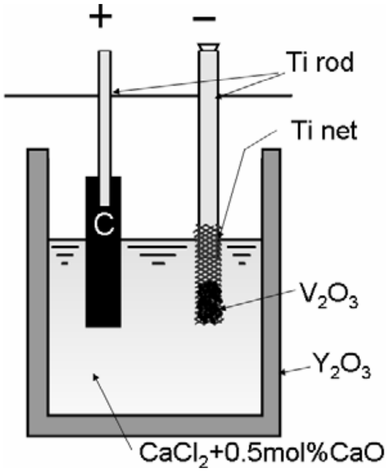


Figure 7. Schematic illustration of experimental arrangement when V_2O_3 was used.

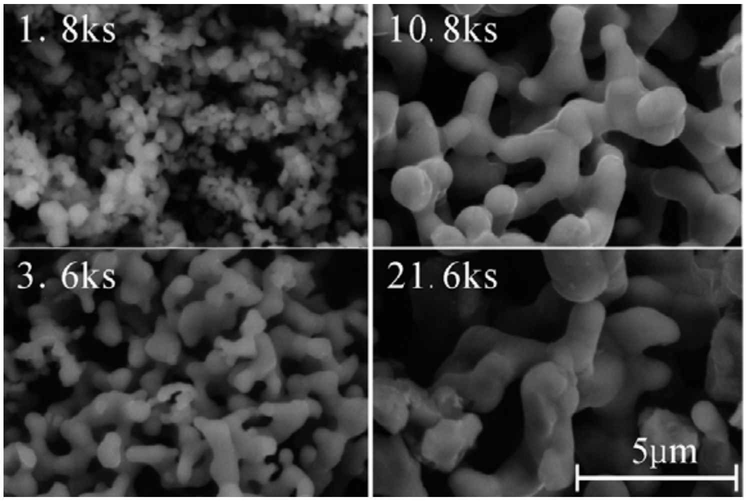


Figure 8. SEM image of the powders obtained from V_2O_3 at 1173 K.

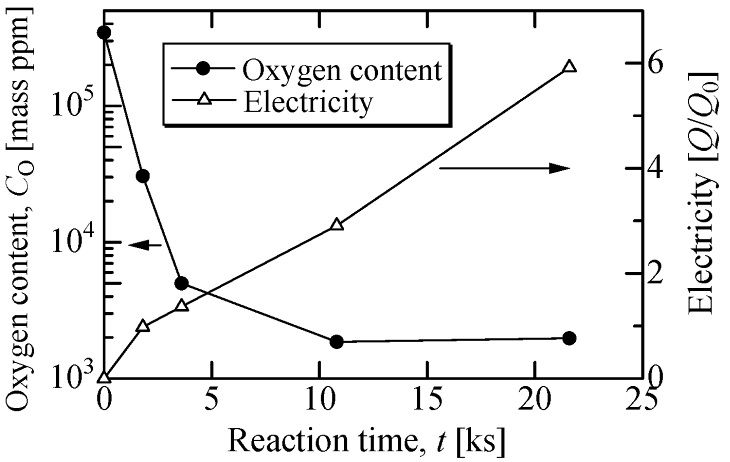


Figure 9. Oxygen concentration in the powder from V_2O_3 at 1173 K, and the supplied electrical charge, Q, where the required charge for Ca production is Q_0.

Deoxidation of V

The commercial V powder containing 1.45 mass% oxygen was deoxidized using the same setup as shown in Fig. 7. Instead of oxide powder, V powder with 100 μm in size was filled in the cathode. This arrangement was known as the electrochemical deoxidation for Ti plate or wire (31,32).

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

The morphology of this V powder before the reaction was shown in Fig. 10. It should be compared with the size of V particles starting from oxide. The commercial powder was about 100 times larger than the reduced particles.

Figure 10. SEM image of the commercial V powder used for the deoxidation experiment.

The electrochemical deoxidation of the commercial V powder was performed for 10.8 ks at 1173 K by applying 3.0 V between the electrodes. The oxygen concentration in the V powder was analyzed to be as low as only 10 ppm oxygen at this experimental condition, where the oxide powder of V_2O_3 was converted to the metal with 0.43% oxygen.

The electrochemical reactions in the bath, Eq.[2],[4] and[5] can be summarized as,

$$\underline{\text{CaO}}\text{ (in CaCl}_2\text{)} + \text{C} = \text{CO/CO}_2\text{ (gas)} + \underline{\text{Ca}}\text{ (in CaCl}_2\text{)} \qquad [7]$$

At the higher concentration of CaO, the larger current are served because the larger amount of the solute, CaO, contributes to the electrolysis below the decomposition voltage of $CaCl_2$. This means that the larger amount of Ca can be formed in the bath for a unit time. The precipitated Ca at the cathode dissolves into the $CaCl_2$ melt, and the $\underline{\text{Ca}}$ concentration near the cathode, i.e., the thermochemical activity of Ca, becomes the higher. Therefore the deoxidation seems to be enhanced at the higher concentration of $\underline{\text{CaO}}$.

Fig. 11 shows the relationship between the supplied electricity Q and the oxygen concentration in the commercial V powder as function of the initial CaO concentration.

The electrolysis was conducted for 10.8 ks at 1173 K by applying the constant voltage of 3.0 V. At the higher CaO concentration, the larger Q was obtained as mentioned above. However, it is surprising that the oxygen concentration in the commercial V powder increased as the initial CaO concentration became higher, namely, that it increased as the supplied electricity increased, or as the amount of formed Ca from CaO increased. The oxygen concentration in the V powder should decrease thermodynamically, when the activity ratio r (= a_{Ca} / a_{CaO}) in equation [6] becomes greater. Therefore, if a_{CaO} can be set constant because of the small oxygen supply from the V powder, and if the local equilibrium was achieved at the surface of V powder, the reason of higher residual oxygen at the higher CaO concentration should be that the local Ca concentration near the cathode was not higher at the higher CaO concentration. This conclusion conflicts with the larger Q. Therefore, we need the other reasons why the residual oxygen was high.

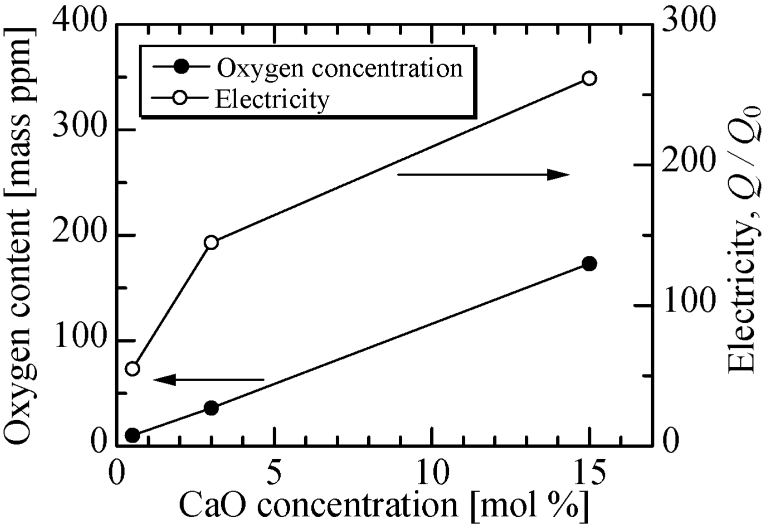


Figure 11. Oxygen content and the supplied electric charge, Q, after deoxidation of V-1.45%oxygen powder. Q_0 is defined as the theoretical electricity to remove 1.45% oxygen. The initial concentration of CaO was taken in the molten $CaCl_2$.

The two facts that the metallic vanadium powder contained 1.45% oxygen could be electrochemically deoxidized to the level of 10 ppm oxygen and that the residual oxygen remained as high as 2000 ppm after reduction from the oxide suggest that the large amount of by-product, CaO, due to reduction and the large surface area of the fine particles are the possible reasons of the higher oxygen content in the powder reduced directly from the oxides.

The third source of oxygen is the residual CaO (adhered to the particles) even after the repeated leaching. The Ca contents were examined by ICP-AES analysis for the aqueous solution after dissolving the obtained V powder, and it was found that the Ca content was less than 600 ppm. It is certain that the residual CaO among the sintered particles (see Fig. 8) was not completely separated from the V particles during the leaching, but its contribution to the overall oxygen concentration is only as large as 200 ppm. Therefore, the surface oxidation of fine powder will be one of the reasons, because the V can be easily contaminated by the atmospheric oxygen even at room temperature.

It may be effective if we can extract the by-product CaO near the cathode. The diffusivity of CaO in the molten salt will be reported separately (33).

Conclusion

The proposed process was experimentally applied to prepare metallic vanadium directly from V_2O_5 or V_2O_3. The process combines the electrolysis of CaO in the molten $CaCl_2$ with the simultaneous calciothermic reduction. The fine metallic powder containing 1860 mass ppm oxygen was obtained from V_2O_3, when the 0.5mol%CaO-$CaCl_2$ melt was electrolyzed for 10.8 ks at 1173 K. The oxygen level from the oxide did not decrease further even when twice electricity was supplied, while the commercial grade powder contained 1.48% oxygen was well deoxidized to 10 ppm. The large amount of by-product, CaO, due to reduction and the large surface area of the fine particles are the possible reasons of high oxygen content in the reduced powder.

Acknowledgments

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