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Mechanistic insight into the influence of Al_2O_3 concentration on the electro-reduction of V_2O_3 to vanadium in molten Na_3AlF_6

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Abstract

The influence of Al₂O₃ concentration on the direct electrochemical reduction of porous vanadium sesquioxide precursors in molten Na₃AlF₆ was investigated by constant voltage electrolysis and cyclic voltammetry. The products obtained by electrolysis at various Al₂O₃ concentrations were examined by XRD and SEM. Specifically, the morphologies of the outer metal layer initially formed were characterized by SEM and EDS, also their effects on the electrolysis process were systematically studied. The results indicate that the Al₂O₃ concentration in molten Na₃AlF₆ has a significant impact on the reduction process. When 0.5 mass% Al₂O₃ is added into molten Na₃AlF₆, the reduction rate of V₂O₃ can be improved because of the appropriate increase of aluminium reductant and relatively high oxide ion transfer rate. However, a high Al₂O₃ concentration (1.0–3.0 mass%) causes the massive precipitation of aluminium at cathodic outer metal layer and further forms Al–V alloy, causing the densification of the outer metal layer and hampering the reduction reaction kinetics.

Key words: Molten salt electrolysis; Al₂O₃ concentration; V₂O₃; Vanadium; FFC Cambridge

process.

1. Introduction

Recently, the FFC (Fray-Farthing-Chen) Cambridge process for producing metal has triggered worldwide research activities because the metal oxide can be directly reduced to pure metal. In the process, the oxygen ions of solid oxide can be expelled from cathode and dissolved in electrolyte then discharged at anode, leaving the pure metal at the cathode [1]. Considerable research efforts have been devoted to the synthesis of various metals and alloys via the direct electrochemical reduction of oxide precursors. The recent development of the FFC process has been described in several excellent reviews [2-6]. As so far, this novel method has been successfully applied to the preparation of, in particular, high-melting-point metals, such as titanium, chromium, niobium, and tantalum. Meanwhile, it also enables the successful preparation of many alloys directly from relevant oxide mixtures [7-16], including Ti–Fe, Ti–Ni, Ni–Cr, Ta–Nb, Ti–Nb–Ta–Zr, Ti–Nb–Ta–Zr–Hf, Nb–Hf–Ti, etc.

There have been attempts to prepare metal vanadium via electrochemical methods, i.e. electrodeposition [17-18] and electro-deoxidation [19-22]. Some studies have focused on the direct electro-reduction of vanadium oxides in molten chloride salt. R.O. Suzuki et al. [19] firstly extended the direct electro-reduction process into the preparation of metal vanadium. The reduction of solid V₂O₃ powder was completed at 1173 K in molten CaCl₂-CaO and fine metal vanadium powder containing 0.186 mass% oxygen was obtained. They proposed a new concept for the direct reduction of oxide in molten CaCl₂, named the OS (Ono-Suzuki) process. Distinguishing from the FFC process, the OS process involves the deposition of metal calcium from CaO in molten CaCl₂ and the calciothermic reduction of the metal oxide. S. Wang et al. [20] performed the electrochemical reduction of V₂O₃ in molten CaCl₂-NaCl-CaO by using compact V_2O_3 pellet as the cathode. They also explored the reaction pathway of the reduction of vanadium sesquioxide based on time-dependent changes of the phase composition; metal vanadium can be prepared within the processing time of 8 h. Z. Cai et al. [21] reported the preparation of metal vanadium by direct electrochemical reduction of V_2O_5 in molten CaCl₂–NaCl. The results demonstrate that the electrochemical reduction of vanadium pentoxide to metal vanadium is accompanied by the decomposition of CaO and

calcium thermal reduction, which act as underlying mechanism in the process.

The future looks bright for this new electrochemical process, because the simple operation, little energy consumption and low pollution. In addition, it offers a new way for the preparation of high-melting-point metals, alloys and nonstoichiometric compounds these are difficult to be achieved through conventional metallurgical techniques. However, further development of the FFC process for scaled production of metal is tardy due to the poor current efficiency. There also still existed some major issues to be solved, one of them is the need of long electrolysis time. For instance, as reported by C. Schwandt et al. [23] the electrolysis preparation process of titanium metal from titanium dioxide precursors in molten CaCl₂ would extend over the reaction time up to several days. In order to promote the process, some work so far has been done concerning the preparation of oxide precursors [24-26], the selection of electrolyte [27-29], anode materials [29-30] and the electrolysis cell [31]. Notably, many efforts have been devoted to study the effect of oxygen ion concentration in the electrolyte on the direct electro-reduction process [32-33]. C. Schwandt et al. [32] reported the electro-reduction of titanium dioxide in molten calcium chloride with the addition of calcium oxide. They found that the presence of CaO in molten CaCl₂ can accelerate the overall rate of the reduction process. The reasons they reported are that the transfer rate of O²⁻ ions is proportional to their concentration and the moderate concentration of CaO in molten CaCl₂ can facilitate the cathodic reduction kinetics. They also reported that a high CaO concentration, e.g. 5 mol% CaO in CaCl₂, shows an adverse effect on the reduction process. The main reason seems to be that a high concentration of CaO leading to local saturation of CaO in the reaction region, which would clog the transmission channel inside the cathode and terminate the reaction. R.F. Descallar-Arriesgado et al. [33] confirmed the suitable amount of CaO for the reduction of NiO in molten CaCl₂ is in the range of 0.5-3.0 mol%. They explained the influence of oxygen concentration on the process by OS mechanism. That is, when intermediate amount CaO is initially added in molten CaCl₂, larger amount of Ca metal reductant can generate in the cathode region than that generate in pure CaCl₂. Hence, the transition rate of nickel metal from NiO can be substantially enhanced through calcium thermal reduction. However, when 5.0 mol% CaO is added in molten CaCl₂,

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the reduction is found to be incomplete. Their interpretation about the unfavorable condition at high CaO concentration is the possibility of liquid calcium precipitation on the cathode. That is to say, a great quantity of calcium can generate when 5.0 mol% CaO is electrolyzed in CaCl₂ melt and the calcium metal may start to precipitate and deposit on the outer surface of the cathode. This precipitation phenomenon would hinder the transmission of oxide ions, making the reduction ineffective.

In our early published paper [22], the electrochemical reduction of porous V_2O_3 pellet, using ammonium polyvanadate as raw material, was performed in molten Na_3AlF_6 salt. Our findings suggest that both the direct electrochemical reduction of V_2O_3 and aluminothermic reduction reaction occur during the reduction process, amongst which the latter plays a key role. The oxygen content of the metal vanadium product can decrease to 0.218 mass% after 4 h of electrolysis. However, further effort is required to optimize the process parameters, in particularly the proper oxygen ion concentration for the direct electro-reduction process in molten Na_3AlF_6 salt should be investigated. Because it is well established that the oxide ion concentration plays a critical role in the FFC process basing on the numerous studies performed in molten chloride salts. And yet no relevant study has devoted to the molten fluoride salt electrolysis process. In addition, the results reported on the influence of oxygen ion concentration in molten chloride salts are mostly based on theories or qualitative analyses. It is difficult to experimentally prove the deductions due to the harsh experimental conditions in high-temperature molten salt bath, thus systematic studies are still required.

The purpose of present study is to investigate the optimum oxygen ion concentration, i.e. alumina concentration, in molten Na_3AlF_6 salt for the electrochemical reduction of porous vanadium sesquioxide precursors, aiming to reduce the electrolysis time and increase the current efficiency. And the mechanism on the influence of the oxygen ion concentration in electrolyte on the FFC process is experimentally proved.

2. Experimental

2.1 Preparation of electrolyte and cathode

Vanadium sesquioxide cathode was prepared using ammonium polyvanadate powder (\geq

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99.5%, particle size range: 100–200 mesh, Dalian Galaxy Metal Material Co., Ltd.) as raw material. Initial ammonium polyvanadate pellets (3.0 g, 20 mm in diameter and about 3.7 mm in thickness) were prepared by moisturizing the powder with a few drops of deionized water and then pressing under 30 MPa in a cylindrical mold. The obtained ammonium polyvanadate pellets were heat-treated at 350°C for 1 h in a tube furnace under argon atmosphere (>99.99%, 1 L/min) and then reduced by coal gas (50% hydrogen, 35% methane, 10% carbon monoxide, 5% ethylene, Shenyang Gas Co., Ltd.) at 850°C for 1 h. At last, the reduced pellets were sintered at 1300°C for 3 h at a heating rate of 5°C/min in argon atmosphere. The obtained oxide pellets were connected to a direct current (DC) power supply by using nickel chromium wire (1mm in diameter) as the current lead. More detailed information about the preparation and assembly of the vanadium sesquioxide cathode was provided in the foregoing study [22].

The electrolyte was prepared using analytical reagent NaF and AlF₃ (3:1 in mole ratio, Sinopharm Chemical Reagent Co., Ltd.) with 0–3.0 mass% Al₂O₃ (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.). The salt mixtures (about 500 g) were placed in a high-purity graphite crucible with an inner diameter of 70 mm and depth of 100 mm. The graphite crucible was also used as the anode in the constant voltage electrolysis experiments or as the counter electrode in the cyclic voltammogram experiments. Prior to the experiments, the salt mixtures were dried at 150°C for 24 h in a vacuum drying oven.

2.2 Solubility of V₂O₃ in molten Na₃AlF₆

About 100 g of electrolyte was contained in a platinum crucible (50 mm in inner diameter, 50 mm in depth) and heated to 1010°C in argon atmosphere. When the electrolyte was

melted, the sintered vanadium sesquioxide pellet was then put into the melt. The temperature was kept at 1010°C for 1 h and the melt was stirred every ten minutes by using a molybdenum rod. At the end of the experiment, a sample of the melt was then withdrawn by dipping with molybdenum rod and subsequently quenched. The content of vanadium in the taken sample was then analyzed by Inductively Coupled Plasma (ICP, Optima 8300).

2.3 Constant voltage electrolysis

The power supply (DP1308A, Rigol Technologies Inc.) was used to perform the constant voltage electrolysis experiment. The graphite crucible containing the salt mixtures was placed in a sealed stainless steel reactor with argon gas flushing into continuously. The temperature was gradually increased and hold at 1010°C to melt the electrolyte. Then the cathode pellet was submerged into the molten salt and a constant voltage of 3.5 V was applied to the cathode and the graphite crucible anode. The electrolysis current was recorded every 5 seconds by digit multimeter (34401A, Keysight Technologies). After electrolysis for 3-4 h, the cathode was lifted out from the molten salt and cooled down to room temperature in argon atmosphere. The product obtained after electrolysis for 4 h in molten Na₃AlF₆ was polished and analyzed using scanning electron microscopy (SEM, Ultra Plus). The products obtained after electrolysis for 3 h in molten Na₃AlF₆ with the addition of Al₂O₃ were ground and then washed in 15% AlCl₃ solution (at 80 °C for 3 h) and distilled water, dried in vacuum and characterized by X-ray diffraction (XRD, D/max-2500PC). The oxygen contents of the products were determined by oxygen nitrogen analyzer (TC-436, LECO Corporation) and all the oxygen content data are measured by using the whole pellet as the test sample.

2.4 Cyclic voltammogram

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A three-electrode system was used for the cyclic voltammogram experiment. Molybdenum rod (>99.95%, 5 mm in diameter, 600 mm in length) was used as the working electrode. The high-purity graphite crucible was used as the counter electrode. A platinum wire (>99.95%, 0.5 mm in diameter, 50 mm in length) processed into spiral shape was used as the pseudo-reference electrode Pt/PtO_x/O²⁻. In order to guarantee that the working electrode kept the same active area, the immersion depth of the electrode was control strictly by using a self-made device. The experimental apparatus for the cyclic voltammogram experiment are shown in Fig. 1. The cyclic voltammogram experiments were performed with an electrochemical workstation (IM6e, Zahner Elektrick, Germany).

3. Results and discussion

3.1. Current versus time curves and characterization of products

Fig. 2(a) shows the current-time curves recorded during the electrolysis process in molten Na₃AlF₆ with the addition of 0–3.0 mass% Al₂O₃. Except for the Al₂O₃ concentration, the experimental conditions were the same for all the runs, especially for the immersion depth of the cathode pellet. As shown in the figure, the overall current increased with the increase of Al₂O₃ concentration in general. All the plots show much higher initial current values and then declined rapidly in the subsequent 10 min due to the diffusion of oxide ions expelled from the cathodic vanadium sesquioxide is fast during the initial stage of the electrolysis process.

Fig. 2(a) also shows that the currents measured at the initial stage of the electrolysis process performed in molten Na_3AlF_6 with Al_2O_3 are higher than that in pure molten Na_3AlF_6 . It was reported that during the direct electro-reduction process of solid oxide, the transport of oxide ions through the electrolyte is only driven by the concentration gradient [34] and the transfer

rate of oxide ions is proportional to their concentration in the electrolyte [35]. Obviously, the addition of Al_2O_3 in molten Na_3AlF_6 accelerates the transmission of oxide ions from the cathode toward to the anode and thus speeds up the reduction reaction occurred in the initial stage of the process, leading to the higher current than that in pure molten Na_3AlF_6 .

It also can be seen in Fig. 2(a) that the currents maintain steady at time-independent constant values at the later stage of the electrolysis process, except for the electrolysis processed in molten Na_3AlF_6 without Al_2O_3 . Fig. 2(b) shows the increase in termination current as the Al_2O_3 concentration increases. This termination current represents a complex electrolysis process, involving the decomposition of alumina in electrolyte [22] and the background current arising from the conductivity of the electrolyte [4, 23]. As reported, the continuous addition of Al_2O_3 inside the molten cryolite would decrease the conductivity of electrolyte [36] and the decomposition potential of alumina decreases in a Nernst-type fashion when the concentration increases. So it reasonable to concluded that the increase of Al_2O_3 concentration in the electrolyte can promote the decomposition of alumina and generate more metal aluminium during the electrolysis process.

Fig. 3 shows the XRD patterns of the as-prepared samples electrolyzed at 3.50 V for 3 h in molten Na₃AlF₆ with 0–3.0 mass% Al₂O₃. It can be seen that the Al₂O₃ concentration has a significant influence on the electro-reduction process of V₂O₃. As shown in Fig. 3(b), the product obtained at 0.5 mass% Al₂O₃ is mainly composed of metal vanadium, indicating the complete reduction reaction of V₂O₃. However, the cathodic product obtained after 3 h of electrolysis in pure molten Na₃AlF₆ is found to be consisted of metal vanadium and low-valence vanadium oxide, i.e. V₉O. As a small amount of water always existed in the

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electrolyte, introduced by inefficient drying procedure inevitably, this would cause a relative low oxygen ion concentration in the electrolyte. This low oxygen concentration sets up a transport limitation for the oxide ions expelled from the cathode towards to the anode and thus causes the sluggishness of the electro-reduction process in molten Na₃AlF₆.

When Al_2O_3 concentrations were increased to 1.0–3.0 mass%, the diffraction peaks of Al₈V₅ appears in the XRD patterns shown in Fig. 3(c-f), indicating that the electrodeposition of metal aluminum is promoted at the cathode area. It can be deduced that the produced aluminium can reacts with V₂O₃ and thus enhances the reduction. On the other hand, the excessive aluminium has also brought along some side effects: i) alloying with the reduced metal vanadium and forming vanadium aluminium alloy, e.g. Al₈V₅; ii) hindering the continuous progress of the reduction process, since some oxide phase still retained in the products. The oxygen content values of the products are exhibited in Fig. 4. It can be seen that the oxygen content determination results are in accord with the XRD results. The oxygen content of the formed metal vanadium after 3 h of electrolysis in molten Na₃AlF₆ with 0.5 mass% Al₂O₃ was decreased to 0.207 mass% and the current efficiency was calculated to be 55%. When the Al₂O₃ concentration continued to increase, the oxygen concentration of the products began to increase significantly. The detailed influence mechanism about the Al₂O₃ concentration on the process will be discussed in the latter sections.

It is noteworthy to address the presence of AIV_2O_4 phase in the products. In some of published articles about the preparation and properties of the vanadium spinels, the valence states of vanadium ions in AIV_2O_4 were reported to be V(II) and V(III) [37-38] and the similar vanadium compounds can be synthesized by solid-state reactions between vanadium oxides and other metal oxides at 900–1200°C, e.g. MnO, CoO, ZnO, MgO [39]. Thus, it is reasonable to suggest the chemical equation for the generation of AIV_2O_4 in this molten salt system as follow:

$$Al_2O_3 + 2VO + V_2O_3 = 2AlV_2O_4$$
 (1)

3.2. Microstructure of products prepared at different Al₂O₃ concentrations

Fig. 5(a) and (b) show the SEM images of the starting cathode V_2O_3 pellet and the product reduced in molten Na₃AlF₆ for 4 h, all taken at the surface of the pellets. As shown in Fig. 5(a), the starting cathode V_2O_3 particles is consisted of irregular polyhedral particles with uniform size of about 400–500 nm. During the electrolysis process, cathode V_2O_3 showed a good stability in molten Na₃AlF₆ because of the low solubility (the solubility was measured to be 0.19 mass%). The SEM image of the reduced sample in Fig. 5(b) shows the grain coarsening behavior of vanadium metal. The EDS analysis result shown in Fig. 5(c) reveals that no oxide phase is detected and the metal phase is composed of vanadium. The formed metal phase shows a porous reticular structure. This porous metal layer provides a diffusion pathway for the molten salt and oxide ions expelled from the inner regions. As revealed in Fig. 5(d), the EDS analysis result shows the molten salt and oxygen filled in the pores of metal phases.

Chen et al. [5] proposed a 3PI (three-phase interlines) model to describe the cathode reduction kinetic process of solid oxide in molten salt. That is, the direct electrochemical reduction of the solid oxide begins at the metal (or current collector) / metal oxide / electrolyte interlines. At the beginning of electrolysis, the 3PI only presents next to the metal wire. Upon providing electrons, the oxide particles next to the metal wire can be reduced to

metal firstly and the metallized area then operates as the current collector propagating the 3PI to the core part. This model holds when the oxide precursor is an electronic insulator. However, since V_2O_3 is an electronic conductor at high temperature (the conductivity of V_2O_3 is about 4.6 S·cm⁻¹ at 1010°C [40]), the 2-phase interface mechanism is more applicable, i.e. only the solid oxide phase and liquid electrolyte phase presenting at the reaction interface. Based on the results reported by D.S.M. Vishnu et al. [41], it can be certain that the oxide pellet can act as the electron conductor. Hence the electro-reduction begins at the whole electroactive surface of the cathode and induces a high initial current, as illustrated in Fig. 2(a). Subsequently, the oxide surface next to the electrolyte is converted to metal, forming a metal layer covering the inner oxide. This initially formed metal layer must be porous to allow the electrolyte to access the inner oxide and oxide ions can move out through the pellet, insuring the reduction continues.

After electrolysis for 1 h in molten Na₃AlF₆, the cathodic product was cut into cross-section and analyzed by SEM and EDS, shown in Fig. 6. As indicated in Fig. 6(a-b), the outer layer of cathode pellet contacting with the bulk electrolyte is reduced, leaving a metal vanadium layer. The oxygen scattered in this outer area, shown in Fig. 6(c), may be corresponding to the oxygen dissolved in the molten salt. Fig. 6(d-f) show the EDS elemental maps of the electrolytic composition, i.e. sodium, fluorine and aluminium elements. By SEM backscattering analysis, it can be seen clearly that the reduced metal layer is sufficiently porous and the electrolyte distributes in the pores and the unreduced core. The formed porous metal layer provides an accessible way for the electrolyte to access the oxide in the inner layer and allows the oxide ions diffusing through the solid cathode pellet and entering the bulk

electrolyte. Hence, there is no denying that insuring a high porosity of the formed outer metal layer is essential for guaranteeing the continuity of solid electro-reduction process.

To gain a better understanding of the influences of Al_2O_3 concentration on the microstructure of the products and reaction kinetics, the SEM images of the samples taken at the metal layer area are shown in Fig. 7. The samples were obtained by electrolysis for 3 h in molten Na₃AlF₆ with the addition of 0–3.0 mass% Al₂O₃. It can be seen that the outer metal layer is composed of metal phase distributed in light zone and molten salt phase distributed in black zone. Apparently, with the increase of Al₂O₃ concentration in the electrolyte, the metal grains were agglomerated into large blocks, which would compress the volume of the molten salt phase inevitably. This would make the reduction process kinetically difficult because the diffusion of oxide ions from the inner layer towards to the electrolyte is blocked by the formed dense metal layer.

In order to obtain quantitative data about the volume ratio of molten salt phase, for each sample more than five SEM images of the metal layer area were taken. The volume ratios of molten salt phase were quantified by Image Pro-Plus 6.0 software. The obtained data is displayed in Fig. 8. Obviously, the volume ratio of molten salt phase almost presents decreased line shape with the increase of Al₂O₃ concentration. That is to say, with the increase of Al₂O₃ concentration, more metal phases are generated in the outer metal layer. In the view of reaction kinetics, the dense metal layer delays the diffusion of oxide ions and electrolyte, slowing down the reduction process.

3.3. Influence mechanism of Al₂O₃ concentration on the reduction process

The findings mentioned above provide concrete evidences for exploring the influence of

 Al_2O_3 concentration on the electro-reduction process of V_2O_3 by observing and analyzing the microstructure of the formed outer metal layer. As will be described later, detailed study about the electrochemical behavior of aluminium ions and the growth mechanism of the metal grains in metal layer are provided.

Fig. 9 shows the cyclic voltammograms recycled for 10 times continuously on a molybdenum electrode in molten Na₃AlF₆ with the addition of 1.0 mass% Al₂O₃. In line with the previous findings [22], the appearance of c1/a1 couple demonstrates the electrodeposition of aluminium ions and the reoxidation of formed aluminium metal. It can be seen that the reduction current and oxidation current increase as the scan cycle repeats. The increase of the reduction current is explainable. As the solubility of aluminium in molten cryolite is only 0.1–1.5 mass% [42], together with the delayed dissolution of aluminium in the bulk molten salt, all these factors cause the adhesion of aluminium on the molybdenum electrode. This phenomenon may enlarge the reaction interface on the working electrode and then more aluminium generates, causing the increasing current as observed in Fig. 9.

The cyclic voltammograms obtained on the first scan cycle for aluminium deposition in molten Na_3AlF_6 with the addition of 0.0–3.0 mass% Al_2O_3 illustrate the differences among various Al_2O_3 concentrations, as shown in Fig. 10. It can be seen that with the increase of Al_2O_3 in electrolyte, the deposition potential of aluminium ions are almost constant, but the reduction currents increase. This indicates that larger amount of aluminium is formed per unit time at higher Al_2O_3 concentration.

According to the electrochemical measurement results and the previous studies [32-33], the improvement of electro-reduction process at around 0.5 mass% Al₂O₃ can be explained by the

appropriate increase of aluminium reductant [33] and the relatively high transfer rate of oxide ions [10]. When the Al₂O₃ concentration was increased to 1.0–3.0 mass%, a certain amount of oxide phase still existed in the products, as shown in Fig. 3, implying the incomplete reduction of V₂O₃ at high Al₂O₃ concentration. Fig. 11(a) shows the SEM image taken at the metal layer of the sample obtained after electrolysis for 3 h at 2.0 mass% Al₂O₃. In line with the previous finding, the metal layer is composed of metal phase and molten salt phase. But it is notably mentioning that the metal phase exhibits heterogeneity in chemical component, which can be observed clearly by SEM back-scattering analysis. Fig. 11 (c-d) shows the EDS spectrums of the metal phase. It can be seen that the external layer is composed of vanadium aluminium alloy and the inner layer is mainly vanadium, with little aluminium. This finding is consistent with the XRD results. The synergistic effects of the substantial increase of metal aluminium and the decrease in aluminium solubility at high Al₂O₃ concentration may trigger liquid aluminium precipitation in the electrolyte. This inference can be proved by analyzing the elemental distribution of the molten salt phase filled in the pores of the metal layer. As shown in Fig. 11 (b), the EDS result shows that the content of aluminium is much higher than that of sodium and fluorine, indicating that liquid aluminium presents in the electrolyte. Therefore, liquid aluminium may deposit on the surface of metal vanadium initially formed in the outer layer of cathode and form Al–V alloy. The formation of alloy can cause the growth of metal grains, which decreases the porosity of the outer layer and forms a dense metal layer covering the inner oxide layer, as shown in Fig. 7. Then the diffusion of oxide ions expelled from the inner oxide towards to the bulk electrolyte is hindered, making the whole reduction process ineffective. Moreover, the increase of metal layer area could provide a larger active

surface area for the electrodeposition of aluminum ions. Thus, it will consume more electric energy for the aluminium electrodeposition and cause the increase of electrolysis current, as illustrated in Fig. 2 (a). This is supported by the EDS line-scan profile data shown in Fig. 12, which indicates that the aluminium content within 400 μ m of distance range from the cathode pellet surface is higher evidently than that of inner layer.

4. Conclusions

The suitable Al_2O_3 concentration in molten Na_3AlF_6 for the direct electro-reduction of V_2O_3 to vanadium was studied. The addition of Al_2O_3 into molten Na_3AlF_6 has a significant impact on the reduction process. The optimum Al_2O_3 concentration is around 0.5 mass% and this value can improve the reduction rate of V_2O_3 . The electrolysis time can be shortened to 3 h, meanwhile the oxygen content of the product could be decreased to 0.207 mass% at a current efficiency of 55%. In contrast, adding too much Al_2O_3 in the electrolyte would impede the reduction process. The experiment proves that an abundance of aluminium can electrodeposit at high Al_2O_3 concentration and liquid aluminium would adhere on the surface of metal vanadium in the outer layer of the cathode and further form Al-V alloy, causing the densification of the outer metal layer. This would block the pathway for the diffusion of electrolyte and oxide ions, making the reduction process ineffective.

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Figure Captions

Fig. 1. Experimental apparatus for cyclic voltammogram.

Fig. 2. Current versus time curves (a) obtained during the electrolysis for 3 h at 1010°C under 3.5 V in molten Na₃AlF₆ with 0–3.0 mass% Al₂O₃, cathodic geometric surface area: 7.49 cm², the currents (b) recorded at the end stage of the electrolysis process as a function of Al₂O₃ concentration in the electrolyte.

Fig. 3 XRD patterns of the as-prepared samples electrolyzed at 3.50 V for 3 h at 1010°C in molten Na₃AlF₆ with different Al₂O₃ concentrations; a: 0 mass% Al₂O₃, b: 0.5 mass% Al₂O₃, c: 1.0 mass% Al₂O₃, d: 1.5 mass% Al₂O₃, e: 2.0 mass% Al₂O₃, f: 3.0 mass% Al₂O₃. Reference standard data from JCPDS cards: V: NO. 089-3842, V₉O: NO. 042-1263, Al₈V₅: NO. 071-0141, AlV₂O₄: NO. 025-0025, V₂O: NO. 039-0773.

Fig. 4 Influence of Al_2O_3 concentration on the oxygen content of the products electrolyzed at 3.50 V for 3 h.

Fig. 5. SEM images of the porous V₂O₃ pellet (a) and the entirely reduced product (b) obtained after electrolysis for 4 h at 1010°C in molten Na₃AlF₆ (w(Al₂O₃) = 0 mass%), with the EDS spectrums (c-d) measured over the specified positions in (b).

Fig. 6. SEM image (a) and EDS elemental map images (b-f) of the cross-section of the product obtained after electrolysis for 1 h at 1010°C in molten Na_3AlF_6 ($w(Al_2O_3) = 0$ mass%).

Fig. 7. SEM images of metal layer area in the samples obtained after electrolysis for 3 h at 1010°C in molten Na₃AlF₆ at different Al₂O₃ concentrations: a: 0 mass% Al₂O₃, b: 0.5 mass% Al₂O₃, c: 1.0 mass% Al₂O₃, d: 1.5 mass% Al₂O₃, e: 2.0 mass% Al₂O₃, f: 3.0 mass% Al₂O₃.

Fig. 8. Volume ratio of the molten salt phase as a function of Al_2O_3 concentrations in the electrolyte.

Fig. 9. Cyclic voltammograms recycled for 10 times continuously on a molybdenum metal electrode at 1010°C in molten Na₃AlF₆ with 1.0 mass% Al₂O₃. Scan rate: 100 mV/s. Fig. 10. Cyclic voltammograms obtained on the first scan on molybdenum metal electrode at 1010°C in molten Na₃AlF₆ with the addition of 0.0–3.0 mass% Al₂O₃. The insert shows the cathodic peak currents recorded at -1.6 V vs. Pt/PtO_x/O²⁻. Scan rate: 100 mV/s. Fig. 11. SEM image and EDS spectrums of the metal layer area of the sample obtained after

electrolysis for 3 h at 1010°C in molten Na₃AlF₆ with 2.0 mass% Al₂O₃.

Fig. 12. The cross-sectional SEM image and corresponding EDS line scan along the white line of the sample obtained after electrolysis for 3 h at 1010° C in molten Na₃AlF₆ with 2.0 mass% Al₂O₃.





























A State











