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Electrodeposition of vanadium from a molten salt bath

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1. Introduction

Vanadium has attracted attention in view of its excellent combination of properties such as high temperature strength, high thermal conductivity, low neutron absorption cross section, low inelastic scattering cross section, favourable strength-to-weight ratio, resistance to corrosion, high elastic modulus and high creep strength [1, 2]. Vanadium has been used in a variety of applications: as an alloy additive to various grades of steel and in heat treatable titanium alloys, in nuclear engineering, magnetic alloys (permendur, supermendur and vicalloy), superconducting materials (V_3Si, V_3Ga), in the chemical and polymer industries and as a colourant in ceramic materials [3–9]. Several of these applications demand high purity vanadium.

Commercially, vanadium is obtained either by calcio or aluminothermic reduction of V_2O_3/V_2O_5 [10, 11] and also by magnesiothermic reduction of vanadium chlorides [4]. However, the metal obtained by these routes needs further purification. Among the refining techniques [12–15], electrorefining in a molten salt bath has been found to be successful for removing the impurities, both metallic and nonmetallic [16–21].

The present investigation was aimed at preparing a low cost vanadium intermediate which could further be refined to high purity metal. The process consisted of (i) preparation of vanadium nitride (VN) by carbothermic reduction of V_2O_5 under nitrogen flow, (ii) thermal decomposition of VN to vanadium intermediate (V, N) and (iii) electrorefining of (V, N) in NaCl–KCl–VCl_2 bath to high purity vanadium. The specific objective of the investigation was to improve the vanadium purity by removing the interstitial impurities (carbon, nitrogen, oxygen and silicon).

2. Theoretical considerations

The electrorefining of vanadium in the cell

$$V_{(\mathrm{impure})}\quad \mathrm{NaCl{-}KCl{-}VCl_2}\quad V_{(\mathrm{pure})}$$

is based on the following two mechanisms:

anode

$$V_{(\mathrm{impure})} + 2\mathrm{Cl}^- \longrightarrow \mathrm{VCl_2} + 2e^-$$

cathode

$$\mathrm{VCl_2} + 2e^- \longrightarrow V_{(\mathrm{pure})} + 2\mathrm{Cl}^-$$

net

$$V_{(\mathrm{impure})} \longrightarrow V_{(\mathrm{pure})}$$

The refining cell consists of (V, N) as the anode, molybdenum strip as the cathode and a molten NaCl–KCl bath with VCl_2 as functional electrolyte. As the electrolysis progresses at a given cathode current density (CCD), V^{2+} in the electrolyte around the cathode is reduced to elemental vanadium, which is subsequently deposited on the cathode. Depletion of V^{2+} ions from the bath due to the cathodic process is compensated by the supply of V^{2+} from the anode. Since both the cathodic and anodic processes are the reverse of each other, electrolysis takes place at small applied potential to take care of the iR drop in the electrolyte and polarization, if any, at the electrodes, provided the activity of the metal ion at the cathode is close to that of the metal ion at the anode.

The extent of refining of the impure metal in the molten salt bath depends on several factors such as the nature of the anode impurities, electrolyte composition, electrolysis temperature, cathode current density and voltage. Nobler impurities (Table 1) remain in the anode and do not enter the electrolyte during electrolysis. On the other hand, baser impurities are concentrated in the molten salt phase and may eventually be transferred to the cathode if their concentrations in the electrolyte, and the cathodic potentials are favourable. Interstitial impurities such as carbon, nitrogen, and oxygen which are present in the anode as carbide, nitride and oxide, respectively, have low solubilities in the chloride bath and do not take part in the cell reaction.

3. Experimental details

High purity V_2O_5 (Table 2) and graphite (99.5% pure) powder were used to prepare vanadium nitride. The nitrogen gas was provided from an oxygen-free nitrogen cylinder. NaCl and KCl were of AR grade. The preparation and subsequent decomposition of vanadium nitride were performed in a medium frequency 30 kW laboratory induction furnace.

The electrorefining was carried out in a 0.15 m diameter argon atmosphere electrolytic cell (Fig. 1). The cell consisted of a lower chamber, electrolytic chamber and an upper chamber, the receiver. The receiver was equipped with a water cooled receiver-lock where the cathode deposit was held for cooling

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Table 1. Electromotive force series. Equimolar NaCl–KCl at 700–900 °C

Couple	E_x^0, *700 °C*	E_x^0, *800 °C*	E_x^0, *900 °C*
Th(IV)–Th(0)	−1.642	−1.598	
Mn(II)–Mn(0)	−1.206	−1.190	−1.170
Zr(IV)–Zr(0)	−1.018		
Ti(III)–Ti(0)	−1.046		
Zn(II)–Zn(0)	−0.860	−0.835	−0.810
Cr(II)–Cr(0)	−0.758	−0.740	−0.728
Fe(II)–Fe(0)	−0.520	−0.510	−0.498
Pb(II)–Pb(0)	−0.390	−0.376	−0.355
Sn(II)–Sn(0)	−0.370	−0.354	−0.340
Co(II)–Co(0)	−0.324	−0.300	−0.275
Ni(II)–Ni(0)	−0.140		
Ag(I)–Ag(0)	0.000	0.000	0.000
Cu(II)–Cu(0)	+0.600	+0.616	+0.644
Cl_2–Cl^-	+0.845	+0.820	+0.798

before removal from the cell. A graphite crucible (0.12 m internal dia., 0.14 m outer dia. and 0.25 m long) was used to contain the electrolyte and the anode. This crucible also acted as the anode. A molybdenum strip 0.16 m long and 0.025 m wide was used as cathode. A full wave selenium rectifier with variable output was used for the electrolysis.

Table 2. Semiquantitative spectrographic analysis of V_2O_5

Element	*Concentration*/wt %
Si, Fe, Mn, Cr, Sn, Bi, In, Ca	> 0.05 (each)
Co, Be, B, Sb, Mg, Pb, Au	< 0.05 (each)

The detailed procedure and experimental conditions for the preparation of the anode have been discussed elsewhere [22].

The cell for electrorefining was tested for leaks at the operating temperatures under both vacuum and pressure conditions. The chloride electrolyte was prepared by drying NaCl and KCl at 400 °C under vacuum. The salts were then melted in argon atmosphere. VCl_2 was added to the molten bath by *in situ* chlorination of vanadium in a graphite chlorinator, immersed in the molten salt bath. Chlorination was carried out by allowing a mixture of chlorine and argon to pass through an Inconel tube to the electrolyte chamber at 700 °C for 8 h at a chlorine flow rate of $1.66 \times 10^{-4}\, m^3\, s^{-1}$. The anode material was then placed at the bottom of the cell through the receiver-lock. An argon atmosphere was maintained throughout the experiment in order to prevent oxidation of

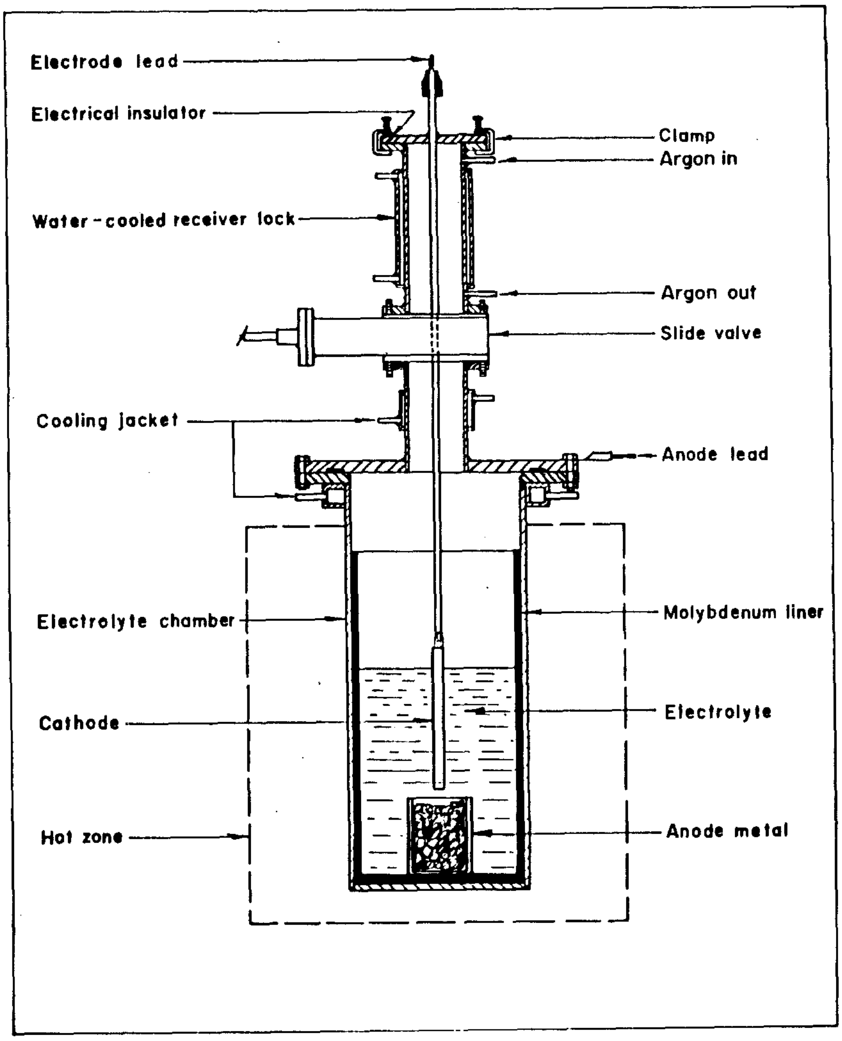

Fig. 1. Insert atmosphere electrolytic cell assembly.

Table 3. Operating data and results of electrorefining of decomposed vanadium nitride

Bath composition (wt %)	44.5 NaCl–44.5 KCl–11% VCl_2
Bath temperature (°C)	700–900
Operating voltage (V)	5.6–1.1
Initial cathode current density ($A\,m^{-2}$)	2152.8–3229
Duration of electrolysis (Ah)	20–180
Cathode current efficiency (%)	60–70
Number of deposits	16
Metal yield (%)	70
Purity (%)	99.4
Hardness of anode feed (VHN)	250
Hardness of arc-cast electrorefined V (VHN)	90

Table 5. XRF analysis of the electrorefined vanadium obtained at 3229 A m^{-2} and 800 °C

Element	*Concentration*/wt %
V	99.40
Ca	0.03
Fe	0.10
Mn	0.04
Zr	0.03
Cr	0.03
Ni	0.02
Mo	0.02
Cu	0.01
Ga	0.01
Nb	0.001

(i) VCl_2 and (ii) vanadium metal, deposited at high temperatures.

Upon completion of electrolysis, the cathode deposit was lifted to the receiver chamber, locked and permitted to cool to room temperature before removal. The metal deposits, thus obtained, were dipped in dilute hydrochloric acid solution, stripped from the cathode, washed and rinsed repeatedly, first with water and then with acetone in order to remove the entrained electrolyte from the crystals. The electrodeposit was vacuum dried and then melted in a non-consumable vacuum arc furnace.

4. Results and discussion

The first few runs were made for the purpose of conditioning the electrolyte. A total of 90 A h at 0.7 V was utilized to condition the electrolyte. Fine metal deposits were obtained which were subsequently discarded.

The results and operating parameters of electrorefining are given in Table 3. It was observed that coarser crystals were obtained at applied voltages between 0.95 and 1.1 V, when the temperature and cathode current density were 750–800 °C and 2422–3229 A m^{-2}, respectively. No deposition was found to take place at a voltage less than 0.7 V. Maximum yield was obtained at 800 °C and a CCD of 3229 A m^{-2}. The metal quality was found to improve with the succeeding runs.

Lower temperature (700–750 °C) resulted in higher electrolyte drag out and higher temperatures (> 900 °C) resulted in an increase in the impurity level of the refined metal. Similarly, at lower cathode current densities (< 2691 A m^{-2}), the yield was very poor, whereas higher cathode current densities (> 3229 A m^{-2}) yielded finer deposits.

An increase in hardness of the deposits after storage was observed. This could be due to the (i) sensitivity of the lower hardness metal to oxidation and (ii) smaller reaction activity of the higher hardness metal.

Refining was continued until 50% of the anode was electrolysed. Fresh material was then charged to replenish the anode in the cell. In this manner, approximately 70% of the metal value in the anode could be deposited in pure form with a reasonably good current efficiency.

Production of soft, coarse and crystalline metal is affected partly by the anode area. A large anode area with fresh metal surface results in a high-quality product [23]. Hardness of the metal product was found to decrease after the addition of fresh anode feed to the cell.

Based on the fact that vanadium transported itself as V^{2+}, current efficiency was found to be in the range 60–70%.

Tables 4 and 5 show the quality of the anode material and the refined product respectively. It can be seen from Table 4 that the major impurities in the anode were carbon, nitrogen and oxygen with some of the metallic impurities in very low quantities. The hardness of the refined vanadium (Table 3) was determined on a 5g sample of crystals which were arc-melted into a button. Arc-melted buttons were also analyzed for carbon, nitrogen and oxygen. The analysis showed that the concentration of all four interstitials could be reduced to a significant extent (Table 6).

Table 4. Analysis of the anode feed

Element	*Concentration*/wt %
Vanadium	92.0
Carbon	1.0
Nitrogen	2.5
Oxygen	3.0
Others (metallic)	1.5

Table 6. Chemical analysis of the arc-cast electrorefined vanadium button

Element	*Concentration*/wt %
Vanadium	99.400
Carbon	0.214
Nitrogen	0.0098
Oxygen	0.054
Silicon	0.035

5. Conclusion

Preparation of high purity vanadium was accomplished in a molten NaCl–KCl–VCl_2 bath employing an anode material containing 92% vanadium. This investigation has shown the feasibility of applying this technique to electrodeposit high purity vanadium from an impure metal containing low metallic and high nonmetallic impurities with a reasonably good current efficiency as well as recovery.

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