# Preparation of vanadium nitride and its subsequent metallization by thermal decomposition

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# Abstract

The preparation of high purity (greater than 99.8%) ductile grade vanadium is extremely difficult owing to its exceptionally high affinity towards carbon, nitrogen and oxygen. The removal of these interstitial impurities by conventional melt-refining routes is rather difficult. Specialized techniques such as pyrovacuum treatment, iodide decomposition and fused salt electrorefinement are normally adopted to prepare ultrapure vanadium. In the present investigation a new technique which involves the preparation and subsequent thermal decomposition of vanadium nitride (VN) has been attempted to obtain vanadium metal. The vanadium nitride in this study was prepared by carbonitrothermic reduction of vanadium pentoxide ( $V_2O_5$ ) at a temperature of 1500 °C. The VN thus formed was thermally decomposed at 1750 °C under reduced pressure ( $3 \times 10^{-2}$  Pa) to metallic vanadium. Consolidation of the product metal sponge (by arc melting) under a low pressure, high purity argon atmosphere yielded vanadium of purity better than 97%. The arc-melted metal can be further refined by fused salt electrolysis, leading to a purity better than 99.5%.

#### 1. Introduction

The present-day science and technology of vanadium and its alloys have been progressing at an accelerating pace, resulting in the development of new and attractive uses for this metal in a diversity of applications [1–5]. Some important areas of application where vanadium plays a crucial role are: in the iron and steel industry, where vanadium is used as an important alloy additive to improve strength, grain size and hardness; in the aerospace industry (Ti–6Al–4V alloy); as one of the ingredients in commercial magnets (Permendur and Supermendur); as a structural material for fast breeder nuclear reactors owing to its low cross-sections for fission neutrons and inelastic scattering; and in the chemical industry as a versatile oxidation catalyst.

The production of vanadium metal from its oxide is possible by reduction either by a metal such as aluminium [6] or calcium [7] or a non-metal such as carbon [8]. Aluminothermic reduction can be performed in an open reactor, a bomb-type sealed reactor or a flowing inert gas copper (water-cooled) reactor, whereas carbothermic reduction is carried out under vacuum. Carbothermic reduction of niobium pentoxide in the presence of nitrogen to prepare niobium nitride (NbN) followed by its pyrovacuum decomposition and subsequent consolidation and purification (by electron beam melting) has been reported to be an alternative method for the preparation of high purity (greater than 99%) niobium [9]. However, the same method offers limited possibilities with respect to the removal of interstitial elements such as C, N and O from the vanadium matrix during various stages of the process [10–12], thereby affecting the final purity of the metal.

In the present investigation an attempt has been made to prepare vanadium by carbonitrothermic reduction of the oxide  $(V_2O_5)$  in the presence of nitrogen followed by thermal decomposition of the product (VN) leading to its subsequent metallization. The influence of various process parameters such as charge composition, pellet size, temperature and duration of pyrovacuum treatment on the final purity of the nitride and the metal has been studied.

## 2. Theoretical considerations

Generally speaking, the high melting nitrides of refractory metals can be prepared by the action of  $N_2$ or NH<sub>3</sub> on the respective metals, their hydrides, oxides or other compounds. Pure vanadium nitride can be obtained by (i) heating pure vanadium powder under very pure N<sub>2</sub> or NH<sub>3</sub> at 1650 °C [13], (ii) the reaction of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) with NH<sub>3</sub> at

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900–1100 °C or with an  $N_2-H_2$  mixture at 600–1400 °C [14] or (iii) reacting vanadium chloride or oxychloride (VCl<sub>4</sub> and VOCl<sub>3</sub> respectively) with NH<sub>3</sub> at 1100–1600 °C [14–16].

The preparation of nitride by heating an oxide-carbon mixture in the presence of  $N_2$  or  $NH_3$  [17, 18] is economical because of the use of inexpensive starting materials but usually it yields relatively impure products. However, the purity of vanadium nitride can be improved to a great extent when a calculated mixture of oxides of vanadium ( $V_2O_3$  and  $V_2O_5$ ) and carbon are heated in a stream of nitrogen at a temperature greater than 1100 °C.

# 2.1. Preparation of vanadium nitride

Vanadium nitride cannot be prepared by heating  $V_2O_5$  alone in a nitrogen atmosphere at high temperature, since the oxide is more stable than the nitride and the free-energy change of the reaction

$$2VN + \frac{5}{2}O_2 \Longrightarrow V_2O_5 + N_2 \tag{1}$$

is about -1000 kJ at all temperatures. The oxide can, however, be converted to nitride if it is heated with a reductant in a nitrogen atmosphere. The formation of vanadium nitride by carbonitrothermic reduction can be represented by the following sequence of steps

$$V_2O_5 + \frac{1}{2}C \Longrightarrow V_2O_4 + \frac{1}{2}CO_2 \quad (650 \ ^\circ C) \tag{2}$$

$$V_2O_4 + \frac{1}{2}C \implies V_2O_3 + \frac{1}{2}CO_2 \quad (700-900 \ ^\circ C)$$
 (3)

$$V_2O_3 + 3C + N_2 \implies 2VN + 3CO \quad (1350-1400 \ ^\circ C) \quad (4)$$

with the overall reaction being

$$V_2O_5(s) + 4C(s) + N_2(g) \Longrightarrow$$
  
 $2VN(s) + 3CO(g) + CO_2(g)$  (5)

It has been observed that at higher temperatures  $(T > 1000 \,^{\circ}\text{C})$  the presence of carbon in excess of the stoichiometric requirement leads to the formation of carbides (both VC and V<sub>2</sub>C) which will remain in the final product as an impurity. Similarly excess oxygen in the charge will remain as a residual impurity. It is thus important to maintain an optimum O/C ratio in the initial charge. For the present investigation the optimum O/C ratio has been found to be 1.25.

The free energy of formation of vanadium nitride (Fig. 1) [19] indicates that the nitride could be obtained by heating vanadium metal in a nitrogen atmosphere at 1200 °C [14]. However, it has been observed that the rate of reaction (5) is appreciable only around 1350 °C.

#### 2.2. Pyrovacuum decomposition of vanadium nitride

The vanadium-nitrogen phase diagram indicates the formation of three nitride phases, namely VN,  $V_2N$ 

and  $\delta$ -V<sub>32</sub>N<sub>26</sub>; and a solid solution of vanadium and nitrogen. However, the only stable phases at higher temperatures (T > 500 °C) are VN and V<sub>2</sub>N [20]. Both these nitrides exhibit a wide range of homogeneity and their nitrogen contents change remarkably as a function of temperature and nitrogen partial pressure ( $p_{N_2}$ ) [21].

Thermodynamic predictions show that vanadium nitride decomposes at 1000 °C in a high vacuum [22]. From a vapour pressure measurement study of VN it was observed that the removal of an appreciable amount of nitrogen from VN takes place at a temperature higher than 1400 °C [23]. The decomposition of VN proceeds in two distinct steps

$$VN \implies V_2N$$
 (T=1277-1577 °C, P=10<sup>-1</sup> Pa) (6)

$$V_2 N \implies (V,N)_{(ss)} \quad (T = 1707 - 1727 \ ^\circ C, P = 10^{-1} \ Pa)$$
(7)

The equilibrium nitrogen pressures over the VN to V<sub>2</sub>N region are 5 and 9 kPa at 1300 and 1600 °C respectively [24]. Such a high decomposition pressure thus facilitates the easy conversion of VN to  $V_2N$ . The decomposition of  $V_2N$  to  $(V,N)_{(ss)}$  has a much lower equilibrium pressure (0.25 kPa). This decomposition, however, occurs along with moderate loss of vanadium by vaporization. Further degassing of  $(V,N)_{(ss)}$  appears difficult, since in the solid solution range the vapour pressure of vanadium is higher than the equilibrium nitrogen pressure (Fig. 2). The lowest concentration of nitrogen in vanadium that can be achieved by pyrovacuum treatment (2000-2100 °C) under 3 mPa is 0.3% [12], which suggests that under the combined effects of high temperature and high vacuum the removal of gaseous nitrogen from VN will only be possible if the initial nitrogen content is more than 0.3%. In contrast, if the nitrogen content is less than 0.3%, there will be a preferential loss of vanadium resulting in an increase in nitrogen concentration.

# 3. Experimental details

#### 3.1. Materials

Vanadium pentoxide  $(V_2O_5)$  and graphite powder were used as the starting materials for carrying out the experimental investigations. High purity  $V_2O_5$  (Table 1) was obtained by decomposing ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), whereas the graphite powder (99.5% pure) was taken from an imported lot (Le Carbone, France). The nitrogen gas was drawn directly from a commercial oxygen-free nitrogen cylinder.

## 3.2. Equipment

Both nitriding and denitriding were conducted in a medium frequency, 35 kW laboratory induction furnace.



Fig. 1. Free energy of formation of metal nitrides.

A high density graphite crucible (inner diameter 102 mm, outer diameter 105 mm, length 180 mm) was used as the susceptor-cum-container for the charge. In the centre of the crucible lid an orifice (which served as the black hole) of 1 cm was made for measuring the temperature. Graphite felt was wrapped around the crucible to provide thermal insulation. The bottom of the crucible was perforated to facilitate effective contact of the charge with nitrogen. The temperature was measured using a disappearing-filament-type optical pyrometer and the values were corrected for the transmissivity of the window and prism. The graphite crucible was placed inside a silica tube furnace chamber (inner diameter 220 mm, length 880 mm), which in turn was coupled with a diffusion pump backed by a rotary pump to provide a reasonably good vacuum (up to 10<sup>-4</sup> Pa).

The melting of decomposed VN was carried out in a non-consumable (0.25 in) tungsten electrode arc furnace.

## 3.3. Procedure

Stoichiometric quantities of  $V_2O_5$  and graphite powder (in the molar ratio of 1:4 respectively) were homogenized in an agate pestle and mortar. The powder mixture was compacted into pellets of sizes ranging from 10 to 20 mm diameter under a pressure of 180 MPa and using a binder (5% camphor in acetone). The pellets were then gradually heated to 1500 °C in the presence of a flowing nitrogen atmosphere until the reaction was over.

The denitriding experiment was performed in the same set-up by progressively heating VN to higher



Fig. 2. Vapour pressure of vanadium and decomposition pressure of vanadium nitride *vs*. temperature.

TABLE 1. Semiquantitative spectrographic analysis report on vanadium pentoxide  $(V_2O_5)$ 

Elements	Concentration (ppm)		
Si, Fe, Mn, Cr, Sn, Bi, In, Ca	500 (each)		
Co, Be, B, Sb, Mg, Pb, Ag, Au	<500 (each)		

temperatures (up to 1750 °C) under a dynamic vacuum  $(3 \times 10^{-2} \text{ Pa})$ .

# 4. Results and discussion

#### 4.1. Effect of pellet size and compacting pressure

The percentage weight loss of different pellets at various stages of nitriding and denitriding treatments indicates that the pellet size and compacting pressure do not have any significant influence on the rate and extent of the reaction.

The vanadium nitride was not found to be sintered and could be easily crushed. Similarly the metallized vanadium obtained after pyrovacuum treatment was found to be of a spongy texture with a high porosity (30% at 1750 °C). This large porosity of the product facilitated easy transport of the gaseous reactant and product, thereby eliminating the possible influence of pellet size and compacting pressure on the rate of the reaction.

# 4.2. Nitriding temperature and time

The nitriding started at around 1100 °C as observed by monitoring the evolution of carbon monoxide (CO) gas at the exit channel of the nitrogen gas line. The results given in Table 2 indicate that the carbonitrothermic reduction did not undergo completion even after 3.5 h of holding at temperatures up to 1400 °C. Nitriding at 1600 °C was found to be vigorous, resulting in disintegration of the nitride pellets. The nitriding time of 3 h at 1500 °C was found to be independent of the amount of oxide-carbon charge. This was anticipated, since the rate of nitriding would depend upon the availability of sufficient nitrogen followed by subsequent removal of CO, which in turn would depend on the nitrogen flow rate. Although it has been reported that a composition of VN<sub>1.0</sub> can be obtained under atmospheric pressure of N<sub>2</sub>, a recent study by Lengauer and Ettmayer [25], showed that such a stoichiometric nitride could be formed only at a higher pressure of  $N_2$ . A nitrogen flow rate of 800 cm<sup>3</sup> min<sup>-1</sup> during nitridation was found to be adequate for preparing the stoichiometric nitride VN<sub>1.0</sub>.

The nitride obtained under these conditions contained quite high amounts of residual carbon and oxygen (Table 2). Some of these impurities were, however, readily removed during the subsequent denitriding stage.

In a similar investigation Guidotti *et al.* [17] have reported a process for the preparation of vanadium nitride by allowing  $V_2O_5$  to react with NH<sub>3</sub> in the temperature range 1000–1050 °C for 5–5.5 h using alumina or Vycor as the container material.

Even though both reactions are feasible and yield nitrides of about the same purity, carbonitrothermic reduction occurred at a faster rate and yielded a nitride with less residual carbon and oxygen, which could be removed during pyrovacuum decomposition by carbon

TABLE 2. Analysis of vanadium nitride obtained at various nitriding temperatures

Temperature (°C)	Time (h)	O/C molar ratio (initial)	Analysis (wt.%)		
			N	С	0
1200	4.0	1.25	7.0	8.0	11.0
1300	3.66	1.25	14.56	4.59	5.81
1400	3.5	1.25	18.23	3.2	2.78
1500	3.0	1.25	20.98	3.0	2.25

TABLE 3. X-ray analysis of vanadium nitride at various stages of pyrovacuum treatment

Temperature (°C)	Phase	
1500	VN	
1600	VN	
1700	$V_2N$ (major)	
1750	v	



Fig. 3. Percentage weight loss of (V,N)(ss) with time.

deoxidation. On the other hand, the reaction with  $NH_3$  results in a nitride with residual oxygen only and removal of this is possible only by sacrificial deoxidation, which will lead to substantial metal loss.

#### 4.3. Denitriding

The results in Table 3 indicate that the decomposition of vanadium nitride proceeded with the formation of a lower nitride  $(V_2N)$  followed by the formation of  $(V,N)_{(ss)}$ . The ultimate decomposition of vanadium nitride was carried out at 1750 °C under a pressure of  $3 \times 10^{-2}$  Pa. Further decomposition beyond 1750 °C was discontinued for two reasons, namely (i) the charge was found to sink into the graphite crucible when attempting to carry out the refining at a temperature greater than 1800 °C and (ii) loss of vanadium (Fig. 3) was observed even at 1750 °C and  $3 \times 10^{-2}$  Pa because of the higher vapour pressure of vanadium over the decomposition pressure of vanadium nitride.

#### 4.4. Arc melting

The shiny (silvery white) and spongy metallized vanadium was subjected to arc melting in the presence of a high purity, low pressure (0.1 Pa) argon atmosphere. The buttons prepared by arc melting were repeatedly remelted five or six times by reversing the side. Analysis of the buttons (Table 4) has shown the vanadium content to be a little over 97%, the rest being the total interstitial impurity concentration.

The arc-melted vanadium metal thus obtained was found to undergo further refinement in a fused salt (all chloride) bath to a purity better than 99.5%.

Based on the above studies, a new flow chart is suggested for preparing ductile grade vanadium from its oxide  $(V_2O_5)$  via the nitride intermediate (Fig. 4).

TABLE 4. Chemical analysis of arc-melted vanadium buttons

Element	Concentration (wt.%)	
Vanadium	97.1	
Carbon	2.11	
Nitrogen	0.524	
Oxygen	0.204	
Others	~0.1	



Fig. 4. Flow chart for preparation of vanadium from  $V_2O_5$  through nitride intermediate.

# 5. Conclusions

The feasibility of a new process for the extraction of vanadium from its oxide  $(V_2O_5)$  through the nitride intermediate was established. The process involved the nitriding of a pelletized charge of  $V_2O_5$  and carbon at 1500 °C in a stream of nitrogen followed by the pyrovacuum decomposition of vanadium nitride at temperatures up to 1750 °C and a pressure of  $3 \times 10^{-2}$  Pa to yield vanadium sponge. The subsequent consolidation of the product in an arc-melting furnace resulted in the formation of vanadium with a purity better than 97%. While vanadium prepared by this method is suitable for many commercial applications, its further refinement (leading to a purity better than 99.5%) was achieved by fused salt electrolysis.

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