On the thermal decomposition of vanadium nitride

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Vanadium nitride, prepared by carbonitrothermic reduction of a $V_2O_5 + C$ mixture at a temperature of 1500 °C under continuous nitrogen flow, was thermally decomposed to metallic vanadium. The extent of removal of nitrogen from VN was found to depend upon temperature, time and reduced pressure. A portion of the residual oxygen and carbon, present in VN, was also removed, in the form of CO, during denitrogenation. The optimum decomposition temperature, time and pressure were 1750 °C, 1 h and 0.05 Pa for a charge of 500 g. The vanadium, obtained at the end of the pyrovacuum heating, is suitable for catalytic applications in industrial processes.

1. Introduction

Transition metal nitrides are generally less stable than their respective oxides and as a consequence lose nitrogen when heated to high temperatures under vacuum. However, because of the much higher binding energy of nitrogen (941 kJ mol^{-1}) compared to oxygen (499 kJ mol^{-1}), sometimes the decomposition of these nitrides occurs even at much lower temperatures.[1] Nevertheless, it is possible to convert a transition metal oxide to its nitride by judiciously selecting both the charge composition of the reactant materials, containing oxide as the principal component, and the processing parameters.

The conversion of metal oxides to their respective nitrides by carbonitrothermic reduction is a fairly common process and has been adopted for a number of metals such as aluminium, uranium and plutonium.[2–4] However, subsequent decomposition of these nitrides to their respective metals has offered limited scope. For example, while it is possible to convert group IVB metal oxides (TiO_2, ZrO_2 and HfO_2) to their respective nitrides (TiN, ZrN and HfN), it is almost impossible to decompose these nitrides to the respective metals owing to (i) the extremely high stability of these nitrides and (ii) the higher vapour pressure of these metals over the equilibrium nitrogen pressure in the M–N phase (M = metal) under pyrovacuum conditions. On the other hand, the preparation of group VB transition metals, through their respective nitride intermediates, stems from the fact that although these nitrides are thermodynamically stable up to moderate temperatures, they, however, decompose to the corresponding metal and molecular nitrogen when subjected to pyrovacuum conditions. Among group VB metal nitrides, both niobium nitride (NbN) and tantalum nitride (TaN), when heated to high temperature under high vacuum, give off nitrogen as the predominant vaporizing species.[5] Vanadium nitride (VN), on the other hand, exhibits the characteristics of both Groups IVB and VB metal nitrides. Nevertheless, it is possible to convert VN to commercial grade vanadium metal (~90% pure), low in total interstitial species, by subjecting it to pyrovacuum decomposition.

This paper discusses the effects of experimental parameters, such as (i) denitriding temperature, (ii) order of vacuum and (iii) holding time, *etc.*, on the extent of transformation of VN to vanadium.

2. Theoretical considerations

Thermodynamic calculations show that vanadium nitride undergoes decomposition at temperatures higher than 1000 °C under vacuum (better than 0.1 Pa).[6] The vapour pressure *vs.* temperature data (Table 1) suggest that the decomposition of vanadium nitride, into vanadium and molecular nitrogen, takes place at a relatively faster rate above 1100 °C.

The decomposition of vanadium nitride, at elevated temperature and under vacuum, proceeds according to the following two equations:

$$2VN \rightarrow V_2N + 0.5N_2 \tag{1}$$

and

$$V_2N \rightarrow (V,N) + 0.5N_2 \tag{2}$$
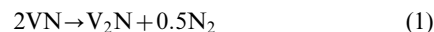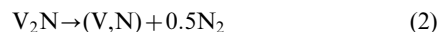
In the first step (equation 1), a lower vanadium nitride (vanadium saturated with nitrogen) is formed between 1277–1577 °C under a vacuum of 0.1 Pa. A further transformation of V_2N to (V,N) (equation 2), a solid solution of vanadium and nitrogen, takes place in the temperature regime 1707–1727 °C.[7] The equilibrium nitrogen pressure for the above two reactions can be computed using the following empirical equation

$$\log p_{N_2}(\text{kPa}) = 2.527 - 2920/T \tag{3}$$

According to equation 3, the values of equilibrium nitrogen pressures over the VN$\rightarrow$V$_2$N phase are about 5 and 9 kPa at 1300 °C and 1627 °C respectively and that over V$_2$N$\rightarrow$(V,N) is about 0.25 Pa at around 1627 °C.[7] The relatively higher value of equilibrium nitrogen pressure over the VN$\rightarrow$V$_2$N phase suggests that it is possible to convert VN to V$_2$N by removing a

Table 1 Vapour pressure data of some selected metal nitrides

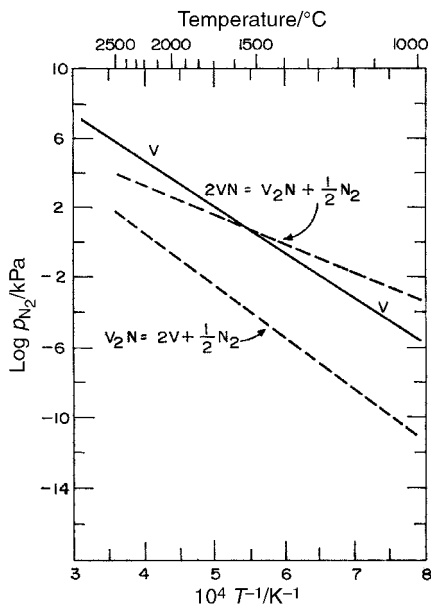| Nitride | Temperature at the given vapour pressure/K | | | | | |
	10^{-6} Torr	10^{-5} Torr	10^{-4} Torr	10^{-3} Torr	10^{-2} Torr	10^{-1} Torr
TiN	1605	1710	1822	1959	2109	2286
ZrN	1968	2104	2259	2404	2576	2742
HfN	1837	1968	2109	2239	2404	2570
VN	986	1052	1130	1220	1300	1400
NbN	1435	1531	1633	1742	1829	2018
TaN	1507	1607	1722	1845	1991	2148

Fig. 1 Vapour pressure of vanadium and decomposition pressure of nitrides of vanadium at different temperatures.

major portion of the nitrogen from vanadium nitride at a temperature $\sim 1600\,^{\circ}$C and moderate vacuum (~ 0.1 Pa). This can be achieved by heating VN in a conventional vacuum system containing only a rotary pump. The decomposition of V_2N to (V,N) has a much lower equilibrium pressure (0.25 Pa). This decomposition, however, occurs along with a moderate loss of vanadium by vaporization. Further removal of nitrogen from the single phase vanadium–nitrogen solid solution, (V,N), at still higher temperatures appears to be difficult as in the solid solution range the vapour pressure of vanadium is higher than that of the equilibrium nitrogen pressure (Fig. 1). No systematic data on the degassing of (V,N) at higher temperatures are available in the literature.

During pyrovacuum heating, residual carbon, from VN, is removed in the form of CO. Although some of the residual oxygen is also removed (along with carbon in the form of CO), it is not possible to achieve complete removal of oxygen on
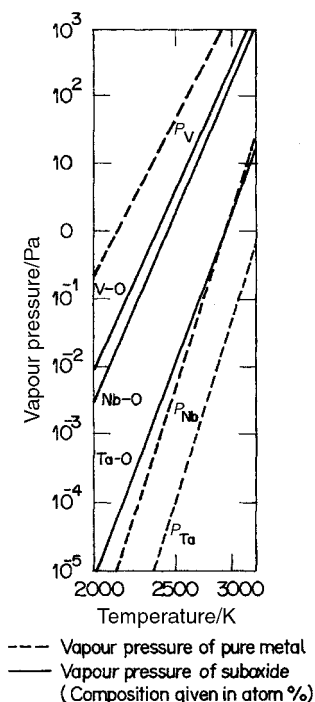

Fig. 2 Vapour pressures of group VB metals and their suboxides.

account of the lower vapour pressure of VO as compared to that of vanadium (Fig. 2).

3. Experimental

3.1. Chemicals

A mixture of V_2O_5 (98.5% pure) and graphite powder (99.5% pure) was used as the starting material. Commercially available nitrogen, IOLAR-2 grade, was directly taken up for use as the nitriding source. The nitrogen gas was rendered moisture free, before use, by passing it through columns of silica gel and molecular sieve.

3.2. Equipment

The pelletized charge was kept in a high density (0.2 m long, 0.1 m internal diameter and 0.006 m thick) graphite crucible-cum-susceptor, which, in turn was placed in a 30 kW, medium frequency (3.8 kHz) laboratory vacuum induction furnace. The susceptor was wrapped with graphite felt and yarn in order to provide adequate heat insulation. The furnace has the provision to be evacuated by a three-stage 200 mm diameter oil diffusion pump of a capacity of $900\,l\,s^{-1}$, backed by a rotary mechanical pump of $450\,l\,m^{-1}$ capacity. The system pressure was measured by a cold cathode penning type ionization gauge in the high vacuum range and by a thermocouple gauge in the mechanical pumping range. The temperature was measured with a disappearing filament type optical pyrometer.

3.3. Procedure

The oxide and graphite powders were mixed, in a mol ratio of 1:4 respectively, and blended with a binder (5% camphor in acetone). The blended powder mixture was compacted into cylindrical pellets of 0.015 m diameter under a dynamic load of 180 MPa in a locally available laboratory hydraulic press unit. The pelletized charge mixture (0.5 kg) was then heated up to a temperature of 1500 °C, under continuous nitrogen flow, for 3 h. The vanadium nitride (VN) so formed assayed vanadium: 73, nitrogen: 20.98, oxygen: 2.5, carbon: 3.0 and others: 0.5%.

The VN thus obtained was then decomposed in the same induction furnace by progressively (and slowly) heating it to higher temperatures under high vacuum. Initially, the heating was carried out at a relatively lower temperature ($T\sim 1000\,^{\circ}$C) under low vacuum (~ 0.1 Pa). The temperature was gradually raised to 1800 °C as the vacuum in the system went on improving till it reached a value of 0.05 Pa.

4. Results

The decomposition of VN to V took place in the following sequential order

$$VN \rightarrow V_2N \rightarrow (V,N) \rightarrow V \qquad (4)$$
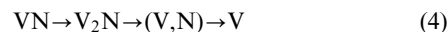
During the first stage of decomposition, i.e. up to a temperature of $\sim 1600\,^{\circ}$C, VN was identified as the only phase from the XRD pattern. When the temperature was raised beyond 1600 °C, VN was found to convert to V_2N. This phase appeared at a temperature $\sim 1700\,^{\circ}$C. XRD analysis of the product, obtained at temperature(s) $\geqslant 1750\,^{\circ}$C, showed the presence of only vanadium lines. Because of the lower concentrations of nitrogen, oxygen and carbon present in vanadium at 1750 °C (Table 2), it was difficult to establish/identify their phases (binary/ternary/quaternary) with vanadium in the V–N–C–O system by XRD alone. However, is has already been established that vanadium forms solid solutions with these elements in these concentration ranges.[8] Further heating of (V,N), beyond 1800 °C, was discontinued for two reasons, viz. (i) the denitrided pellets were found to sink into the

Table 2 Chemical analysis of vanadium nitride, obtained at 1750 °C and 0.05 Pa

Element	Amount (wt%)
Vanadium	94.40
Nitrogen	2.50
Carbon	1.60
Oxygen	1.20
Silicon	0.12
Iron	0.05
Chromium	0.03
Nickel	0.03
Manganese	0.02
Magnesium	0.025
Calcium	0.015
Aluminium	0.010

graphite crucible at a temperature above 1800 °C, presumably because of the formation of lower melting eutectic composition(s) and (ii) loss of vanadium, to an extent $\sim 12\%$, was observed to take place even at 1750 °C and 0.03 Pa (Fig. 3).

The impure vanadium, (V,N,C,O) pellet, obtained at the final stage of the pyrovacuum treatment, was found to be of a spongy texture with high porosity (30% at 1750 °C). This large porosity facilitated easy transport of N_2 and CO into the gas phase, during pyrovacuum heating.

During the denitriding process, along with nitrogen, a part of the residual carbon and oxygen also escaped into the gas phase, in the form of CO, thereby refining vanadium further. This is evident from the chemical analysis of the product, obtained at 1750 °C and 0.05 Pa (Table 2).

5. Discussion

5.1. Removal of nitrogen

Studies pertaining to the removal of nitrogen from vanadium present confusing results. Various authors have reported a decrease,[9] an increase[10–15] and almost unchanged[16–18] nitrogen concentrations during the melting of vanadium alloys containing different amounts of nitrogen. Kruger and Winterhager observed a decrease in nitrogen concentration during electron beam melting of vanadium.[13] However, they observed an increase in the nitrogen value for those alloys which had an initial nitrogen concentration less than 0.15%. According to Horz, vanadium containing 0.27% nitrogen could not be denitrided further even after heating the alloy at 1550 °C and under high vacuum.[14] Anable has reported an increase in the nitrogen contents during both electron beam melting and
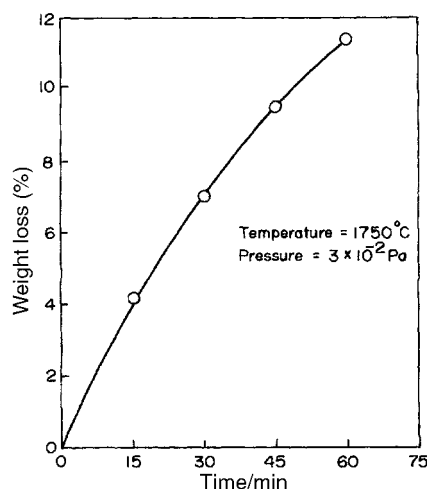

**Fig. 3** Percentage loss of vanadium at different time intervals.

vacuum heating of vanadium–nitrogen alloys.[15] Horz observed that vacuum annealing of solid solutions of vanadium and nitrogen at 1400 °C and 10^{-4} Pa liberated no nitrogen to the gas phase.[19] Similarly, Kruger in his observation concluded that vanadium containing 0.3 wt% nitrogen was not found to undergo degassing even at 1550 °C and 10^{-7} Pa pressure.[20] Gottwald *et al.* observed that pyrovacuum treatment of a vanadium–nitrogen solid solution at 2000–2100 °C under 2.7×10^{-3} Pa resulted in the lowest ever possible nitrogen concentration in vanadium.[21] They concluded that if the initial nitrogen concentration in vanadium is greater than 0.3%, than degassing of vanadium with respect to nitrogen is possible. Guidotti *et al.* reported that while attempting to decrease the nitrogen content in vanadium from 1.8% to 0.6%, they observed a loss of vanadium to the tune of $\sim 80\%$.[22] These considerably differing results might have arisen due to (i) difficulties in analytical procedures, (ii) the presence of lower quantities of nitrogen in the alloys and (iii) different experimental conditions.

Krishnamurthy has studied the decomposition pattern of VN in a thermobalance.[23] According to him, the conversions of VN to V_2N and V_2N to (V,N) took place between the temperature ranges 1275–1575 °C and 1680–1700 °C respectively. The latter change, according to him, was accompanied by a change in nitrogen concentration from 8 to 4%. At temperatures higher than 1700 °C, the thermogram still recorded the weight loss which has been ascribed to (i) vanadium vaporization and (ii) deoxidation of (V,N). But the present investigation has shown that the conversion of VN to V_2N and V_2N to (V,N) essentially took place at temperatures slightly higher than 1600 °C and 1700 °C respectively. Probably, this discrepancy arose because of the use of different temperature measurement devices. In the present investigation, we measured the temperature with the help of an optical pyrometer where the accuracy of measurement was within $\pm 1\%$ of the recorded values.

Extensive pyrovacuum treatment could not be carried out in order to denitride VN to metallic vanadium with very low (<1000 ppm) nitrogen content because of the extremely low equilibrium nitrogen pressure over vanadium, containing about ~ 1 at% ($\equiv 0.3$ wt%) nitrogen at the operating temperature regime, resulting in significant vanadium loss.

5.2. Removal of oxygen and carbon

The residual carbon and oxygen contents of vanadium nitride were 3.0% and 2.5% respectively. However, such concentrations did not interfere in the subsequent pyrovacuum decomposition. During heating under vacuum, removal of both carbon and oxygen took place simultaneously along with nitrogen. This is indicated by a decrease in their respective values (Table 2). The removal of both carbon and oxygen took place independently and by different mechanisms. Initially, when the concentrations of both carbon and oxygen in vanadium nitride are relatively high, the refining takes place by recombination of carbon and oxygen to form carbon monoxide followed by its subsequent escape to the gas phase.[8] This mode of removal of carbon and oxygen is known as carbon deoxidation which can be represented as

$$[C]_V + [O]_V \rightarrow (CO) \tag{5}$$
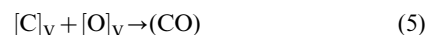
However, during pyrovacuum heating, when the respective concentrations fall below a critical value, the removal of oxygen takes place through suboxide (vanadium monoxide, VO) vaporization. This mode of removal of oxygen is known as sacrificial deoxidation and can be denoted as

$$[O]_V + V \rightarrow (VO) \tag{6}$$

Besides being dependent on temperature, the relative ratio of

carbon-to-sacrificial deoxidation is dependent on the concentration of carbon and is independent of oxygen concentration. The value of this ratio, at 2000 K, is

$$p_{CO}/p_{VO} = 6 \times 10^{-2} C_C \qquad (7)$$

Equation 7 indicates that when the concentrations of both carbon and oxygen are relatively high, significant amounts of carbon and oxygen are removed by carbon deoxidation. Krishnamurthy[23] observed an increase in carbon values from 1.7 to 1.8% and from 1.57 to 5.87% upon heating VN pellets at 1700 °C under 0.007 Pa and 1800 °C under 0.8 Pa respectively. In contrast, he observed a decrease in oxygen values from 1.0 to 0.3% and 0.34 to 0.002% respectively under the above experimental conditions.[23] The decreases in oxygen values are due to the vaporization of both vanadium and VO. According to Krishnamurthy, the rate of sacrificial deoxidation became appreciable when the carbon concentration fell below approximately 1.6%.[23] However, the present investigation has shown that a moderate loss of vanadium, *via* sacrificial deoxidation, took place even before the carbon content reached a value of 1.6%.

The extent of purification by sacrificial deoxidation is ascertained by a factor R, which has been defined by Brewer and Rosenblatt as follows[24]

$$R = [C_O/C_M]_{Vapour} / [C_O/C_M]_{Metal} \qquad (8)$$

C_O and C_M being the concentrations of oxygen and vanadium (in at%) in the phases indicated as subscripts. The R value essentially gives the relative value of oxygen in the vapour phase to that in the condensed phase. At a given temperature, the value of R changes with a change in the oxygen content. However, if the vapour phase constitutes only monoxide and monoatomic metal atoms and the concentration of oxygen obeys Henry's law (at low concentration, the vapour pressure of the solute is proportional to its mol fraction), then R approaches a limiting value which is independent of composition at any time.[25] This limiting R value determines the feasibility of sacrificial deoxidation. If this value is more than one, the metal can be purified by means of sacrificial deoxidation. In most cases, sacrificial deoxidation takes place simultaneously along with vaporization of metal of interest.

The R value for vanadium is only 6.3 at 1927 °C which indicates that vanadium can be refined by sacrificial deoxidation at the cost of a considerable amount of metal loss. As an example, it can be calculated that vanadium loss to the extent of 35% will take place in order to decrease the oxygen content from 1 to 0.1 at%.[8] Several studies have shown that when vanadium is heated under high or ultra-high vacuum to a temperature above 1500 °C, a reduction in oxygen content takes place along with an intense and simultaneous loss of vanadium by vaporization. Rosenblatt and Brewer calculated that a 10% loss of vanadium takes place, as a result of VO evaporation, during which the oxygen content of the melt is reduced to half of its initial value.[24] Anable also reported a 20% loss in vanadium after treating the alloys at 1600 °C for a period of 1.5 h.[15] Similarly, Kothe and Schlat reported 33% loss of vanadium after heating vanadium–oxygen alloys at 1600 °C for a period of over 50 min.[17] This loss in vanadium causes an apparent increase in the residual carbon content as oxygen is no longer available for carbon deoxidation to take place. Moreover, the high operating temperature favours both vanadium and vanadium monoxide evaporation rates, thereby diminishing the rate of CO evaporation further.

From the present studies, a temperature of ~1750 °C and a pressure of 0.05 Pa seem to be the optimum conditions for ensuring minimum vanadium loss during pyrovacuum heating with a view to removing carbon and oxygen.

5.3. Removal of silicon

The decrease in silicon content, after pyrovacuum heating, from an initial value of 0.35% (as SiO_2 in V_2O_5) to a final value of 0.12 [as Si in (V,N,C,O)] (Table 2) suggests that a portion of the silicon present in the oxide was removed in the form of SiO[8] according to the following reaction

$$[Si]_V + [O]_V \rightarrow (SiO) \qquad (9)$$
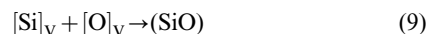
6. Merits of the present process

(1) A major advantage of the present process is that the nitriding and denitriding experiments can be carried out sequentially in a single step and in the same experimental set-up without carrying out any intermediate operation(s). Thus, this process appears to be better than carbothermic reduction which involves multistep operations.

(2) An important characteristic of the carbonitrothermic reduction (to prepare VN) is that although the reduction reaction is initiated in the densely compacted oxide–carbon mixture, owing to gas–solid combination of the reactants the product VN becomes porous. Besides being porous in nature, VN also maintains its structural integrity during denitrogenation as well as deoxidation.

(3) During denitriding, carbonitrothermically prepared vanadium could be refined *via* carbon deoxidation, in the initial stage of the pyrovacuum heating when the residual carbon concentration was relatively higher, whereas VN obtained *via* ammonia reduction of V_2O_5/V_2O_3 could only be refined by sacrificial deoxidation which resulted in significant vanadium loss.[22]

A major limitation of carbonitrothermic reduction is that this process did not give relatively pure VN and hence may be considered disadvantageous as far as the preparation of high purity VN *per se* is concerned. However, if considered from the metal preparation point of view, carbonitrothermic reduction of V_2O_5 to VN is just an intermediate step with few complications.

7. Conclusion

The thermal decomposition of carbonitrothermically prepared VN at 1500 °C and a vacuum of 0.5 Pa yielded 94.4% pure vanadium metal. The present process shows promise for preparing commercial grade vanadium metal by using cheaper reactant materials. The other attractive features of this process include the fewer steps, the environment-friendly process and the relatively higher vanadium yield.

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