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On the carbonitrothermic reduction of vanadium pentoxide

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Vanadium nitride was prepared by heating a mixture of vanadium pentoxide and graphite powder under a flowing nitrogen atmosphere. The resultant nitride was evaluated by powder X-ray diffraction and chemical analysis. The effects of various experimental parameters, such as oxide-to-carbon ratio, nitrogen flow rate, nitriding temperature and time, compacting pressure, *etc.*, on the extent of nitridation as well as the purity of the vanadium nitride, were studied.

1. Introduction

Transition metal nitrides and carbides have generated considerable interest because they exhibit technologically useful properties. These materials combine high hardness and excellent strength with high melting points and hence are preferred to conventional metals and/or alloys for providing good wear resistance and thermal as well as electrical conductivity, particularly in high temperature operations/processes. The traditional applications of these materials range from cutting tools and structural materials[1,2] to magnetic and electric components[3] and superconducting devices.[4–6] In recent times there has been a renewed interest in the application of transition metal nitrides/oxynitrides and carbides/oxycarbides in heterogeneous catalysis. On account of their superior behaviour, in terms of their selectivity, activity, stability and resistance to poisoning, these materials are being preferred to some of the other well known transition metals such as platinum, palladium and rhodium.[7–12] Vanadium nitride (VN), besides being used in the synthesis of low porosity polycrystalline composites,[13] has also been found to exhibit excellent activity and selectivity in catalytic hydroprocessing such as (i) dehydrodenitrogenation (HDN), (ii) dehydrodesulfurisation (HDS) and (iii) dehydrodeoxygenation (HDO).[14,15] Some of the transition metal nitrides, particularly NbN and TaN, have also been reported to be used as intermediate compounds in the production of the respective (high purity) metals.[16] The objective of the present investigation was to synthesize a vanadium nitride intermediate, from vanadium pentoxide, for its subsequent conversion to vanadium metal.

Friederich and Sittig were among the first to prepare vanadium nitride by heating a mixture of V_2O_3 and pine charcoal (in the ratio 1 : 3), in a molybdenum boat, to a temperature of 1200 °C under very pure nitrogen flow conditions.[17] The resulting product contained 78.3% vanadium, 21.1% nitrogen and 0.5% silica. However, there was no residual carbon in their product! In another investigation Guidotti *et al.* prepared VN by heating V_2O_5 in NH_3 in a vycor/alumina boat in two successive steps. The resulting nitride contained 20–21 wt% nitrogen and less than 0.9 wt% oxygen.[18] Although the nitride obtained by Guidotti *et al.* contained less residual oxygen, its rate of formation was found to be slower. Moreover, subsequent denitriding of VN, prepared by them, was found to result in a relatively higher loss of vanadium.

In the present investigation, the synthesis of vanadium nitride (VN) has been carried out by carbonitrothermic reduction of vanadium pentoxide (V_2O_5) to surmount these difficulties. A pelletized charge mixture comprising a mixture of V_2O_5 and graphite powder was heated to high temperatures (up to 1800 °C) under nitrogen flow in a vacuum induction furnace. The effects of various experimental parameters on the extent of nitridation of the oxide–carbon charge mixture and upon the quality of the nitride obtained are discussed.

2. Theoretical background

Vanadium nitride can not be prepared by heating V_2O_5 alone in a nitrogen atmosphere as the free energy change of the reaction

$$2VN + 5/2O_2 \rightarrow V_2O_5 + N_2 \qquad (1)$$

is ~ -1000 kJ mol^{-1} at all temperatures. However, the oxide can be converted to nitride if it is heated to high temperature in the presence of a suitable reducing agent under a nitrogen atmosphere. The reducing agents that can be used are either metallic (aluminium, calcium and magnesium) or non-metallic (carbon and silicon). Among these reductants, carbon is inexpensive and is abundantly available and hence is preferred for preparing the nitride. The reaction of nitrogen on the mixture of vanadium monoxide and carbon can be described as

$$VO + C + 1/2N_2 \rightarrow VN + CO \qquad (2)$$

The free energy change of the above reaction becomes favourable at atmospheric nitrogen pressure and at a temperature higher than 1000 °C (Fig. 1). In the presence of excess carbon, formation of vanadium carbide also occurs concurrently with vanadium nitride.

3. Experimental

3.1. Materials

High purity vanadium pentoxide (Table 1) and graphite powder (Le Carbone, France, 99.5% pure) were used as the starting materials. An IOLAR-2 grade nitrogen cylinder was used as the source of nitrogen. The gas was made moisture free by passing it through a column of silica gel and a molecular sieve prior to use.

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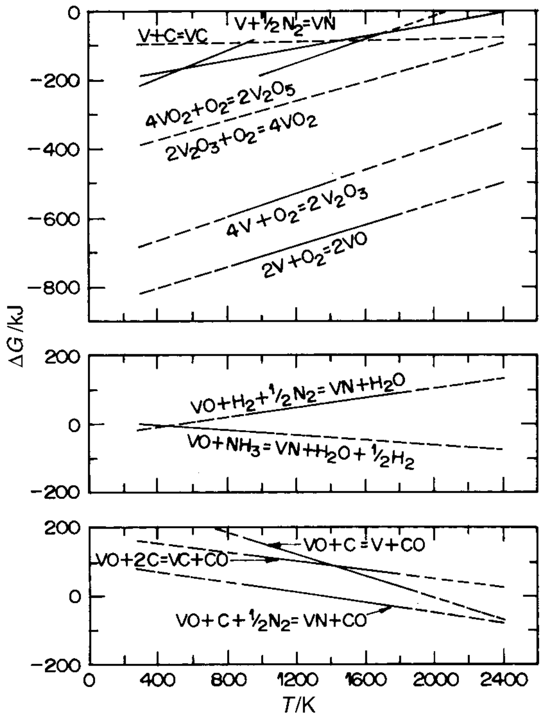

Fig. 1 Free energy changes of reactions involving the formation of vanadium nitride.

Table 1 Analysis of vanadium pentoxide

Name of the element/compound	Concentration
Co, Be, B, Sb, Mg, Pb, Ag and Cu	< 500 ppm (each)[a]
Fe, Mn, Cr, Sn, Bi, In and Ca	> 500 ppm (each)[a]
SiO_2	0.35%[b]
Al_2O_3	0.05%[b]
P	0.01%[b]
S	0.01%[b]

[a]From spectrographic analysis. [b]From chemical analysis.

3.2. Equipment

3.2.1. Pelletization press. A laboratory hydraulic press unit, locally available, was used for the pelletization of the oxide–carbon mixture.

3.2.2. Nitriding furnace. The nitriding of pelletized charge was carried out in a 30 kV medium frequency (3840 cycles s^{-1}) laboratory vacuum induction furnace. In this furnace, the charge was heated conductively from the susceptor, which, in turn, was heated by the induction field. The susceptor was a 0.2 m long, 0.1 m internal diameter and 0.006 m thick high density graphite crucible. The susceptor was wrapped with graphite felt, for heat insulation, and graphite yarn. The wrapped susceptor was placed on a steel pedestal. A 0.23 m diameter, 1.0 m long quartz tube was placed around this assembly and then the induction coil was lowered into position. On the flat, polished head of the quartz tube rested a water cooled stainless steel flange provided with an 'O' ring. The viewing port assembly carried four sight glasses, mounted on a rotating disc for temperature measurement. The temperature was measured with a disappearing filament optical pyrometer. Nitrogen flow in the system was maintained by providing inlet and outlet ports with flow meter and needle valve attachments. A schematic diagram of the induction furnace assembly is shown in Fig. 2.

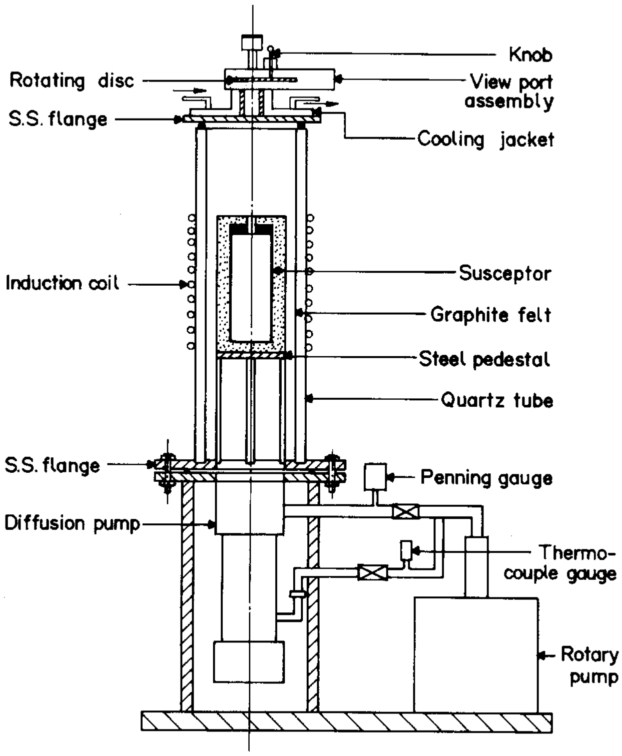

Fig. 2 Schematic diagram of the vacuum induction furnace.

3.3. Procedure

The charge mixture, comprising V_2O_5+C, was blended with a binder (5% camphor in acetone) and then pelletized into a 0.015–0.020 m diameter under a dynamic load of 180 MPa. The pellets were then kept in the graphite crucible, which, in turn, was placed inside the induction furnace. The inlet and outlet ports, after ensuring a proper flow of gas, were tightened in order to prevent the entry of outside air into the furnace. The charge was flushed three times with nitrogen and then heated slowly under a continuous flow of nitrogen. The extent of the reaction was monitored by burning off carbon monoxide at the exit channel. The VN thus formed was cooled to room temperature under a continuous argon flow.

4. Results and discussion

The formation of vanadium nitride (VN) started at a temperature of ~1200 °C, as was observed by the evolution and subsequent burning of carbon monoxide (in the form of a greenish violet flame with a golden yellow tip) near the exit port of the nitrogen gas line. The length of the flame was observed to increase with rising temperature and increases in the reaction duration. The carbonitrothermic reduction of V_2O_5 was essentially a reduction-cum-nitriding reaction. Initially, up to a temperature of about 1000 °C, V_2O_5 was successively reduced to V_2O_3 and the latter was finally converted to VN at a temperature higher than 1000 °C. The extent of the nitriding reaction was found to depend on a number of parameters such as oxide-to-carbon ratio, particle size of the reactants, pellet size, compacting pressure, nitriding temperature and time, nitrogen flow rate, *etc.*

4.1. Effect of oxide-to-carbon ratio

Vanadium has a valency ranging from 2 to 5 and thus has a strong affinity for both carbon and oxygen. Thus, the presence of excess carbon and/or oxygen in the initial charge composition, over the stoichiometric requirement, is reflected in the form of residual impurities in the final product. The purity of the resulting vanadium nitride was studied by varying the

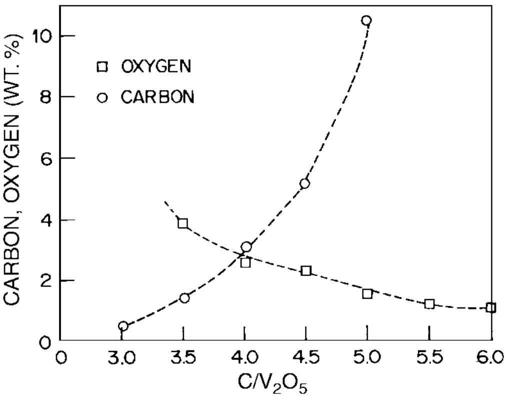

Fig. 3 Dependence of the carbon and oxygen contents of vanadium nitride on the C : V_2O_5 ratio at 1500 °C and 3 h.

carbon content from 3 to 6 mol per mol V_2O_5. Fig. 3 shows the dependence of the carbon and oxygen concentrations in vanadium nitride on the C : V_2O_5 ratio at a reaction temperature of 1500 °C and a duration of 3 h. The optimum mixing ratio was found to be 4.0 which was somewhat less than the stoichiometric ratio of 5.0. When the mixing ratio was less than 4.0, the residual oxygen in the product increased due to the shortage of carbon for reduction. Conversely, when the mixing ratio exceeded 5.0, the presence of excess carbon led to the formation of a V–C solid solution, thereby increasing the residual carbon content of vanadium nitride.

4.2. Effect of particle size

4.2.1. Effect of particle size of V_2O_5. Finer fractions of V_2O_5 were found to exhibit an enhanced nitriding reaction rate as finer particles have a higher specific surface area for the reaction per unit mass. The variation of the extent of the nitriding reaction with the particle size of V_2O_5 is shown in Fig. 4.

4.2.2. Effect of particle size of carbon. A reduction in the grain size of carbon increases both the contact area between V_2O_5 and carbon as well as the number of nucleation sites. Hence finer graphite powder is expected to enhance the percentage conversion of V_2O_5 to VN. The effect of the grain size of carbon on the extent of the reaction is shown in Fig. 5. It can be seen from this figure that while the percentage conversion remained more or less unchanged when the particle sizes were in the ranges 88–105 μm and 74–88 μm respectively, there was a marginal increase in the percentage conversion when the particle sizes were in the ranges 44–53 μm and 37–44 μm respectively. However, a sharp increase in the reactivity occurred when the particle size was decreased from 74–88 μm to 53–74 μm. Besides causing an increase in the overall reactivity, in general, fine grained carbon also produces either a less sintered or unsintered product. Vanadium nitride, prepared by using graphite powder with a particle size between 37–44 μm VN, was not found to be sintered and hence could be easily crushed into powder.

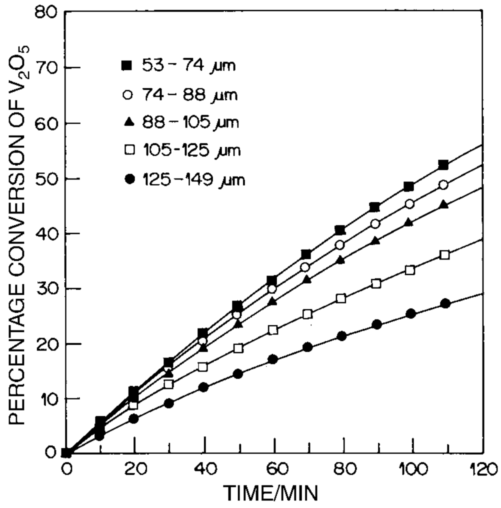

Fig. 4 Effect of the grain size of V_2O_5 on its nitridation, T = 1500 °C, N_2 flow rate = 13.3×10^{-6} m^3 s^{-1}, C : V_2O_5 = 4.0, carbon grain size = 37–44 μm.

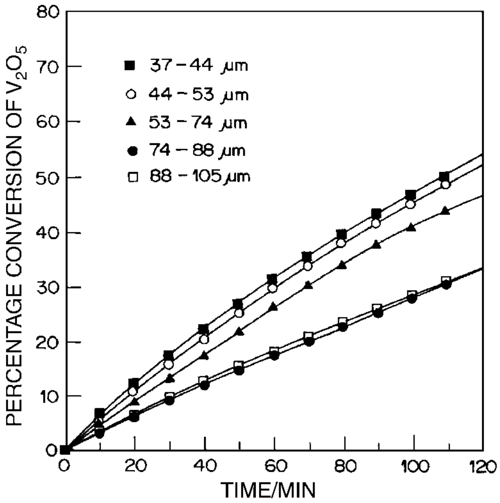

Fig. 5 Effect of the grain size of graphite powder on the nitridation of V_2O_5, T = 1500 °C, N_2 flow rate = 13.3×10^{-6} m^3 s^{-1}, C : V_2O_5 = 4.0, grain size of V_2O_5 = 53–74 μm.

4.3. Effect of pellet size

The reaction for an intrinsic chemical reaction system will take place uniformly and does not depend on the size of the pellets. Generally, if the pellet diameter is less than a critical diameter, the reaction rate becomes unaffected by the pore diffusion resistance. Similarly, for a relatively large diameter pellet, there is the possibility of the formation of the nitride only on the surface layer. However, the percentage weight loss of different pellets at various stages of nitriding and denitriding indicates that a pellet size in the range of 10–20 mm diameter does not have any significant influence on the rate or the extent of the nitriding reaction.

4.4. Effect of compacting pressure

As mentioned previously, the carbonitrothermic process followed a two-stage reaction route where carbon played the role of an effective reductant. Therefore, the physical contact between C and V_2O_5 was essential for CO_2 and CO gas formation. An extremely intimate mixture of fine particles can be obtained by increasing the pellet forming pressure. A higher pellet-forming pressure would also increase the contact area between carbon and V_2O_5. However, Fig. 6 shows that the compacting pressures, in the range 120–200 MPa, had no significant effect on the percentage conversion of V_2O_5 to VN.

4.5. Nitriding temperature and time

It was observed that the rate of formation of VN became appreciable only around 1350 °C. The carbonitrothermic reduction did not undergo completion even after holding the charge for 3.5 h at 1400 °C (Table 2). Nitriding at 1600 °C was found to be vigorous, resulting in the disintegration of the nitrided pellets. A nitriding time of 3 h at 1500 °C was found to be adequate for preparing a nitride with minimum residual carbon and oxygen (Table 2). The nitriding time of three hours at 1500 °C was also found to be independent of the oxide–

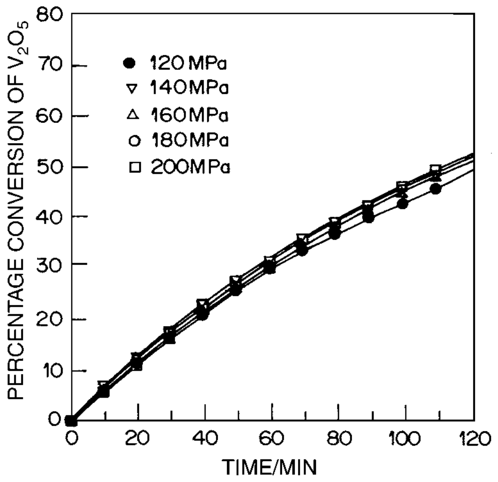

Fig. 6 Effect of compacting pressure on the nitridation of V_2O_5, $T = 1500\ ^\circ C$, N_2 flow rate $= 13.3 \times 10^{-6}\ m^3\ s^{-1}$.

carbon charge composition up to 750 g. This was anticipated since the nitridation rate would depend upon the availability of sufficient nitrogen followed by subsequent removal of carbon monoxide from each pellet, which, in turn, would depend on the flow rate of nitrogen. The vanadium nitride pellets, obtained at 1500 °C, were found to be spongy.

4.6. Effect of nitrogen flow rate

The resistance that may arise due to the external mass transfer in any chemical reaction may be neglected for those reactions where the overall rate is controlled by chemical kinetics. This situation occurs when the flow rate of the reacting gas is larger than that required. The nitridation rate was found to increase with an increase in the nitrogen flow rate. Although it has been reported that a composition of $VN_{1.0}$ can be obtained under an atmospheric pressure of nitrogen, a study by Lengauer and Ettmayer showed that such a stoichiometric nitride could only be formed at a higher nitrogen pressure.[19] Accordingly, the nitriding reaction was carried out by varying nitrogen flow. It was observed that a nitrogen flow rate in the range 1.6–$8.3 \times 10^{-6}\ m^3\ s^{-1}$ proved to be inadequate for the preparation of a stoichiometric nitride (VN) even after carrying out the reaction at 1500 °C for 6 h. However, when the flow rate was maintained in the range 10.0–$11.6 \times 10^{-6}\ m^3\ s^{-1}$, the reaction time required to obtain stoichiometric VN was reduced to 4 h. A flow rate of $13.3 \times 10^{-6}\ m^3\ s^{-1}$ or more at 1500 °C for 3 h was found to be adequate for preparing stoichiometric $VN_{1.0}$. A higher nitrogen flow rate was also required to maintain a low CO concentration in and around the reaction site and provide an efficient reaction of V_2O_5 with N_2.

4.7. Reaction mechanism

The progress of the carbonitrothermic reaction was monitored by interrupting the reaction intermittently at different temperatures and time intervals and then analyzing the representative samples by powder X-ray diffraction as well as chemical analyses. As has already been stated, the overall reaction could broadly be divided into two zones, *viz.* (i) reduction and (ii) nitriding.

Table 2 Chemical analysis of vanadium nitride obtained at different nitriding temperatures

			Analysis/wt%		
Temperature/°C	Time/h	$C:V_2O_5$	N	C	O
1200	4.00	4.0	7.00	8.00	11.00
1300	3.66	4.0	14.56	4.59	5.81
1400	3.50	4.0	18.23	3.20	2.78
1500	3.00	4.0	20.98	3.00	2.50

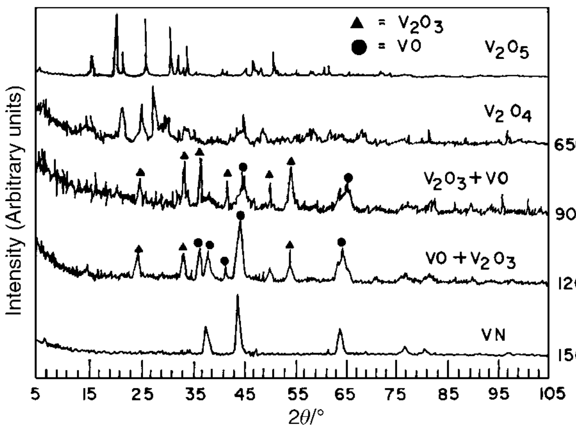

Fig. 7 XRD patterns of V_2O_5, intermediate phases and vanadium nitride.

The transformation of V_2O_5 to VN took place in the following sequential order

$$V_2O_5 \rightarrow V_2O_4 \rightarrow V_2O_3 \rightarrow VO \rightarrow V(N,C,O) \rightarrow VN \quad (3)$$

XRD analysis of the products (Fig. 7) showed that V_2O_5 was initially reduced to V_2O_4 at 650 °C. In the second stage, further reduction of V_2O_4 to V_2O_3 took place in the temperature regime 700–900 °C. A small amount of VO was also found to form along with V_2O_3. Between 1000–1200 °C, the predominant phase was VO along with a little amount of V_2O_3. The representative samples, for XRD examinations, were taken out of the furnace by heating the charge mixture for one hour at 650, 900 and 1200 °C respectively. At temperatures higher than 1200 °C and lower than 1350 °C, the XRD peak did not show the presence of either VO or VN. Between 1350–1500 °C, only VN could be detected. However, chemical analysis of VN, obtained at 1400 and 1500 °C, showed the presence of residual carbon and oxygen in the ranges 3.2, 2.78% and 3.00, 2.5% respectively (Table 2). As vanadium is known to form solid solutions with carbon and oxygen, in these concentration ranges,[20] the residual carbon and oxygen (in VN) were probably present in the form of some oxynitride/carbonitride/carboxynitride phase(s). However, confirmation of the occurrence of these phases by XRD could not be performed due to the lack of any published data on the V–N–C–O system. The formation of some oxynitride phases has been reported during the reduction of V_2O_5/V_2O_3 with ammonia.[18,21] The chemical analysis of VN, obtained after heating the charge for 3 h at 1500 °C (Table 2), showed a small discrepancy in the nitrogen content (20.98 as against the theoretical value of 21.5) of VN. This is due to the remnants of oxygen and carbon, remaining in the bulk as solid solutions, and/or non-stoichiometry.

The formation of VN by carbonitrothermic reduction reaction thus took place in the following sequential steps

$$V_2O_5(s) + 0.5C(s) \rightarrow V_2O_4(s) + 0.5CO_2(g) \quad (4)$$

$$V_2O_4(s) + 0.5C(s) \rightarrow V_2O_3(s) + 0.5CO_2(g) \quad (5)$$

$$V_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2VN(s) + 3CO(g) \quad (6)$$

with the overall reaction being

$$V_2O_5(s) + 4C(s) + N_2(g) \rightarrow 2VN(s) + CO_2(g) + 3CO(g) \quad (7)$$

Although Krishnamurthy has reported the formation of V_2O_4 and V_2O_3 as intermediate phases while carrying out the carbonitrothermic reduction of V_2O_5 in a TG-DTA set up,[22] he, however, has not reported the formation any intermediate phases during conversion of V_2O_3 to VN. He has also reported the possibility of formation of lower oxides, without identifying them, when the heating rate was decreased from 10 °C min^{-1} to 6 °C min^{-1}. In the nitridation of V_2O_5 with NH_3, King and Sebba speculated that V_2O_3 had entered the corundum structure to form VO_2N_2, thereby weakening the lattice structure.[23] Further nitridation was thought to break the corundum structure into a VO–VN substitutional alloy which eventually transformed to VN. In yet another investigation, Kapoor and Oyama have also reported the formation of VN by reduction of V_2O_5 with NH_3.[21] According to the authors, V_2O_5 was first converted to V_2O_3 and then to VO before being transformed to VN. But their findings are not fully consistent with the interpretation of King and Sebba. Although it has been reported that another intermediate phase (V_4O) is formed after VO during the carbothermic reduction of V_2O_5/V_2O_3 prior to the formation of vanadium,[24] we have only detected VO and not the V_4O phase (Fig. 7).

While a good number of data on the kinetics of reaction of nitrogen/ammonia with metallic vanadium have been published by several authors,[25,26] no comprehensive data on the kinetics of carbonitrothermic reduction of oxides of vanadium are available in the literature perhaps because of the inherent complexity of the reaction scheme involving the formation of many intermediate carbonitride/oxynitride/oxycarbide/carboxynitride phases.

5. Conclusion

The present investigation describes the formation of vanadium nitride by heating a mixture of vanadium pentoxide and carbon under a flowing nitrogen atmosphere. The experimental parameters that critically affected the formation of the nitride were: oxide-to-carbon charge composition, particle size of the oxide and graphite powder, nitriding temperature and nitrogen flow rate.

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