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Nitride Intermediates in the Preparation of Columbium, Vanadium, and Tantalum Metals

(In Two Parts)

1. Nitride Preparation

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8079

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NITRIDE INTERMEDIATES IN THE PREPARATION OF COLUMBIUM, VANADIUM, AND TANTALUM METALS

(In Two Parts)

1. Nitride Preparation

by

R. A. Guidotti,[1] G. B. Atkinson,[2] and D. G. Kesterke[3]

ABSTRACT

The Federal Bureau of Mines has studied the reaction of oxides of columbium, vanadium, and tantalum with ammonia in vertical, gas-solids reactors at temperatures ranging from 300° to 1,300° C with the goal of preparing nitride intermediates for subsequent preparation of the metals by a thermal-decomposition step. The best nitride conversions were obtained in nonmetal reactors. With Cb_2O_5, V_2O_3, and V_2O_5, low-temperature maxima in reaction rates occurred at 800°, 800°, and 450° C, respectively, during oxynitride formation (in Al_2O_3) at 1 atm of pure ammonia. Conversion of the oxynitride, in a second step, to the mononitride was optimum at 1,200° C for columbium and 1,050° C for vanadium. In the case of Ta_2O_5, the rate of reaction to form Ta_3N_5 (in a single step) was highest at 900° C, where the presence of up to 5 percent methane was found to be beneficial; improved results were obtained by conducting the nitriding in a rotary kiln. Optimum space velocities (in the vertical Al_2O_3 reactor) ranged from 5,280 hr^{-1} for Cb_2O_5 to 7,950 hr^{-1} for V_2O_3. Oxide particle size had little effect upon reaction rates. Under fully optimized conditions, products containing less than 1 percent oxygen were readily obtained in under 6 hours.

INTRODUCTION

One objective of the Bureau of Mines research program has been the development of new or improved processes for the preparation of metals and alloys from minerals or mineral products. As part of this program, pioneering research indicated the possibility of preparing a number of high-purity, refractory metals from their oxides by use of nitride intermediates.

The most common method of preparing refractory metals, such as vanadium, columbium, and tantalum, involves carbothermic (8, 17, 19, 25)[4] or

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[1] Research chemist.

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[3] Supervisory metallurgist (now Chief, Boulder City Metallurgy Research Laboratory).

[4] Underlined numbers in parentheses refer to items listed at the end of this report.

metallothermic (1, 7, 12, 15, 26, 28) reduction of the oxides in a batch process, followed by consolidation and purification by electron-beam melting. These Group V A metals also can be prepared from their chlorides via metallothermic- or hydrogen-reduction techniques (17, 19, 25), or by electrowinning from molten salt mixtures (14, 18, 29).

In evaluating alternative preparation techniques, the Bureau investigated a method which involves reacting the oxide (generally the pentoxide) of the Group V A metal in question with anhydrous ammonia at temperatures up to 1,300° C to form the nitride, followed by thermal decomposition of the nitride at 1,800° C or higher, under vacuum, to yield pure metal and elemental nitrogen. The nitriding process may have the potential advantage of being suitable for a continuous operation in a fluidized bed or rotary kiln. In addition, no toxic or corrosive gases are generated in the nitriding and denitriding sequence.

The portion of the process dealing with nitride preparation is the subject of this paper; results of nitride decomposition studies will be presented in a second report. The objective of the present work was to study the rate and degree of nitride conversion of the Group V A oxides with ammonia, to optimize experimental conditions, and to obtain a nitride product as low as possible in oxygen in the shortest practical time. Variables examined included reactor material, temperature, space velocity and composition of the nitriding gases, and composition, particle size, and thermal treatment of the oxides. Initial nitriding studies with Cb_2O_5 have previously been reported (11). The results of additional nitriding studies with Cb_2O_5 are reported here, along with the results of similar work with oxides of vanadium and tantalum.

In general, the nitriding reactions proceeded at a nearly constant rate. They were terminated when the rate decreased significantly. Most of the nitride conversion data reported in this document were generated from single experiments. Arrhenius plots were made from these conversion rate data, and the activation energy, E_a, was obtained by a least-squares treatment. The average coefficient of variation of the activation energy data was approximately 8 percent. The Arrhenius plots were similar to those shown in the reported study (11) with Cb_2O_5.

EQUIPMENT AND APPARATUS

The equipment and apparatus used in the study were similar to those used in the earlier work (11). The charge was contained on a frit or metal-felt pad (depending upon the reactor material), internally supported within a 89-mm-long by 38-mm-diameter reactor and capped by a porous lid to allow gas passage while preventing sample loss. In the case of the Al_2O_3 reactor, a custom-fabricated, iron-free Al_2O_3 frit was employed. A small-diameter tube connected to the base of the reactor was used to introduce purge and reactant gases into the system. The gas-solids reactor was contained in a vertical Al_2O_3 tube with gasketed end plates provided with connections for thermocouples and gas. Most of the experiments were performed in the vertical reactor; under the experimental conditions, the charge was not fluidized and exhibited fixed-bed behavior. A limited number of nitriding experiments were also carried out with Ta_2O_5, using a small rotary kiln.

REAGENTS

The Cb_2O_5 and Ta_2O_5 used in the studies were metallurgical grade, or better than 99.9 percent pure. Fluoride impurity in the Cb_2O_5 was removed by calcination at 600° to 800° C for at least 12 hours. The V_2O_5 was prepared by calcining reagent-grade NH_4VO_3 at 400° C for 4 hours with frequent stirring. The V_2O_3 was prepared by hydrogen reduction of V_2O_5 at 600° C.

Commercial anhydrous ammonia, prepurified-grade hydrogen and nitrogen, and chemically pure methane and carbon monoxide were used as received without additional purification. High-purity helium, used as a purge gas and diluent in some experiments, was obtained from the Bureau of Mines Helium Operations.

Calcium carbide was used for monitoring the rate of water evolution during each run. Conventional dessicants were found to be unsuitable: $Mg(ClO_4)_2$ (Anhydrone) was incompatible with ammonia and formed a salt adduct, while $CaSO_4$ (Drierite) had a low water-absorption capacity.[5]

EXPERIMENTAL PROCEDURE

The experimental procedure was the same as that employed in the earlier studies (<u>11</u>). The exhaust gases were passed through tubes filled with calcium carbide which were periodically weighed to determine the rate of water evolution as the nitriding progressed.

Oxygen was determined by neutron activation, carbon by combustion analysis, and columbium and tantalum by ignition to the pentoxide at 800° C. Because of difficulties encountered in accurate analysis of nitride products of columbium and tantalum for nitrogen by neutron activation (due to matrix effects and problems with standards), nitrogen values were obtained by difference for these samples. Difficulties in analysis of such nitride materials have been previously reported by other workers (<u>2</u>, <u>13</u>).

RESULTS

Cb_2O_5

Previous studies with Cb_2O_5 showed that significantly better results were obtained with nonmetal systems than with metal systems (<u>11</u>), and in the current effort, additional studies were undertaken using an Al_2O_3 reactor with an iron-free Al_2O_3 frit, to better define the optimum experimental conditions. Charges of 7.5-g Cb_2O_5 were used for most of the experiments.

Typical nitride conversion data for the Al_2O_3 reactor, at a space velocity of 1,760 hr^{-1} (220 cm^3/min), are shown in table 1. (Space velocity = gas

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[5] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

volume/time/charge volume = time^{-1}.) Unless otherwise stated, values reported are corrected to STP--0° C and 1 atm. It was not practical to estimate the space velocity at temperature because of thermal effects and the dissociation of ammonia which occurred.

TABLE 1. - Nitride conversion data for the reaction of Cb_2O_5 with NH_3 in Al_2O_3 reactor[1]

Temp, ° C	Reaction time, hr	Product analyses, wt-pct		Phases
		[2]N	[3]O	
700	5	13.2	4.6	δ-Cb(O,N)
800	8	13.3	3.5	δ-Cb(O,N)
900	11	12.5	1.8	δ-Cb(O,N) + ε-CbN
1,000	26	12.3	.9	ε-CbN

[1] Space velocity = 1,760 hr^{-1}, 7.5-g charge.
[2] CbN = 13.1 wt-pct N.
[3] Cb_2O_5 = 30.1 wt-pct O.

An apparent activation energy (E_a) of 21.5 kcal/mole was obtained for the conversion of Cb_2O_5 to the nonstoichiometric oxynitride, δ-Cb(O,N), using the Al_2O_3 reactor with the iron-free frit. This compares to 19.2 obtained when a commercial, iron-containing alumina frit was used. An overall range of 15 to 26 kcal/mole was observed in this region for the various reactors. A similar range of E_a values of 17 to 23 kcal/mole was found for the formation of the CbO_2 intermediate from Cb_2O_5. (A value of 18.2 kcal/mole resulted when pure H_2 was used.) Finally, when CbO_2 further reacted to form the high-temperature δ-CbN phase, corresponding E_a values ranged from 10 to 14 kcal/mole. Insufficient data prevented the determination of E_a for the formation of the low-temperature (ε) form of CbN from CbO_2. The E_a data were obtained by a least-squares treatment of conventional Arrhenius plots. The magnitude of the E_a values is typical of reactions where chemical control is rate limiting.

Particle Size

The Cb_2O_5 used for most of the research was a finely divided powder (1- to 2-micrometer average particle size), which tended to agglomerate and sometimes caused difficulties in attaining good gas-solids contact. To alleviate this, Cb_2O_5 "wet cake" (hydrous oxide) was used in preparing a more reactive material. The material was calcined at 600° to 800° C for 24 hours and crushed to particle sizes of minus 10 plus 20 to minus 200 mesh. The best results with material calcined at 700° C were obtained for particle sizes of ≥48 mesh. Total reaction times for the various particle sizes differed little for comparable oxygen levels of the product, however, because of diffusional limitations in the final stages of reaction. Calcination temperatures of 600° to 800° C had little effect upon the observed reaction rates.

Space Velocity

For much of the earlier work in the Al_2O_3 reactor, an ammonia space velocity of 1,760 hr^{-1} (220 cm^3/min) was used with a 7.5-g charge. Subsequent experiments indicated that this was less than optimum for the size charge employed. As a result, additional experiments were carried out at higher space velocities at a temperature of 800° C, where oxynitride formation was most favorable. The results of tests with minus 35- plus 48-mesh Cb_2O_5 indicated that the initial reaction rate reached a maximum at a space velocity of about 5,280 hr^{-1} (660 cm^3/min); comparable results were obtained at the higher temperatures as well. This space velocity was then used for the majority of the subsequent experiments.

Two-Step Nitriding Sequence

In an attempt to reduce the total time required for complete conversion of Cb_2O_5 to CbN with ammonia, the nitriding was conducted in two steps. The relatively high initial surface area of the δ-Cb(O,N) phase formed at 800° C compensated for the loss of surface area caused by sintering during subsequent CbN formation above 1,100° C. Results are presented in table 2 and show that considerable reduction in reaction time occurred when the two-step reduction sequence was employed, relative to a single-stage reduction at the lower space velocity. A further reduction in reaction time occurred at the higher, optimum space velocity, with slightly lower oxygen levels of products being obtained at 1,300° C.

TABLE 2. - Comparison of one-step and two-step reaction of Cb_2O_5[1] with NH_3

Run	Temp, ° C	Sequence	Total reaction time, hr	Space velocity, hr^{-1}	Product analysis, wt-pct	
					O	N
1	1,200	1 step	33.5	1,760	0.07	11.8
2	800/1,200	2 step	8.0	1,760	.36	12.5
3	800/1,200	2 step	4.0-5.0	5,280	.84	12.3
4	800/1,300	2 step	5.0-5.5	5,280	.20	13.1

[1] 7.5-g charge = minus 35 plus 48 mesh.

Gas Composition

A cursory study of the effect of the composition of the nitriding gas mixture upon the rate and degree of nitride conversion was made at a gas space velocity employed in earlier studies of 1,760 hr^{-1}. Gas mixtures of NH_3 with CH_4, CO, and H_2 were studied, as well as H_2-N_2 mixtures.

Nitriding tests with CO-NH_3 mixtures containing up to 50 percent CO indicated that, relative to ammonia, there was no improvement in the rate and degree of nitriding of Cb_2O_5 at 800° C, where the rate of oxynitride [δ-Cb(O,N)] formation was greatest. With comparable CH_4-NH_3 mixtures, there was a significant contamination by carbon.

While a maximum in the initial reaction rate was observed with NH_3-H_2 mixtures at about 70 percent ammonia, at 1,000° C (ε-CbN region), the overall reaction time (relative to pure ammonia) was increased, because of the decrease in the secondary reaction rate which took place with decrease in the ammonia concentration. Thus, no real benefits were derived.

At 800° C, rates of reaction with H_2-N_2 mixtures were relatively low. With a 75-percent H_2-25-percent N_2 mixture--the composition of completely dissociated ammonia--the reaction rate was only 1/10 of that for pure ammonia. There was also a sharp drop in the initial reaction rate at 1,100° C as the nitrogen content of the gas mixture was increased.

V_2O_3

Initial nitriding experiments were carried out in the Al_2O_3 reactor with 5-g charges of V_2O_3, because its higher melting point, relative to V_2O_5, allowed a wider temperature range to be studied.

Space Velocity

The effect of ammonia space velocity upon the initial rate of reaction with V_2O_3 is typified in figure 1 for temperatures of 600°, 700°, and 800° C. (All rates were obtained by least-squares treatment of the linear portion of

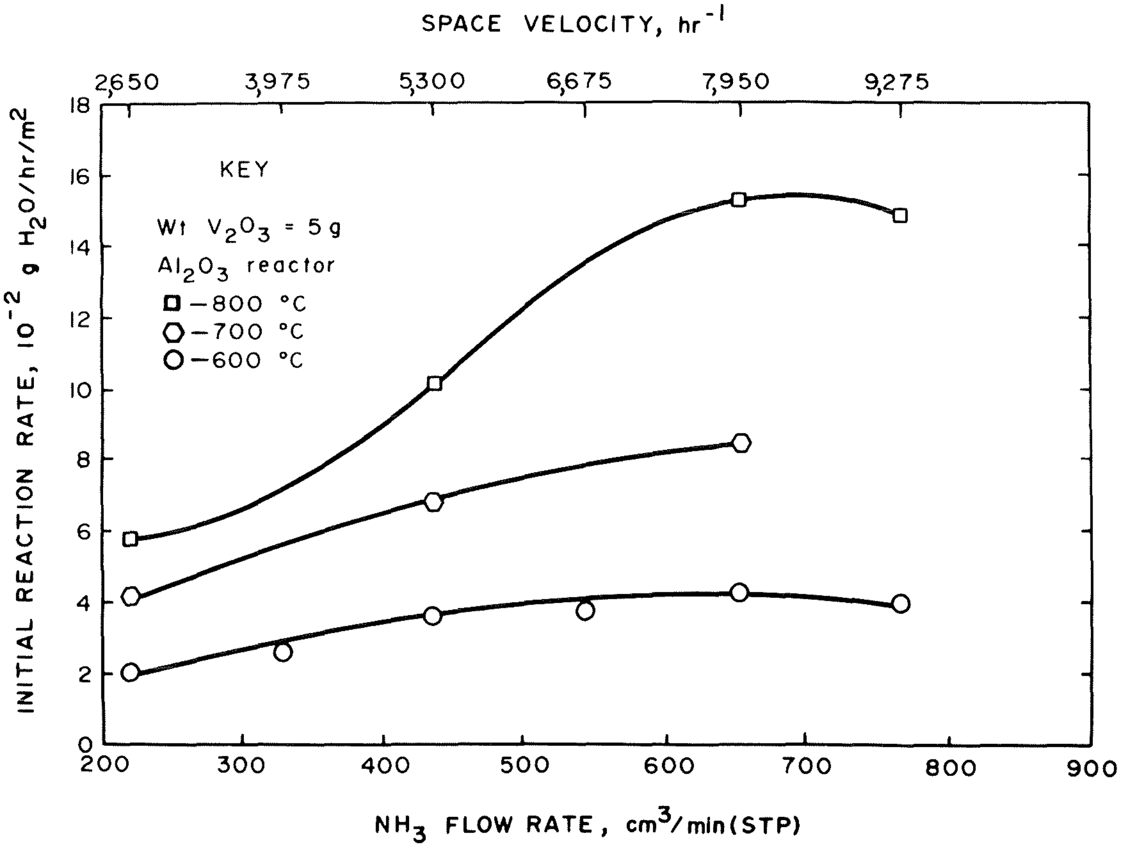

FIGURE 1. - Rate of NH_3-V_2O_3 reaction as a function of flow rate in Al_2O_3 reactor.

the water-time curves.) The best results were obtained at a space velocity of about 7,950 hr^{-1}.

The initial rate of reaction (evolution of water with time) was observed to be linear at the optimum velocity (as was observed with Cb_2O_5 under similar conditions), which is characteristic of reactions where chemical or mixed chemical and transport control is rate limiting (4, 6).

Reactor Material and Temperature

The effect of reactor material upon the rate of reaction at the optimum space velocity for a temperature range of 400° to 1,200° C is shown in figure 2.

At 900° C or higher in the metal reactors and 1,000° C or higher in the nonmetal reactors, VN was the reaction product; below these temperatures, V(O,N) predominated. At 1,000° C in the Al_2O_3 and Vycor reactors, VN formed via the V(O,N) intermediate. This was characterized by a change in slope of the linear water-time plots, which was also noted earlier for Cb_2O_5 under similar conditions. (At ≥1,000° C, where VN formation was favorable, Al_2O_3 was the preferred nonmetal reactor, since Vycor exhibited substantial devitrification at this temperature, while the use of graphite led to carbon contamination of the product and side reactions with product water vapor.)

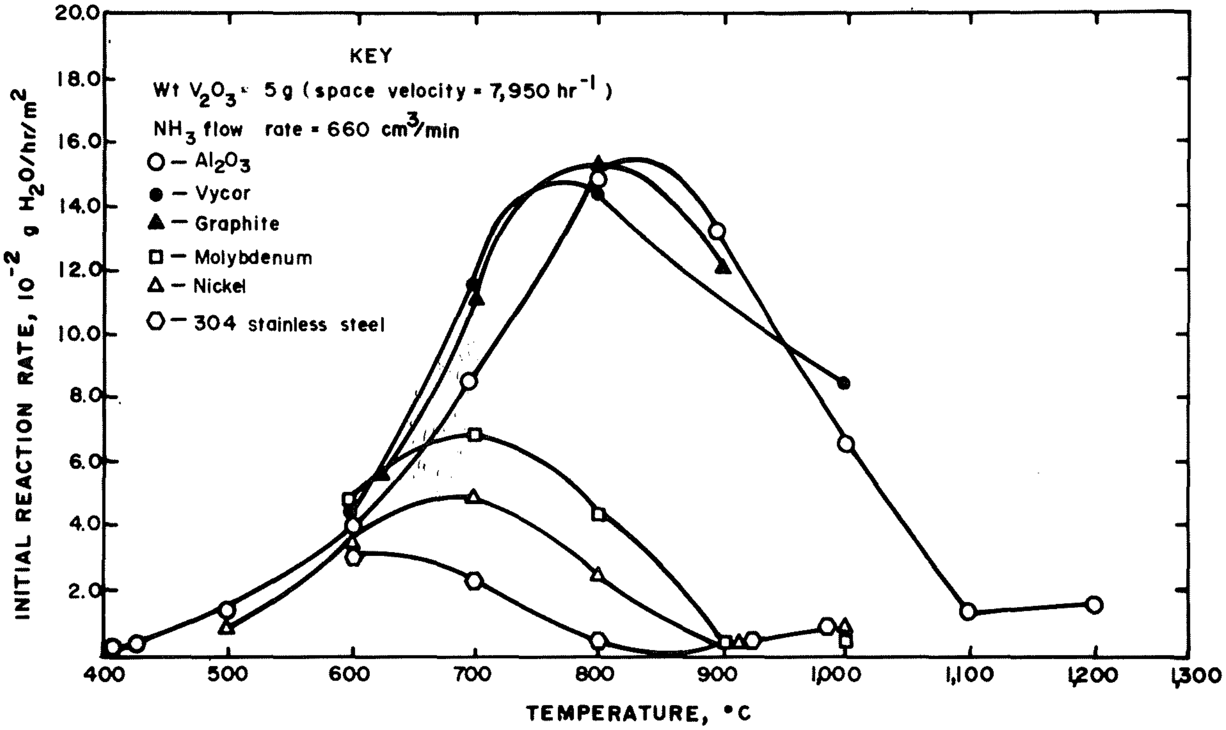

FIGURE 2. - Rate of NH_3-V_2O_3 reaction in various reactors as a function of temperature.

Apparent activation energies for the reaction of V_2O_3 with ammonia are listed in table 3 for the various reactors. The nitriding process can be described by three reaction regions: (1) $V_2O_3 \rightarrow V(O,N)$; (2) $V(O,N) \rightarrow VN$; and (3) $V_2O_3 \rightarrow VN$. For the Al_2O_3 reactor in region 1, a low-temperature (400°-500° C) and a high-temperature (600°-800° C) region of oxynitride formation were evident in the E_a data, with the low-temperature product having a much higher oxygen content and almost three times the apparent activation energy of its counterpart. The E_a values in region 1 are in the range expected for chemical or mixed control as being rate limiting. Insufficient data points prevented accurate determination of E_a values for regions 2 and 3.

TABLE 3. - Apparent activation energies for the reaction of V_2O_3 with NH_3[1]

Reactor	E_a, kcal/mole[2]		
	Region 1: $V_2O_3 \rightarrow V(O,N)$	Region 2: $V(O,N) \rightarrow VN$	Region 3: $V_2O_3 \rightarrow VN$
Al_2O_3	34.0 (400°-500° C)	17.7 (900°-1,000° C)	6.1 (1,100°-1,200° C)
	11.9 (600°-800° C)	([3])	([3])
Vycor	16.1 (600°-700° C)	([3])	([3])
Graphite	19.0 (500°-700° C)	([3])	([3])
Nickel	27.6 (500°-600° C)	([3])	33.0 (900°-1,000° C)
Molybdenum	([3])	([3])	6.8 (900°-1,000° C)

[1] Space velocity = 7,950 hr^{-1}, 5-g charge.

[2] Temperatures in parentheses indicate the range over which the E_a data are valid.

[3] Not available due to insufficient data.

Nitride Conversion

Typical nitride conversion data are presented in table 4 for the Al_2O_3 reactor. While more rapid conversion occurred below 800° C, temperatures of at least 900° C in the metal systems and 1,000° C in the nonmetal systems were required to obtain a nitride product containing 0.5 percent or less oxygen. Under the best conditions, reaction times ranged from 18 to 30 hours, with the nonmetal reactors requiring less time.

As it had been demonstrated that a two-stage nitriding sequence reduced the total reaction time substantially for the reaction of ammonia with Cb_2O_5, similar experiments were carried out with V_2O_3. The results are presented in table 5. A substantial reduction in reaction time was realized with the two-step nitriding process; the best overall results were obtained with a nitride-formation temperature of 1,050° C.

TABLE 4. - Nitride conversion data for the reaction of V_2O_3 with NH_3 in Al_2O_3 reactor[1]

Temp, ° C	Reaction time, hr	Product analysis, wt-pct		Phases
		[2]N	[3]O	
400/500	[4]6/47	17.3	12.6	V(O,N)
500	[4]14.5	15.7	10.1	V(O,N)
600	4.5	17.6	7.3	V(O,N)
700	4	17.7	5.4	V(O,N)
800	2	19.4	3.8	V(O,N)
900	7	19.2	3.3	V(O,N)
1,000	24	21.0	.4	VN
1,100	20	21.4	.2	VN
1,200	20	20.4	.4	VN

[1] Space velocity = 7,950 hr^{-1}, 5-g charge.

[2] VN = 21.6 wt-pct N.

[3] V_2O_3 = 32.0 wt-pct O.

[4] Reaction not carried to completion.

TABLE 5. - Two-step reaction of V_2O_3 with NH_3 in Al_2O_3 reactor[1]

Temp, ° C	Total reaction time, hr	Product analysis, wt-pct		Atomic pct N per hour of run time
		O	N	
1,000	24.0	0.40	21.0	2.04
1,000	20.0	.20	21.4	2.48
800/1,000	4.0	.54	22.8	12.8
800/1,050	3.5	.54	22.4	14.5
800/1,100	4.5	.47	21.7	11.1

[1] Space velocity = 7,950 hr^{-1}, 5-g charge.

V_2O_5

Because of its low melting point (675° C), V_2O_5 was not heated to temperatures over 650° C prior to initiation of a run.

Temperature

Initial experiments were carried out with 5-g charges of V_2O_5 in the Al_2O_3 reactor at an ammonia flow of 220 cm^3/min (space velocity = 2,530 hr^{-1}). Water evolution was linear with time, with a change in slope after partial reduction had occurred; that is, the reaction was taking place in two stages. For runs between 350° and 375° C, this change occurred near a product composition of V_6O_{13}, which then reacted further to form V_2O_3. (The phases were confirmed by X-ray analysis.) At 300° C, the presence of VO_2 was also detected in the product. At 400° to 500° C, V_2O_3 was observed as an intermediate during the formation of V(O,N). At 600° to 650° C, V(O,N) formed directly from V_2O_5.

Additional tests at increased ammonia flow rates indicated that a space velocity of 7,590 hr^{-1} (660 cm^3 NH_3/min) was optimum for a 5-g charge. The secondary reactions and product phases observed at the lower space velocity were also evident at the optimum space velocity.

Reactor Material

The effects of reactor material upon the initial rates of reaction of V_2O_5 with ammonia (at the optimum space velocity) are shown in figure 3. Again, the best results were obtained with the Al_2O_3 reactor.

Apparent activation energies for the reaction of V_2O_5 with ammonia are shown in table 6. Between 300° and 650° C, there appeared to be five distinct reaction regions: (1) $V_2O_5 \rightarrow V_2O_3$; (2) $V_2O_3 \rightarrow$ V(O,N); (3) $V_2O_5 \rightarrow$ V(O,N); (4) $V_2O_5 \rightarrow V_6O_{13}$; and (5) $V_6O_{13} \rightarrow V_2O_3$. In regions 1 and 4, V_2O_3 and V_6O_{13}, respectively, formed as intermediate phases, which reacted further in regions 2 and 5. In regions 3 and 5, the V(O,N) and V_2O_3 phases, respectively, were the final products.

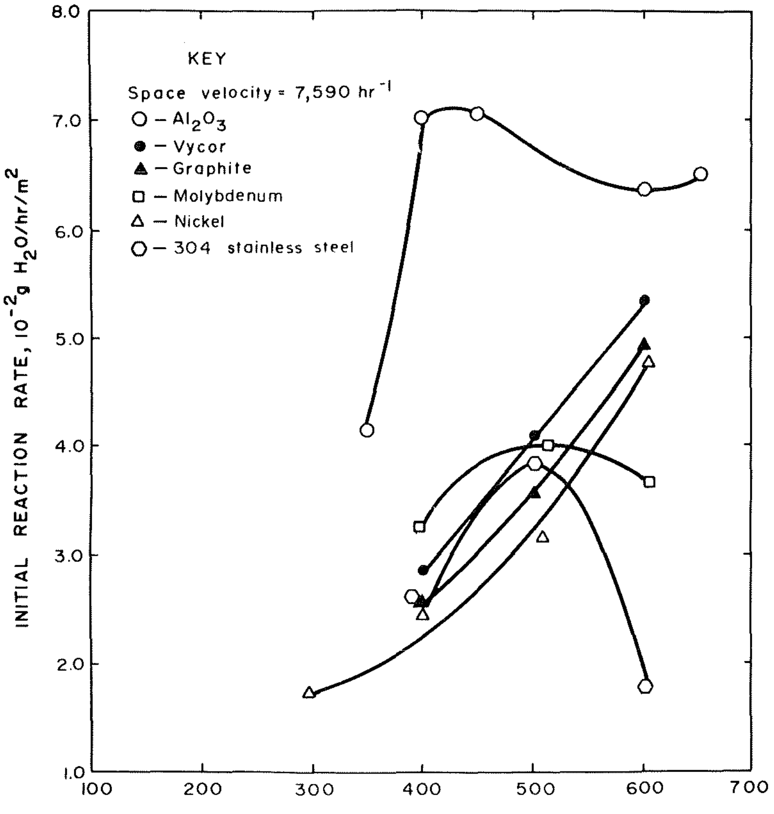

FIGURE 3. - Rate of NH_3-V_2O_5 reaction in various reactors as a function of temperature.

Region 1 ($V_2O_5 \rightarrow V_2O_3$) was characterized by low E_a values of ≤ 4 kcal/mole, which is indicative of a process where diffusion is rate limiting. Select E_a values for the Al_2O_3 reactor in regions 3 [$V_2O_5 \rightarrow$ V(O,N)] and 4 ($V_2O_5 \rightarrow V_6O_{13}$), and for the nickel reactor in region 4, were comparable to those observed for region 1. (Insufficient data points prevented a more detailed compilation of E_a values.) The tendency toward parabolicity of the water-time data in these regions is added support for diffusional limitations.

TABLE 6. - Apparent activation energies for the reaction of V_2O_5 with NH_3[1]

Reactor	E_a, kcal/mole[2]				
	Region 1: $V_2O_5 \rightarrow V_2O_3$	Region 2: $V_2O_3 \rightarrow V(O,N)$	Region 3: $V_2O_5 \rightarrow V(O,N)$	Region 4:[3] $V_2O_5 \rightarrow V_6O_{13}$	Region 5: $V_6O_{13} \rightarrow V_2O_3$
Al_2O_3................	0.12 (400°-450° C)	27.0 (400°-500° C)	0.57 (600°-650° C)	(4)	(4)
Al_2O_3[5]...............	0.11-0.69 (400°-500° C)	22.4-29.0 450°-500° C)	5.90 (600°-700° C)	1.35 (300°-375° C)	22.8 (350°-375° C)
Vycor.................	3.52 (400°-600° C)	19.5 (400°-500° C)	(4)	(6)	(6)
Graphite.............	3.60 (400°-500° C)	20.4 (400°-500° C)	(4)	(6)	(6)
Molybdenum...........	2.02 (400°-500° C)	22.8 (400°-500° C)	(4)	(6)	(6)
Nickel...............	2.34 (400°-500° C)	23.2 (400°-500° C)	(4)	3.00 (300°-400° C)	(4)
304 stainless steel, preheater...........	4.08 (400°-500° C)	23.5 (400°-500° C)	(4)	(6)	(6)

[1] Space velocity = 7,600 hr^{-1}, 5-g charge.
[2] Temperatures in parentheses indicate the range over which the E_a data are valid.
[3] VO_2 also noted at 300° C.
[4] Not available due to insufficient data.
[5] Space velocity = 2,530 hr^{-1}.
[6] Not observed because reactor was not used below 400° C.

Apparent activation energies for region 2 [$V_2O_3 \rightarrow V(O,N)$] were comparable to values observed earlier in nitriding studies with V_2O_3 (in region 1), and as such, are indicative of a process in which chemical control is rate limiting. The tentative E_a value of 23 kcal/mole for the Al_2O_3 reactor in region 5 ($V_6O_{13} \rightarrow V_2O_3$) is evidence for chemical control, also.

Nitride Conversion

Nitride conversion data for V_2O_5 in the Al_2O_3 reactor are presented in table 7 for an ammonia space velocity of 7,590 hr^{-1}. The lowest oxygen level of the product was obtained at the highest temperature of 650° C, after a reaction time of only 2 hours. In their study of the pyrolysis of NH_4VO_3 (V_2O_5, for all practical purposes) in H_2-NH_3 mixtures, Roubin and Paris (20) reported that a mixture of V_2O_3 and V(O,N) was obtained at 500° C. This very likely resulted from insufficient reaction time. Specific details as to gas composition, flow rate, sample size, etc., were not given, making direct comparison with our data difficult.

TABLE 7. - Nitride conversion of V_2O_5 with NH_3 in Al_2O_3 reactor[1]

Temp, ° C	Reaction time, hr	Product analysis, wt-pct		Phases
		[2]N	[3]O	
350	13	1.1	34.0	V_2O_3
400	7	.6	32.1	V_2O_3
450	23	19.1	9.5	V(O,N)
500	7	16.9	9.6	V(O,N)
600	2	17.1	8.2	V(O,N)
650	2	19.3	6.3	V(O,N)

[1] Space velocity = 7,590 hr^{-1}, 5-g charge.
[2] VN = 21.6 wt-pct N.
[3] V_2O_5 = 44.0 wt-pct O; V_2O_3 = 32.0 wt-pct O.

The two-step nitriding sequence successfully used with V_2O_3 was also applied to V_2O_5. With an oxynitride reaction temperature of 600° C and a nitride conversion temperature of 1,000° to 1,050° C, a nitride product with <0.9 percent oxygen and 20 to 21 percent nitrogen was obtained after 5 to 5-1/2 hours, using the Al_2O_3 or Vycor reactors.

To determine whether hydrogen reduction of V_2O_5 followed by reaction with ammonia would be preferable to direct reaction of V_2O_5 with ammonia, a cursory examination was made to obtain information on specific rates of reaction of V_2O_5 with hydrogen. The rate of water evolution during hydrogen reduction of V_2O_5 was quite linear, with a change in slope occurring at an intermediate product composition of V_6O_{13} for runs between 300° and 400° C. Above this temperature, V_2O_3 was formed directly in a single step. The rate was maximum at 600° C, and reached a plateau at a space velocity of 7,600 hr^{-1}.

Hydrogen reduction of V_2O_5 at 600° C, followed by reaction with ammonia at 800° C and then at 1,050° C, required a total time of 6-1/2 hours at the optimum space velocities (in the Al_2O_3 reactor); this compares to 5 hours for direct reaction with ammonia at 600° C and then at 1,050° C to form a comparable product.

Ta_2O_5

In nitriding studies with Ta_2O_5, a 12.5-g sample was used to obtain a volume comparable to those of the oxides previously studied. Initial experiments were carried out in the Vycor reactor, and results indicated that an ammonia space velocity of 4,750 hr^{-1} (660 cm^3/min) was close to optimum at temperatures between 900° and 1,000° C, where nitride formation was most rapid.

During reaction of Ta_2O_5 with ammonia, the initial rate of water evolution was linear, as previously noted for the other Group V A oxides. A typical curve of oxygen removal with time is shown in figure 4 for a reaction temperature of 600° C in the Al_2O_3 reactor; similar data for V_2O_5 and V_2O_3 are included for comparison. (Comparable data for Cb_2O_5 were not available under these exact conditions.) The corresponding initial rates of reaction, on a unit area basis, were 0.0069×10^{-2} g $H_2O/hr/m^2$ for Ta_2O_5, compared with 0.643×10^{-2} and 0.421×10^{-2} for V_2O_5 and V_2O_3, respectively.

Reactor Material and Temperature

The initial, linear reaction-rate data are presented in figure 5 for the various reactors as a function of temperature, at a space velocity of 4,750 hr^{-1}. Poor results were obtained with the metal reactors.

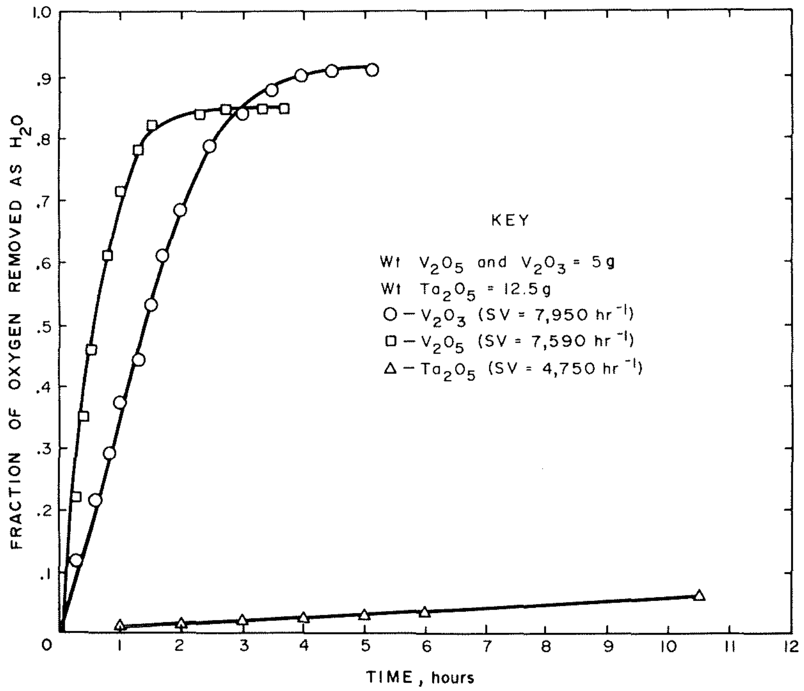

FIGURE 4. - Rate of ammonia-oxide reaction at 600° C in Al_2O_3 reactor.

In the reaction of Ta_2O_5 with ammonia, four major, distinct regions were discernible. In region 1, between 600° and 700° C, Ta_3N_5 was formed directly, but only slowly. In region 2, between 800° and 900° C, the oxynitride, TaON, was formed as an intermediate phase; this then reacted further in a second step, in region 3, to form Ta_3N_5. The mononitride, TaN, was formed directly, but slowly, from the pentoxide in region 4, at temperatures of ≥1,200° C. A less clearly defined reaction zone appeared to exist between 1,000° and 1,100° C,

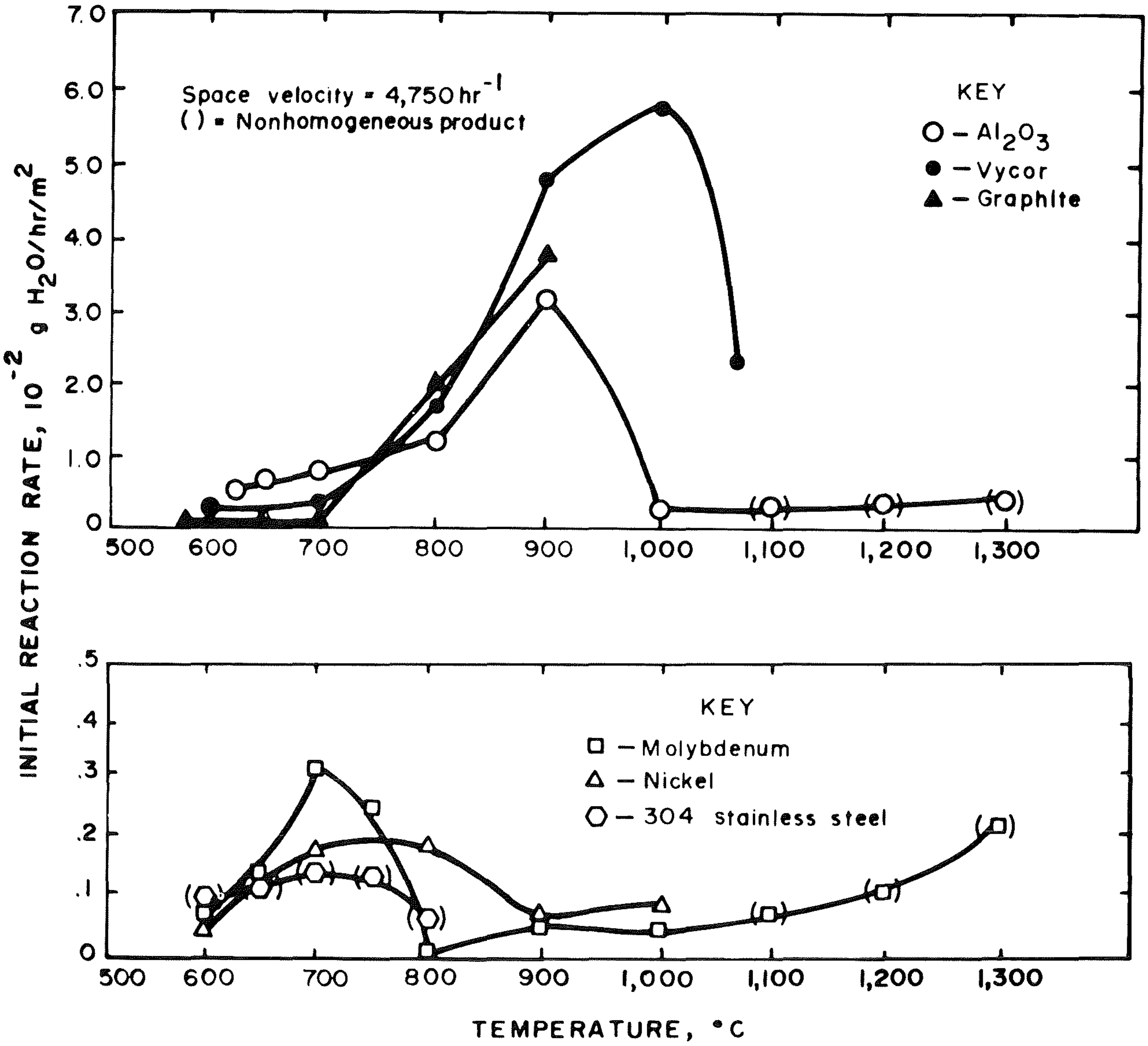

FIGURE 5. - Rate of NH_3-Ta_2O_5 reaction in various reactors as a function of temperature.

where the major product phase was found to be Ta_5N_6, with trace amounts of TaON (in Al_2O_3 and Vycor reactors). Indications were that Ta_5N_6 formed via the oxynitride as an intermediate; insufficient data prevented a more thorough characterization of this reaction region.

Apparent activation energies for the nitriding of Ta_2O_5 with ammonia are presented in table 8. In region 1 ($Ta_2O_5 \rightarrow Ta_2N_5$), E_a values were of the order of magnitude expected for rate limiting by chemical control. Similarly high E_a values were obtained for region 2 ($Ta_2O_5 \rightarrow$ TaON). The tentative E_a value of 11 kcal/mole obtained for region 3 (TaON $\rightarrow Ta_3N_5$) in the Al_2O_3 reactor suggests the presence of a mixed control. Apparent activation energies in region 4 ($Ta_2O_5 \rightarrow TaN$) again were indicative of chemical control as the most probable rate-limiting process.

TABLE 8. - Apparent activation energies for the reaction of Ta_2O_5 with NH_3[1]

Reactor	E_a, kcal/mole[2]			
	Region 1: $Ta_2O_5 \rightarrow Ta_3N_5$	Region 2: $Ta_2O_5 \rightarrow TaON$	Region 3: $TaON \rightarrow Ta_3N_5$	Region 4: $Ta_2O_5 \rightarrow TaN$
Al_2O_3.......	37.4 (625°-700° C)	(3)	10.7 (800°-900° C)	23.3 (1,200°-1,300° C)
Vycor.......	[4]30.2 (600°-900° C)	[4]30.2 (600°-900° C)	(3)	(5)
Graphite....	40.3 (600°-700° C)	21.3 (700°-900° C)	(3)	(5)
Molybdenum..	29.4 (600°-700° C)	(3)	(3)	34.0 (1,200°-1,300° C)
Nickel......	27.8 (600°-700° C)	(3)	(3)	(5)

[1] Space velocity = 4,750 hr^{-1}, 12.5-g charge.

[2] Temperatures in parentheses indicate the range over which the E_a data are valid.

[3] Not available due to insufficient data.

[4] One E_a value over temperature range for both regions.

[5] Not observed because reactor was limited in temperature to <1,200° C.

Because of the low reactivity of Ta_2O_5 towards ammonia, product nonhomogeneity, or the formation of a multiphase product, became pronounced for the metal reactors over 800° C. Incomplete reaction was also evident at ≥1,100° C in the Al_2O_3 reactor, where the upper portion of the charge remained unreacted. The rate data in figure 5 in these regions of nonhomogeneity are thus questionable and are so indicated.

The relative reactivity of the Group V A metal oxides over a range of 350° to 1,300° C is shown in figure 6 for the Al_2O_3 reactor. Because of the lower, less-than-optimum space velocities used with Cb_2O_5, the curve is somewhat less in absolute magnitude than it would have been otherwise. The relative positions of the curves, however, would remain unchanged.

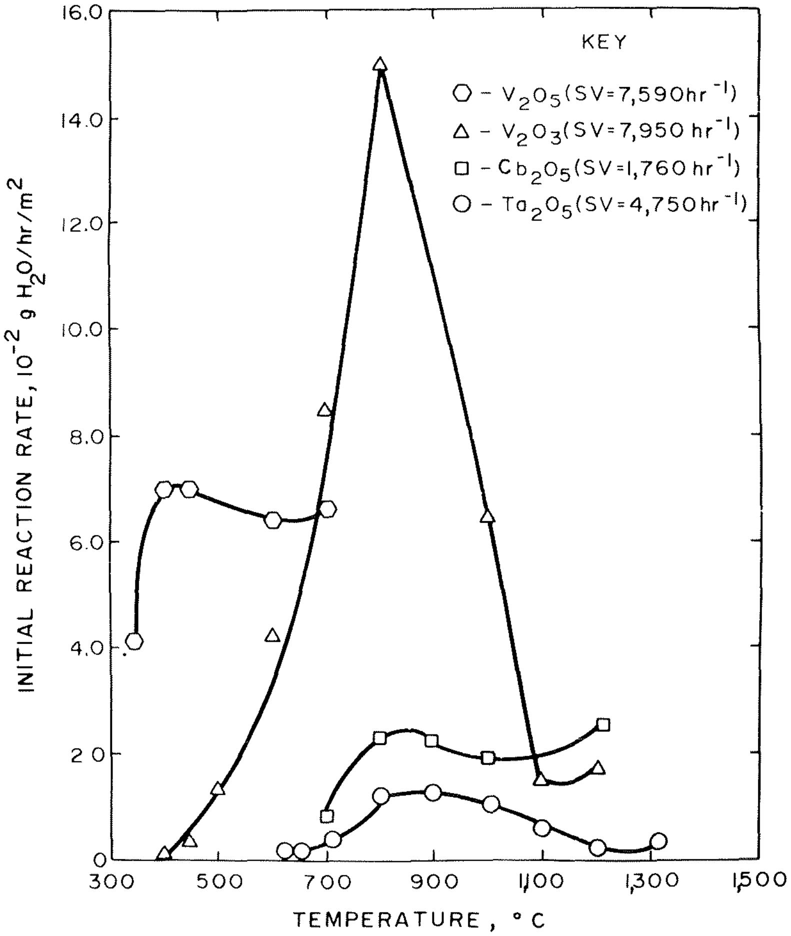

FIGURE 6. - Rate of ammonia-oxide reaction as a function of temperature in Al_2O_3 reactor.

Nitride Conversion

Nitride conversion data for the reaction of Ta_2O_5 with ammonia are presented in table 9 at a space velocity of 4,750 hr^{-1} in the Vycor reactor, where the data obtained were the most complete and reliable.

Formation of Ta_3N_5 was noted as low as 600° C, but did not occur to any appreciable extent below 700° C; a minimum temperature of 900° C was necessary (with the nonmetal reactors) before the oxygen level of this product decreased to near 1 percent. Swisher and Read (22) reported an oxygen level of 0.8 to 1.3 percent after reaction of Ta_2O_5 with ammonia at 827° C. The Ta_3N_5 phase was not stable above 900° C and lost nitrogen to form lower nitrides such as Ta_5N_6 and δ- and ε-TaN, which is in general agreement with data by Brauer, Weidlein, and Strähle (5) and Fontbonne and Gilles (9). The δ- and ε-TaN phases were first observed at a reaction temperature of 1,200° C (in the Al_2O_3 reactor); however, at 1,300° C, only ε-TaN was formed.

TABLE 9. - Nitride conversion of Ta_2O_5 with NH_3 in Vycor reactor[1]

Temp, ° C	Reaction time, hr	Product analysis, wt-pct		Phases
		[2]N	[3]O	
600	[4]31	1.6	15.9	β-Ta_2O_5
700	[4]31	8.8	5.0	Ta_3N_5, β-Ta_2O_5
800	31	10.2	2.6	Ta_3N_5, minor = TaON
900	27	10.5	1.1	Ta_3N_5, trace = TaON
1,000	28	7.7	1.4	Ta_5N_6, minor = TaON
1,075	27	7.5	1.4	Ta_5N_6 (distorted) trace = TaON

[1] Space velocity = 4,750 hr^{-1}, 12.5-g charge.
[2] Ta_3N_5 = 11.4 wt-pct N, Ta_5N_6 = 8.50 wt-pct N, TaN = 7.18 wt-pct N.
[3] Ta_2O_5 = 18.1 wt-pct O.
[4] Reaction not carried to completion.

Auxiliary Reductant

Because of the low reactivity of Ta_2O_5, additional nitriding studies were carried out with methane as an auxiliary reductant. Levels of 1.1, 2.5, and 5 volume-percent were used at temperatures of 900° to 1,200° C in the Al_2O_3 reactor, at a constant space velocity of 4,750 hr^{-1}; the results are presented in table 10.

TABLE 10. - Nitride conversion data for the reaction of Ta_2O_5 with CH_4-NH_3 mixtures in Al_2O_3 reactor[1]

Temp, ° C	Reaction time, hr	CH_4, pct	Product analysis, wt-pct		
			[2]N	[3]O	[4]C
900	37	0	10.6	1.1	0
900	[5]13	1.1	10.8	1.3	0.666
1,000	22	1.1	1.8	.65	4.6
1,100	[5]6	1.1	1.6	9.4	2.0
900	12.5	2.5	10.0	2.4	.25
1,000	15.5	2.5	.5	.85	5.7
1,100	6	2.5	2.4	6.9	3.0
900	12.5	5.0	11.2	1.0	.001
1,000	6.5	5.0	2.1	.85	4.7
1,100	5	5.0	1.4	.38	5.3
1,200	4	5.0	1.1	.17	5.6

[1] Space velocity = 4,750 hr^{-1}, 12.5-g charge.

[2] Ta_3N_5 = 11.4 wt-pct N, Ta_5N_6 = 8.50 wt-pct N, TaN = 7.18 wt-pct N.

[3] Ta_2O_5 = 18.1 wt pct O.

[4] TaC = 6.22 wt-pct C.

[5] Not carried to completion.

At 900° C, the use of methane as an auxiliary reductant resulted in shorter reaction times, for comparable oxygen level in the product, relative to when ammonia alone was used. For example, with a 5-percent CH_4-NH_3 mixture at 900° C, a product containing 1.0 percent oxygen was obtained in one-third the time required with pure ammonia. At higher temperatures, a substantial reduction in oxygen level occurred, along with a dramatic decrease in the nitrogen content of the product, as carburization became more favorable. Thermodynamically, TaC becomes more stable--that is, has a more negative free energy of formation--than TaN above 1,300 K (1,027° C), corroborating experimental observations.

Space Velocity

During cursory experiments at higher ammonia flow rates at temperatures where nonhomogeneity of the charge was observed during TaN formation, the optimum space velocity for the Vycor reactor (4,750 hr^{-1}) was less than optimum for the Al_2O_3 reactor. Because of this, additional tests at higher space velocities were carried out at 900° C, where the preferred formation of Ta_3N_5 was most favorable. It was found that the optimum space velocity in the Al_2O_3 reactor under these conditions was approximately 7,120 hr^{-1}. A nitride product with only 0.60 percent oxygen was obtained after 23 hours, which compares with 1.1 percent oxygen after 37 hours at 4,750 hr^{-1}.

Rotary Kiln

Because of the nature of the reaction between Ta_2O_5 and ammonia, it was not possible to apply the two-step nitriding sequence, and an alternate technique involving a rotary kiln was examined in attempts to enhance gas-solids contact. For this work, a bench-top rotary kiln was constructed using heavy-wall quartz and Al_2O_3 tubes (35- and 45-mm ID, respectively). At a rotational speed of 12 to 15 rpm, the inside peripheral velocity ranged from 2.8 to 3.0 cm/sec. Quartz-wool plugs were used to contain the charge in the heat zone and act as heat baffles. A 10-mm Al_2O_3 tube was used for feeding ammonia into the heat zone of the reactor via a rotary-feedthrough fitting in the end plate.

As a result of the difficulties encountered with the charge adhering tenaciously to the walls during initial tests with the Al_2O_3 kiln, efforts were concentrated on the quartz kiln.

At an equivalent space velocity of 4,750 hr^{-1}, the initial rate of water evolution in the quartz kiln appeared to be parabolic, which would indicate the presence of diffusional limitations presented by partial sintering of the charge into miniballs, about 2 to 3 mm in diameter. Additional tests carried out at 900° C at equivalent space velocities up to 14,250 hr^{-1} indicated that the initial (parabolic) rate of reaction reached a maximum at approximately 10,000 hr^{-1}, or a linear gas velocity of 145 cm/min. Total reaction time was reduced to about 6 hours, compared with 23 hours at 4,750 hr^{-1}, and a <1-percent oxygen level in the nitride product was still readily obtained.

Nitrogen Uptake

While monitoring the evolution of water vapor during the reaction of the Group V A oxides gives a measure of the reaction rate in terms of oxygen removal, it sheds no light on the rate of nitrogen uptake during oxynitride and nitride formation. Therefore, a number of nitriding experiments were carried out whereby samples could be removed periodically during runs for X-ray and oxygen and nitrogen analyses; the charge was contained on a frit sealed in the center of a vertical Vycor tube. The resultant data for Ta_2O_5 are presented in table 11, for a space velocity of 6,600 hr^{-1}, at temperatures of 700° and 900° C. Similar data for V_2O_3 and Cb_2O_5 are included for comparison.

The rate of oxygen loss (as water) was greater than the rate of nitrogen uptake (on an atomic basis)--more so during Ta_3N_5 formation and at the higher temperature. Corresponding data obtained early in the study for V_2O_3 and

Cb_2O_5, but at much lower space velocities (2,650 hr^{-1} and 1,520 hr^{-1}, respectively), showed similar behavior.

TABLE 11. - Relative nitrogen uptake and oxygen loss during reaction of Group V A oxides with NH_3

Oxide	Rate of O loss[1] / rate of N uptake	Remarks
Ta_2O_5:[2]		
700° C.	1.26	Ta_3N_5 formation.
900° C (step 1)	1.11	TaON formation.
900° C (step 2)	1.88	Ta_3N_5 formation.
Cb_2O_5:[3]		
700° C.	1.93	δ-Cb(O,N) formation.
1,000° C (step 1)	4.52	δ-Cb(O,N) formation.
1,000° C (step 2)	NA	ε-CbN formation.
V_2O_3:[4]		
700° C.	1.74	V(O,N) formation.
1,000° C (step 1)	2.50	V(O,N) formation.
1,000° C (step 2)	1.30	VN formation.

NA Not available.
[1] Atomic basis.
[2] Space velocity = 6,600 hr^{-1}, 6-g charge.
[3] Space velocity = 1,520 hr^{-1}, 15-g charge.
[4] Space velocity = 2,650 hr^{-1}, 5-g charge.

The much higher relative oxygen-nitrogen ratios for V_2O_3 and Cb_2O_5 may have been a result of the less-than-optimum space velocities employed in the early portion of the study, so that comparison with the data for Ta_2O_5 may not be completely valid. Time limitations prevented further investigation of the effect of space velocity upon the relative oxygen-nitrogen ratios.

DISCUSSION

Ammonia Dissociation

In the reaction of the Group V A metal oxides with ammonia, the material of construction of the reactors and the gas space velocity (flow rate) were found to have profound effects upon the rate and degree of nitride formation, since they determine the extent to which ammonia dissociation occurs,

$$2NH_3 \rightleftarrows N_2 + 3H_2. \qquad (1)$$

As the ammonia passes through the reactor, prior to contacting the charge, heterogeneous dissociation of ammonia occurs on the walls. The reactor material influences this process by catalytically increasing the rate of dissociation until some steady-state concentration of ammonia is established. This partial pressure of ammonia then effectively determines the reactivity or nitriding potential of the gas mixture. The metal reactors would be more catalytically reactive than the nonmetal reactors, because of the ready availability of low-lying, empty d orbitals for metal-nitrogen bond formation during chemisorption of ammonia prior to dissociation (3, 10, 24).

The improved results obtained with the nonmetal reactors are attributed to the reduced dissociation of ammonia. This was supported by cursory experiments in which ammonia was passed through the various empty reactors at 600° to 1,100° C, while the gases above the frits of the reactors were monitored for nitrogen content. Lower nitrogen contents were found with the nonmetal reactors. The effect of reactor material upon reaction rate was reduced at temperatures over 1,100° C, where homogeneous dissociation of ammonia became important.

The ammonia space velocity also affects the extent of ammonia dissociation. A less-than-optimum flow rate increases the gas residence time in the reactor and charge and allows excessive dissociation to occur. This can lead to a severe, vertical concentration gradient of ammonia in the charge, which would be most evident for a more unreactive oxide. (The layered segregation of products observed under certain conditions with Ta_2O_5 was most likely a result of this.) In the extreme case, the ammonia is completely dissociated and hydrogen becomes the main reactive gas species, with nitrogen taking little part in the reaction. With Cb_2O_5, for example, reaction with completely dissociated ammonia produced mainly CbO_2, instead of the nitride or oxynitride. In the case of Ta_2O_5, under comparable conditions, the absence of lower oxides resulted in no reaction taking place.

The dissociation energy of the first N-H bond in ammonia has been determined to be 104 kcal/mole (23), which is comparable to that for H_2; this compares to 226 kcal/mole for N_2 (16). The much higher dissociation energy of N_2 would account for the considerably reduced activity of N_2-H_2 mixtures observed in nitriding Cb_2O_5, relative to ammonia.

Because of the sensitivity of the observed reaction rates to the activity of the nitriding gas, the experimental data will also be affected by the influence on ammonia dissociation of other physical properties of the reactor, such as mass, size, and shape. To minimize this effect in the study, reactor geometry and dimensions were kept as similar as possible. However, the effective heat zone over which catalytic dissociation of ammonia occurred would differ somewhat for the various reactors, because of differences in thermal conductivity.

The empirically determined optimum reaction conditions for nitriding of the various oxides essentially reflect the influence of the foregoing factors. The determination of absolute reaction rates is not in itself meaningful--even in the absence of the effects discussed--because variations in oxide reactivity would be expected from lot to lot, depending upon the sample history. The rate data and activation energies reported here, however, are believed to be more than adequate for a valid comparison of the relative reactivities of the various Group V A oxides towards ammonia.

Oxide Reactivity

The reactivity of the Group V A metal oxides toward ammonia was generally as expected, with the vanadium oxides being the most reactive and Ta_2O_5 the least so. At 800° C, for example, the reactivity decreased in the order: $V_2O_3 > Cb_2O_5 > Ta_2O_5$. The same trend can be observed in the K_p data for the conversion of the pentoxides to the mononitrides at 1,500 K, where mononitride formation was observed experimentally in all cases. Values of 8.57×10^{14}, 8.52×10^5, and 3.10×10^2 were calculated for vanadium, columbium, and tantalum, respectively, for the following reaction:

$$M_2O_5 + 10/3\ NH_3 \rightarrow 2MN + 5H_2O + 2/3N_2. \qquad (2)$$

ΔF_f° data for TaN and CbN used were from Schick (<u>21</u>), and the other data were from Wicks and Block (<u>27</u>).

This same relative reactivity of the pentoxides is evident in the change in the average effective valence (AEV) of reaction products over the temperature range studied. (The AEV of the metal was calculated from the composition of the reaction product assuming a valence, or oxidation state, of -3 for nitrogen and -2 for oxygen; it essentially indicates the relative state of reduction of the metal in an idealized ionic lattice, which may not be entirely the case.) As the temperature was increased, the initial AEV of 5 (for the pentoxides) dropped to a minimum plateau value of 3 for the reaction products. One would expect the plateau to begin at lower temperatures as the oxide reactivity was increased. This was observed to be true experimentally. For the most reactive oxide, V_2O_5, an AEV plateau value of 3 was observed at 600° C. With the less-reactive Cb_2O_5, this did not occur until 1,000° C. In the case of the least reactive oxide, Ta_2O_5, the initial AEV of 5 remained unchanged from 600° to 900° C, dropping to a value of 3 only at 1,200° C.

The magnitude of the apparent activation energies for the various regions of reaction observed during the nitriding of the Group V A oxides with ammonia, in general, was indicative of chemical control as being rate limiting. Chemical control was most important during the initial stages of reaction, while diffusion control exerted the most influence in the final stages, as evidenced by the lack of dependency of the reaction rate on space velocity. The exceptions were the first-stage reactions observed with V_2O_5, to form V_2O_3, V_6O_{13}, or V(O,N), where diffusional control appeared to be more important. This is what one might expect, in view of the highly reactive nature of V_2O_5, which would lessen the importance of chemical control during initial reaction.

During reaction of the oxides with ammonia, adsorption and dissociation first occur to form species such as atomic hydrogen ($\cdot H$) and nitrogen ($\cdot \dot{N} \cdot$), and amine ($\cdot NH_2$) and imine ($\cdot \dot{N}H$) radicals (<u>3</u>, <u>24</u>). The latter would most likely be the reacting species, since they would serve as a source of hydrogen for removal of oxygen as water, and provide nitrogen for nitride and oxynitride formation as well. Development of a mechanistic kinetic model to explain and predict rate data, however, was beyond the scope of the study. Formulation of such a model would be difficult because of the numerous product phases possible for the various oxides and the number of potential species which could take part in reactions. In addition, the dissociation of ammonia during intraparticle diffusion would complicate diffusion calculations.

CONCLUSIONS

The use of nonmetal reactors resulted in the highest initial rates of reaction during nitriding of the Group V A metal oxides with ammonia in gas-solids reactors at temperatures up to 1,300° C, because of the reduced tendencies to catalyze heterogeneous dissociation of ammonia. The low-temperature maxima in rates were associated with oxynitride formation for V_2O_3, V_2O_5, and Cb_2O_5, and with Ta_3N_5 formation for Ta_2O_5; high-temperature minima in rates occurred during mononitride formation. In general, chemical control appeared to be most important during initial reaction, while diffusion control predominated in the terminal stages. During reaction, the rate of nitrogen uptake was less than the rate of oxygen loss.

A two-step reaction sequence--oxynitride formation followed by nitride formation--provided optimum reaction conditions for V_2O_5, V_2O_3, and Cb_2O_5 in the Al_2O_3 reactor; with Ta_2O_5, a quartz rotary kiln was used to optimize nitride conversion by promoting better gas-solids contact. In all cases, nitride products with <1 percent oxygen resulted after 6 hours or less.

While the use of larger particle sizes (>48 mesh) increased initial reaction rates somewhat, improvement was minimal, because diffusional control predominated in the final stages of reaction. The best overall results were obtained using pure ammonia, except for Ta_2O_5, where up to 5 percent methane was beneficial at 900° C.

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