PREPARATION OF VANADIUM METAL BY CARBON REDUCTION OF VANADIUM OXIDES

by

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INTRODUCTION

Vanadium metal has been used for sometime as an alloying agent, especially in steels. However, until recently it had received little attention with regards to applications as pure metal or as a major constituent in alloys. Materials investigations in areas of reactor technology reveal that vanadium metal exhibits certain characteristics which make it attractive as a material for selected reactor applications. More specifically, its low absorption cross section for fast neutrons and its compatibility with high purity sodium metal, coupled with its elevated melting point and high thermal conductivity, make vanadium of interest as a cladding material in sodium cooled reactors. Vanadium metal or alloy may well offer a superior fuel cladding for fast breeder reactors of current design.

Vanadium is not a rare element; it has been estimated that it ranks 22nd among the elements in the earth's crust (1), being as abundant as zinc or nickel (2). However, vanadium is widely distributed in trace amounts and is rarely found in concentrations greater than about two percent. Vanadium is often recovered as a by-product especially in some uranium ore processing (3). Recovery of the vanadium is usually in the form of the oxide which can be used in metal preparation. The oxide can be converted to other compounds, such as halides, which may be subsequently reduced to give the metal. Although a number of methods have been employed to prepare the metal, a study by Joly (4), in 1958, revealed that the methods which could be extended to an industrial scale type process fell into two general categories. They were:

(1) The reduction of the oxide with a reactive metal such as calcium or with carbon in a vacuum.

(2) The reduction of vanadium halides or halogen containing salts with hydrogen, magnesium or sodium.

Due to the low stabilities of the halides and their tendency to hydrolyze, changing their composition and yielding corrosive products, they offer major problems as a means for metal preparation. Therefore, methods based on the reduction of oxides have attracted greatest interest. Of these, the metallothermic type reductions have, to date, shown the greatest promise. The reduction of oxide by carbon has been considered as unsatisfactory for good grade metal due essentially to the inability to obtain complete reduction under the conditions that have been employed. In view of present technology, however, this method of preparation appears to warrant further study. Thus, the carbon reduction of vanadium oxides has been of primary interest in the investigation reported here.

If a suitable process, based on the carbon reduction can be developed, a number of advantages over metallothermic processes might be realized. Some of these advantages may be seen when a comparison is made with the calcium or aluminum reductions as represented by the following assumed expressions:

$$V_2O_5 + 4C \rightleftharpoons 2V + CO_2 + 3CO \qquad (1)$$

$$V_2O_5 + 5Ca \rightarrow 2V + 5CaO \qquad (2)$$

$$V_2O_5 + 10/3Al \rightarrow 2V + 5/3Al_2O_3 \ . \qquad (3)$$

First of all, about four times as much calcium as carbon would be required to obtain a given amount of vanadium by the reactions as written. Furthermore, experimental investigations have revealed that a 50% to 100% excess of calcium is required to obtain a satisfactory yield of pure product (5). Since the present price of calcium metal (about two dollars per lb.) per unit weight is considerably higher than carbon, calcium as a reductant would cost at least six dollars more per pound of vanadium produced.

The substitution of aluminum in place of calcium substantially reduces the price of the reductant to about forty cents more per pound than the cost by carbon reduction. However, another factor which must be considered, in the aluminum reduction, is the solubility of aluminum in vanadium. Since it alloys quite readily with vanadium, the resulting metal invariably contains undesirable amounts of aluminum which leads to an added purification or refining step to obtain the pure vanadium metal.

Even though carbon as a reductant offers some economic advantages, other factors stemming from the nature of the reactions favor carbon reduction. In the metallothermic reductions, yields of metal are lower than in carbon reduction and furthermore, the reaction products consist of a slag material along with the metal. This requires a clean separation to recover the metal for subsequent processing; otherwise, some contamination of the metal could result. In the carbon reduction, the reaction products, other than the metal are gaseous. Since the reaction is carried out under vacuum type conditions, pure metal and theoretical yields should result providing the reaction conditions (temperature and pressure) are proper for driving the reaction to completion. The problems encountered by a number of investigators in an effort to achieve these conditions will become apparent during the course of this report.

LITERATURE REVIEW

In 1801, del Rio (6) announced that a Mexican ore he analyzed contained a new metal. He named it erythronium, from the Greek work erythros, meaning red, since it formed red salts when treated with acids. He abandoned his opinion a few years later when Collet-Descotils (7) claimed that the new metal was an impure lead chromate. In 1831, Sefström (8) described a new mineral which he found in some Swedish iron ores and suggested for it the name vanadium, after the Scandinavian goddess of love and beauty, Vanadis. Immediately thereafter, Wohler (6) established that Sefström's vanadium and del Rio's erythronium were identical and was indeed a new metal.

Berzelius (9) was the first to attempt the preparation of the metal. By heating a volatile chloride which was really an oxychloride, in an atmosphere of ammonia, he thought he obtained vanadium metal. It was shown later that he had prepared the nitride (10). The first to prepare fairly pure metal was Roscoe (10), in 1869, by the reduction of the dichloride in very pure hydrogen. Although this process was time consuming and resulted in low yields of metal, his work provided an incentive for a number of researchers to attempt the preparation of pure metal using a variety of approaches, including the carbon reduction of the oxide.

The first reported attempts to prepare vanadium metal by the carbon reduction of vanadium oxide were performed by Henri Moissan in the middle 1890's (11,12). He employed vanadium pentoxide and carried out the reduction in an electric furnace. The product which he believed to be the metal, however, was considered by others to be essentially vanadium carbide. The conditions which Moissan employed are known to yield vanadium carbide.

In 1905, von Bolton (13) produced vanadium metal which was ductile enough to absorb the blows of a hammer. His process employed a unique method of thermal dissociation. Initially, a plastic mass of vanadium pentoxide and paraffin was pressed into bars and heated under vacuum by an electric current. In this step, the pentoxide was carbonized to the trioxide which was subsequently separated into its components by dissociation.

Ruff and Martin (14), in 1912, used a similar process and obtained 95 to 97% vanadium by forming mixtures of the trioxide and sugar charcoal into rods and heating them first to sintering in a vacuum resistance furnace, then to fusion in an arc furnace.

In 1935, Morette (15) tried to reduce vanadium oxides with carbon monoxide and with carbon. The reduction of the pentoxide with carbon monoxide proceeded no farther than the trioxide at temperatures up to 1200°C. Using sugar charcoal on these oxides, a metal was obtained, but the vanadium content analyzed to be less than 85% and was highly contaminated with carbides.

Kroll and Schlechten (16) made an extensive investigation of the reduction of vanadium oxide with carbon in a vacuum in 1948. In their research, CP grade vanadium pentoxide was briquetted with minus 100 mesh graphite and heated in a beryllia crucible in an induction furnace. The reaction initiated at 650°C as the charge was being heated. A temperature of 1550°C was maintained until the pressure decreased to 2 microns, after which the heating was stopped; above that temperature, it had been found that melting would occur causing a violent reaction of the molten product with the beryllia crucible. The resulting briquette from this 1550°C treatment was then crushed, mixed, rebriquetted and heated a second time in an effort to complete the reaction. Their metallic product, which never exceeded 93.4% vanadium, contained oxide and unreacted carbon. On the basis of these results, Kroll and Schlechten questioned the practicability of carbon reduction of vanadium oxide for the production of good quality vanadium metal.

Karassev and his coworkers (17), in 1956, and Joly (4), in 1958, succeeded in preparing ductile vanadium metal by extending and modifying Kroll and Schlechten's approach. This was accomplished by adjusting the carbon to oxygen ratio in the charge to unity at various times during the reduction sequence and heating for extended periods up to $1700^{o}C$ with a finishing pressure of $5x10^{-5}$ mm Hg. A typical analysis of the metal produced by this process showed it to contain 1200 ppm carbon and 600 ppm oxygen.

In an effort to reduce the long sintering times required in the processes by Karassev and Joly, Kiefer, Bach and Lutz (18), in 1967, reported on a method of preparing vanadium metal and some vanadium alloys by reducing the specified oxides with vanadium carbide instead of carbon. Their process, like the others consisted of a series of steps. First of all, the charge of oxide and carbide was sintered at $1450^{o}C$ until the pressure decreased to $5x10^{-4}$ torr; this required about eight hours. The sintered mass was then crushed, thoroughly mixed, and analyzed followed by adjusting the carbon to oxygen ratio to unity with vanadium carbide, remixing and rebriquetting. This mass was then sintered a second time at 1500°C for nine hours or until the final pressure was $1x10^{-4}$ torr. The sintered material from the second heating was recrushed and the stoichiometry adjusted again. These first two steps were performed using vacuum induction heating with the charge in a conducting container. The third step was carried out by pressing the readjusted charge into bars and heating them resistively under vacuum. This technique was used because it was felt that the temperature differential in a charge heated by induction was enough to cause the surface to melt before the center of the charge had completely reacted. After heating the bar resistively for six hours at temperatures up to 1650°C and a final pressure of less than $2x10^{-5}$ torr, the bars were then crushed and the stoichiometry adjusted a third time. After thorough mixing, bars were reformed and heating by self-resistance at temperatures up to 1675°C with the pressure going to $5x10^{-5}$ torr. Metal of greater than 99.8% purity resulted.

From an analysis of these previous investigations several observations can be made. They are:

(1) All of the reductions that yielded fair quality metal were performed by reacting the charge at temperatures below the melting point of the sample; this was considered as necessary by these investigators because molten vanadium metal reacted vigorously with all tested container materials.

(2) Since the reaction was carried out in the solid state, a stepwise process, which consisted of a series of sintering, grinding and rebriquetting steps to insure good particle contact, was necessary to complete the reaction in the solid state.

(3) Due to this type of reaction, heating schedules required extended periods of time.

It was on the basis of these observations that it became apparent that, if the carbon reduction of vanadium oxide were to be developed into a practical process for good quality vanadium metal that might have large scale potential, other means for promoting the reaction would have to be derived.

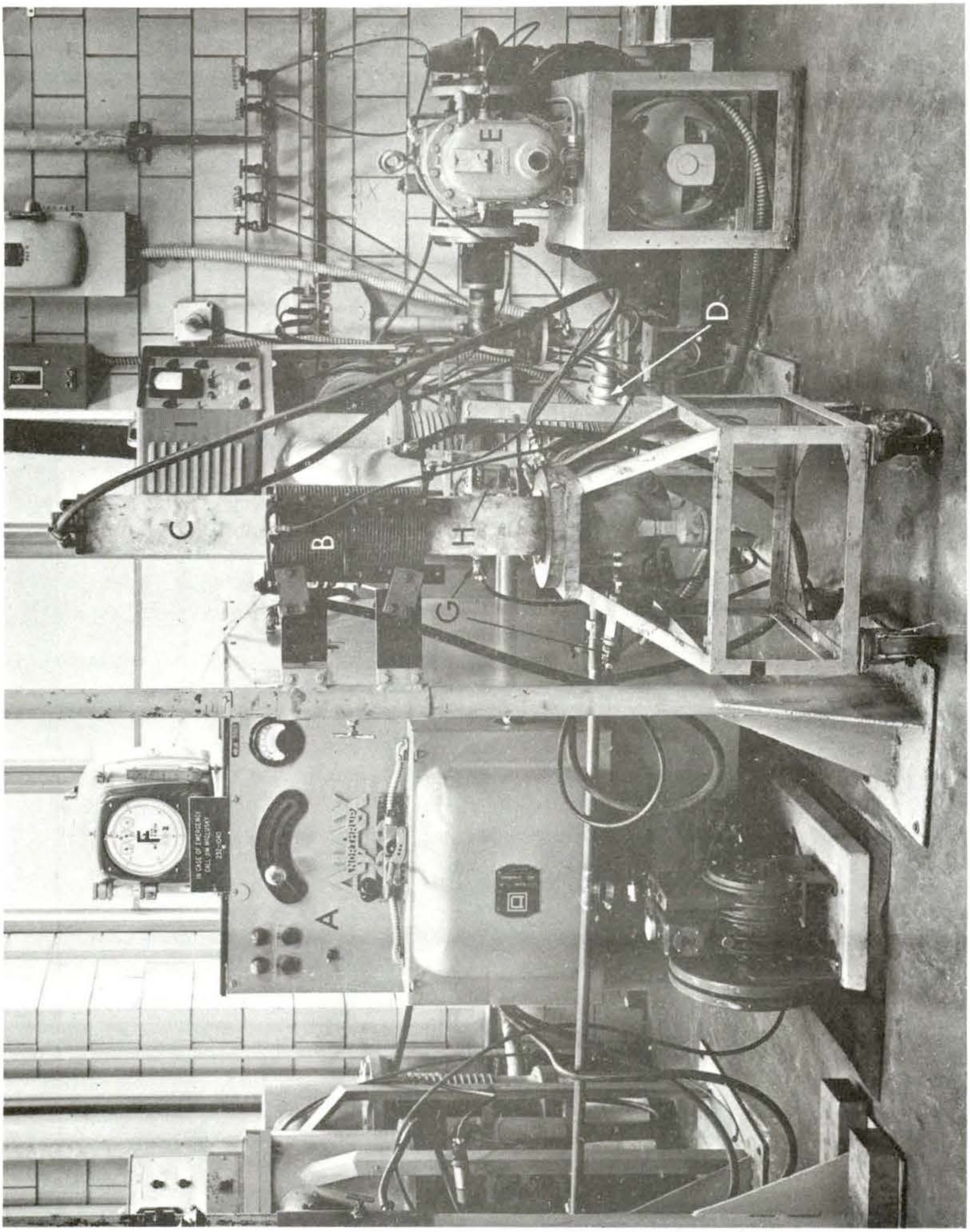
APPARATUS

Two types of induction heating power units, or converters, were used in this investigation. One was an Ajax mercury-arc gap type unit, while the other was a Westinghouse radio-frequency (450 kilocycles) generator. Two sizes of the Ajax units, a 6 KW and a 20 KW, were generally employed with a graphite susceptor as the heater. Most of the initial reductions and exploratory work were carried out using the smaller converter while the 20 KW unit was used for sintering crucibles and reducing larger charge sizes. The Westinghouse RF generator, a 25 KW unit, was used primarily for the self-induction heating experiments. The furnace chamber for each power unit was connected to a vacuum pumping system.

Since the equipment associated with each of the Ajax converters was similar, only a description of the smaller unit will be discussed. A photograph of this setup is shown in Figure 1. Power from the converter is supplied to a hoist-type, water-cooled induction coil four inches inside diameter and ten inches in height consisting of 40 turns. The furnace vacuum chamber used in this setup was composed of a water-cooled base which supported a silica sleeve three and three-eighths inches inside diameter with a one-fourth inch wall

Figure 1. Photograph of 6 KW Ajax vacuum induction furnace

A. 6KW Ajax converter
B. Induction coil (hoist-type)
C. Silica sleeve
D. Oil diffusion pump
E. Roots-type booster pump
F. Wet test meter
G. Thermocouple gauges
H. Ionization gauge
I. Thermocouple and ionization gauge control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thickness and about 32 inches in length. The vacuum seals at the ends of the silica sleeve were neoprene gaskets. A water-cooled head equipped with an observation port served as a lid for the chamber. The port was used to make visual observations during the course of a reduction and to take temperature measurements with an optical pyrometer. Figure 2 is a diagrammatic representation of this chamber.

The vacuum system employed consisted of a three-stage six inch diameter oil diffusion pump with a Roots-type booster pump backed by a Welch Duo-Seal mechanical fore pump. This vacuum pumping system could readily decrease the furnace chamber pressure to less than $5x10^{-5}$ mm Hg. Two thermocouple gauges and an ionization gauge were used to indicate the pressure that developed and a wet test meter connected to the exhaust of the fore pump gave a measure of the quantity of gas evolved during the course of a reduction.

A typical furnace assembly employed with the Ajax units is shown diagrammatically in Figure 3. It is composed of a graphite crucible with carbon powder insulation packed in a silica beaker. The graphite crucible which served as a susceptor was one and seven-eighths inches inside diameter and six inches in height with a three-sixteenths inch wall. This crucible was

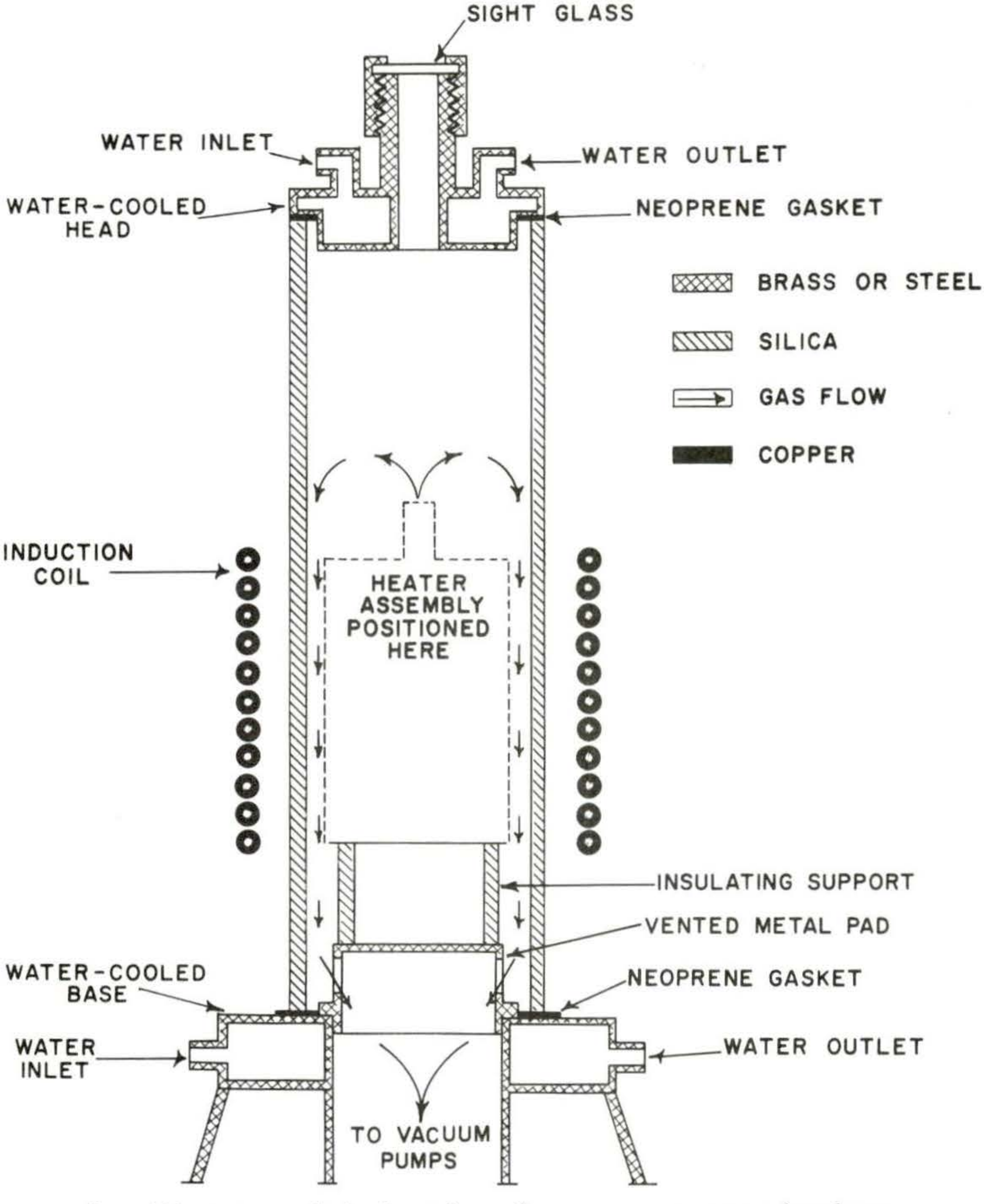

Figure 2. Diagram of induction furnace vacuum chamber

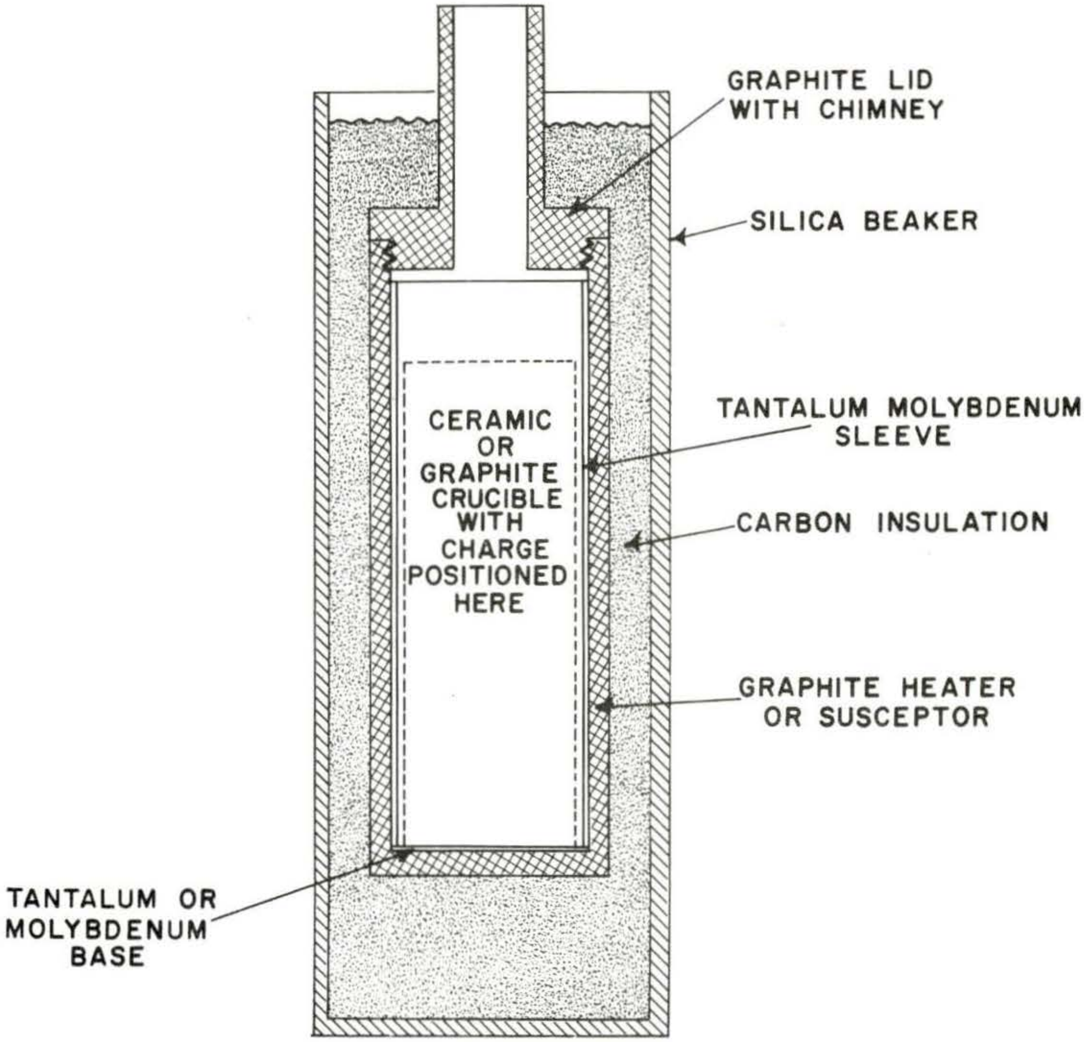

Figure 3. Diagram of furnace assembly used in vacuum induction heating experiments

fitted with a threaded cap that had a chimney which served as an observation port and an exit for product gases during a reduction. Whenever a substance was sintered that could conceivably react with the graphite heater, a liner of 30 mil sheet tantalum or molybdenum was employed. The fused silica beaker was three inches inside diameter and nine inches in height with a one-eighth inch wall. The carbon black insulation was a mixture of Shawinigan Black and Thermax carbon black mixed in a one to one volume ratio.

For a reduction where self-induction heating was used, the Westinghouse RF generator was employed to increase the efficiency or coupling between the induction coil and the conducting charge. This generator supplied power to a stationary water-cooled induction coil four inches inside diameter and six inches in height consisting of ten turns. The furnace vacuum chamber used with this unit is essentially the same as described for the 6 KW Ajax unit. The vacuum pumping system consisted of a three-stage four inch diameter oil diffusion pump with a Welch Duo Seal mechanical pump as the fore pump. The system could evacuate the furnace chamber to pressures less than 5×10^{-6} mm Hg. System pressure was determined using either a thermocouple gauge or an ionization gauge while a wet test meter was used to monitor gas evolution. Figure 4 is a photograph of this entire setup.

The furnace assembly used in the self-heating experiments is shown schematically in Figure 5. The vanadium intermediate product which has been pressed into the form of a right circular cylinder composes the charge. This compacted charge is positioned within an inner refractory oxide crucible and rests on some powdered intermediate which serves as a support. The inner crucible is placed within the larger refractory oxide crucible and covered with a refractory oxide lid. The latter crucible is insulated from the fused silica beaker, which serves as the overall containment vessel, by powdered refractory. The inner crucible measured one and one-half inches outside diameter and two and one-fourth inches in height with a three thirty-seconds inch wall. The larger crucible which measured one and five-eighths inches inside diameter and two and seven-eighths inches in height with a three thirty-seconds inch wall was fitted with a lid, prepared from a refractory oxide material. This lid had a chimney which served as an observation port and as an exit for gases formed during the reduction. The containment silica beaker measured two and one-half inches inside diameter and five inches in height with a one-sixteenth

Figure 4. Photograph of 25 kilowatt Westinghouse RF Generator

A. RF Generator
B. Induction coil (stationary)
C. Silica sleeve
D. Oil diffusion pump
E. Wet test meter
F. Thermocouple gauge
G. Ionization gauge
H. Thermocouple and ionization gauge control

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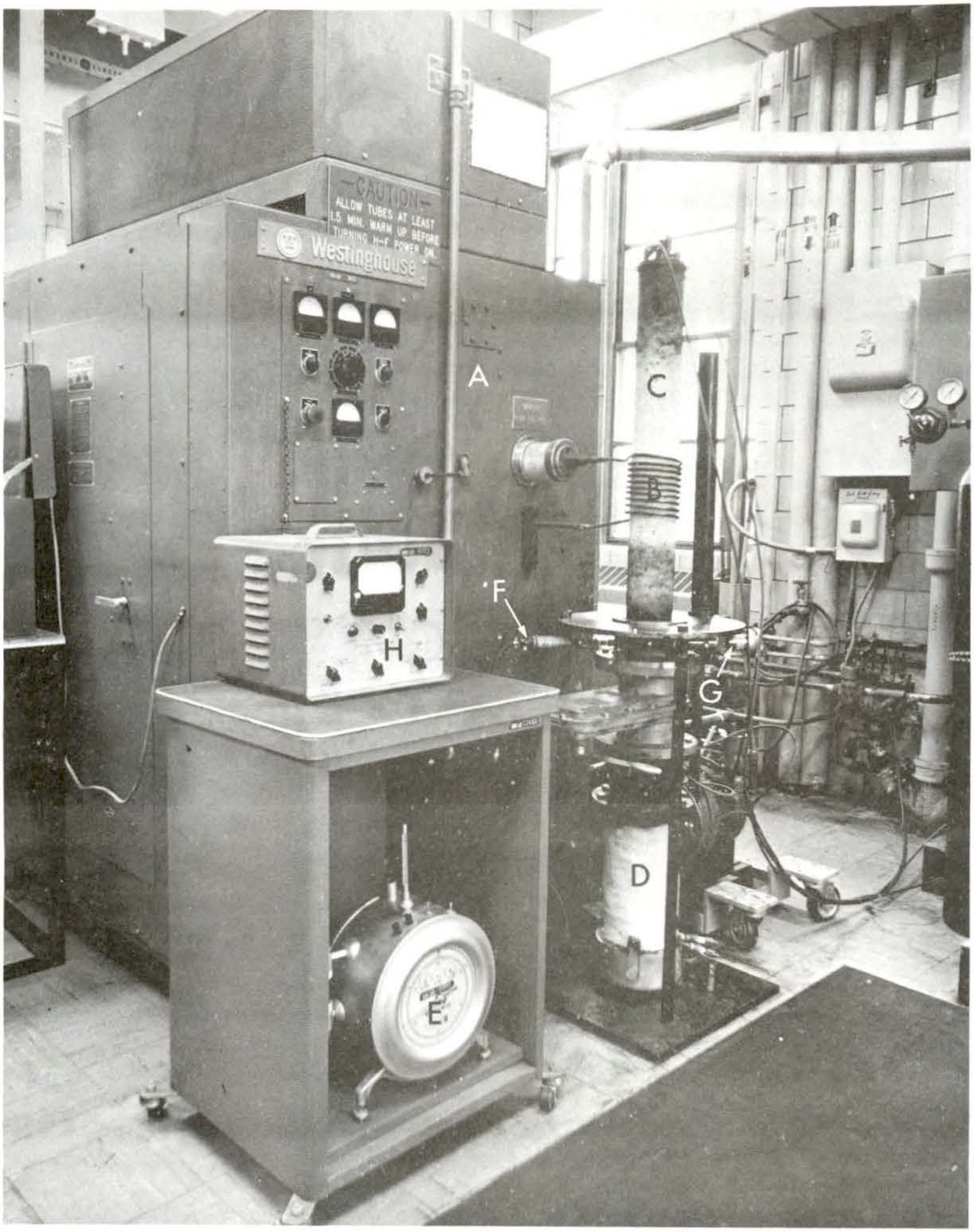
CAUTION
ALLOW TUBES AT LEAST
1.5 MIN. WARM UP BEFORE
TURNING H-F POWER ON.
Westinghouse
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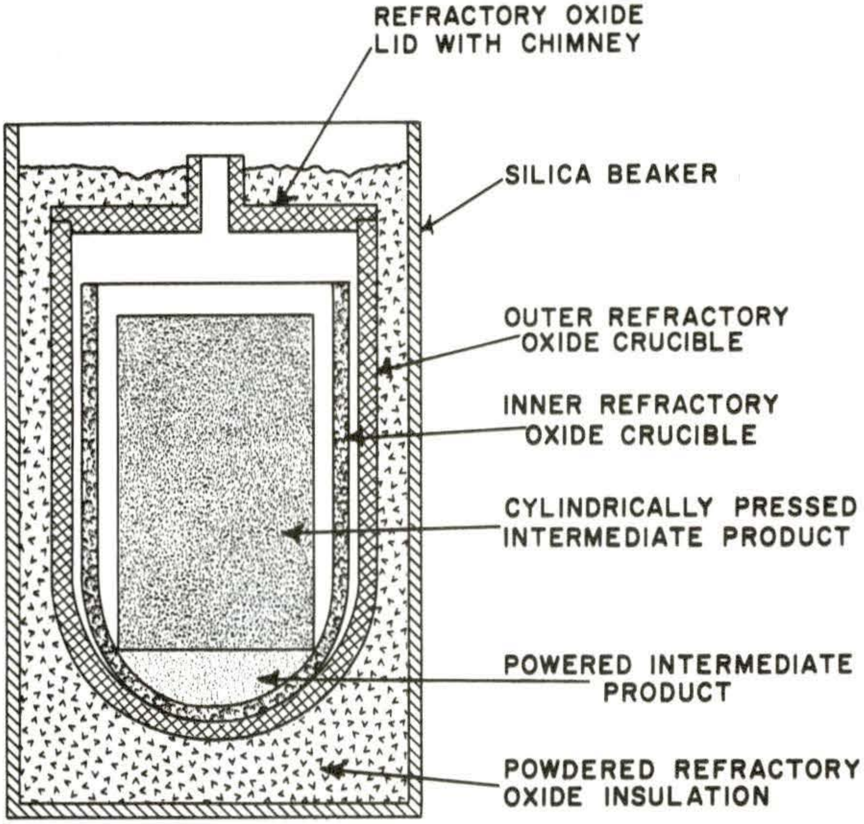


Figure 5. Schematic representation of furnace assembly used in self-induction heating experiments

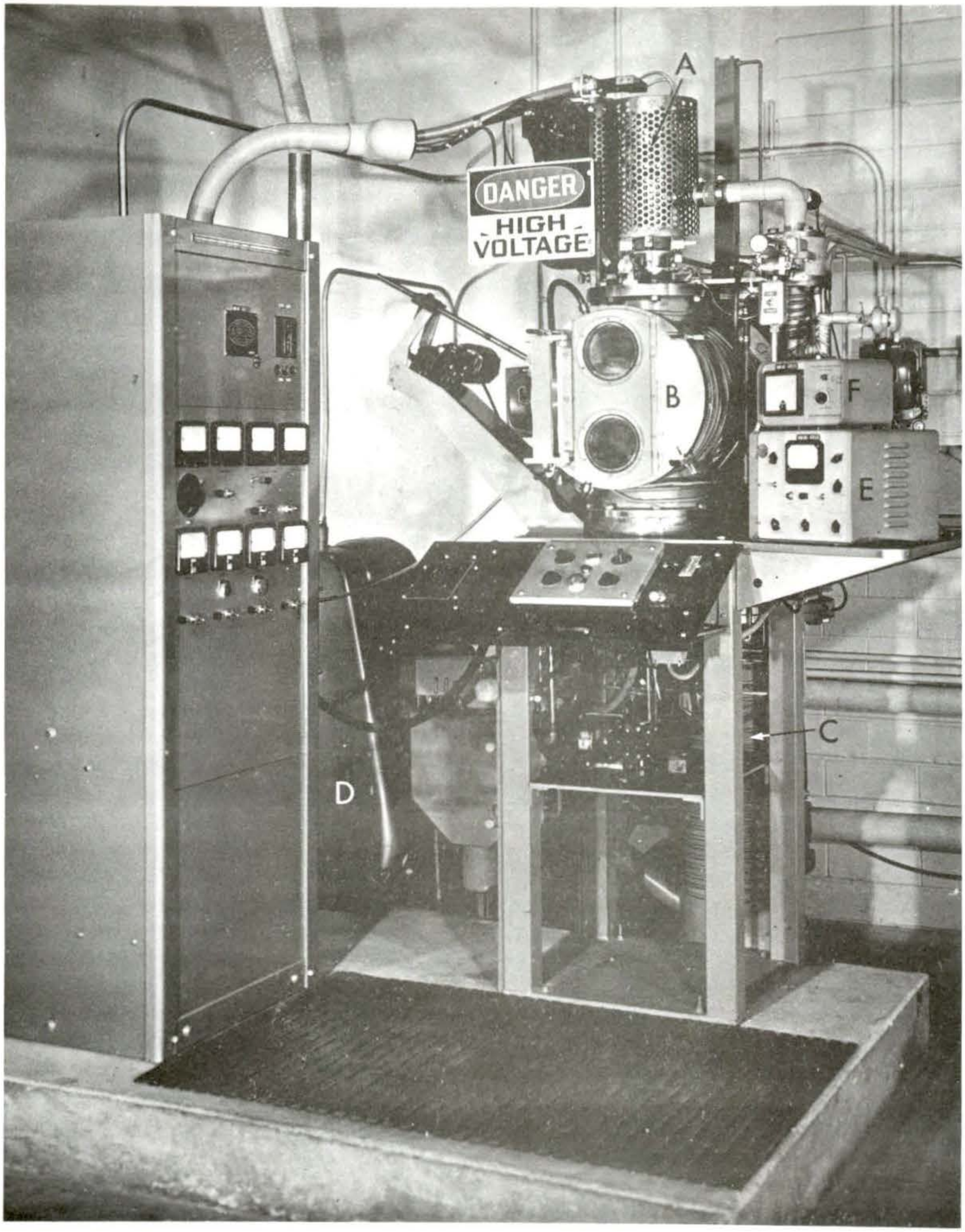
inch wall. The powdered insulation between the outer crucible and containment silica crucible has a thickness slightly greater than one-fourth inch.

Some metal purifications and final reductions were performed using a 9 KVA electron-beam furnace as shown in Figure 6. This unit consists of a water-cooled chamber where the samples are melted by an electron beam from an electron gun which is mounted at the top of the melting chamber. Both the chamber and gun are maintained under a reduced pressure of about 2×10^{-6} mm Hg with a sixteen inch three-stage oil diffusion pump coupled with a Stokes Microvac mechanical fore pump. Pressures above one micron in the melting chamber are measured with an NRC Type 501 Thermocouple Gauge while pressures below one micron are measured with an NRC Type 507 Ionization Gauge. They are controlled by an NRC Model 710 Thermocouple-Ionization Gauge Control. The pressure inside the gun assembly is measured with a Type GPH-100A Discharge Vacuum Gauge.

The gun assembly is shown schematically in Figure 7. A tungsten cathode filament is heated electrically to about 2000^{o}C causing electron emission. The current in the electron beam can be varied between 30 and 600 milliamperes. The cathode potential at the filament is fixed at -15,000 volts with

Figure 6. Photograph of 9 KVA electron-beam furnace

A. Electron gun
B. Melting chamber
C. Oil diffusion pump
D. Stokes fore pump
E. Thermocouple and ionization gauge control
F. Discharge vacuum gauge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DANGER
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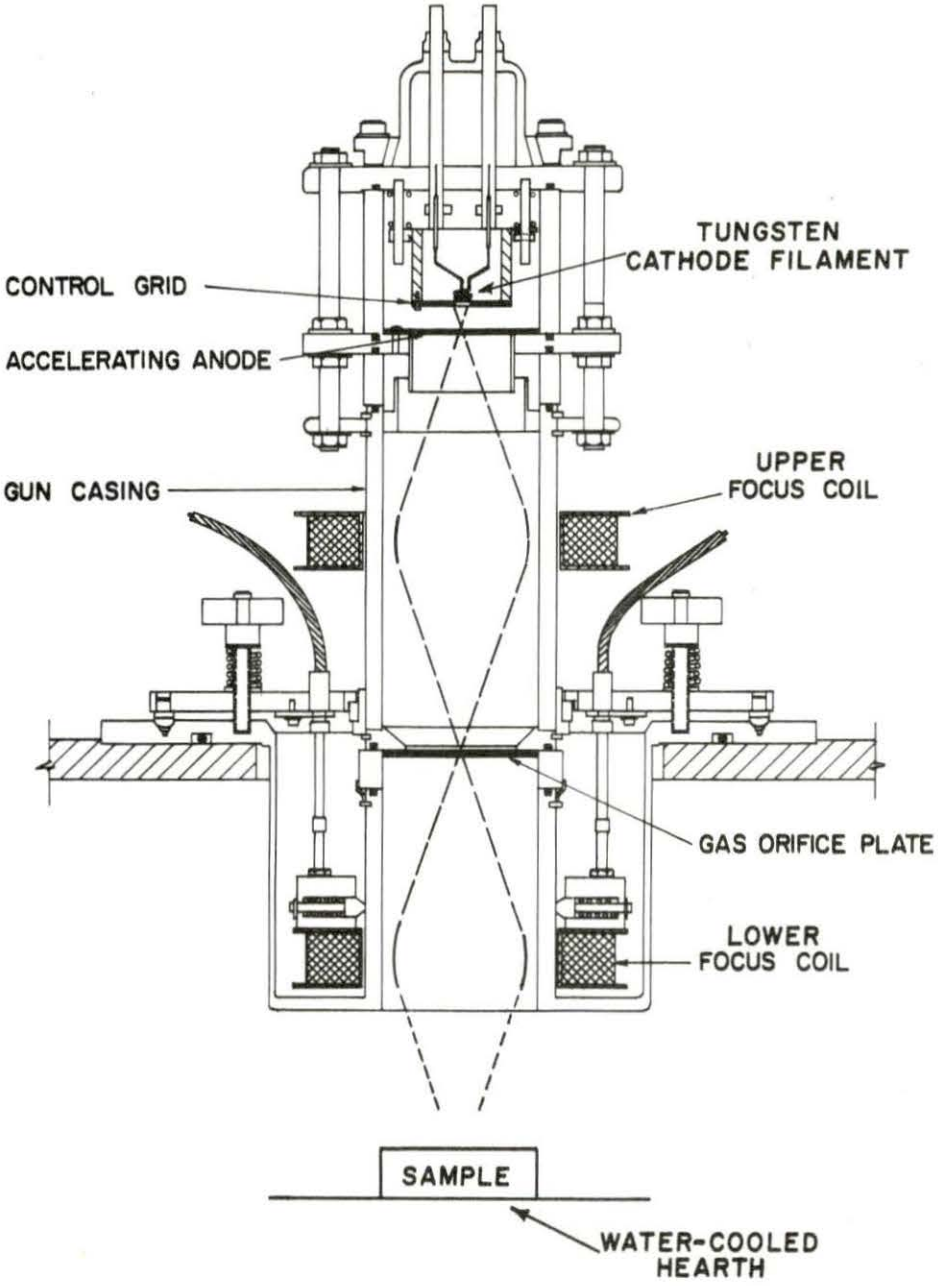


Figure 7. Electron-gun assembly of 9 KVA electron-beam furnace

respect to ground. The accelerating anode voltage which is variable between 0 and -10,000 volts is normally set at -5,000 volts in order to maintain a 10,000 volt differential between the cathode and accelerating anode.

The beam is focused electromagnetically by means of two focusing coils around the casing or barrel of the gun. The upper coil focuses the beam through a hole in a gas orifice plate. This plate serves as a baffle and deters the flow of gases released by the material being melted from entering the upper chamber. The lower coil is used to focus the beam on the material being melted.

MATERIALS

Charge Materials

Vanadium pentoxide

Two sources of commercial grade vanadium pentoxide were employed in this study. At the outset of this investigation, the oxide supplied by the Vanadium Corporation of America was used while the oxide supplied by the Union Carbide Corporation was used in later experiments. Results of chemical analyses on these starting materials are summarized in Table 1. Impurity levels reported in the table, with the exception of carbon and nitrogen were obtained spectrographically; carbon and nitrogen concentrations were obtained by chemical methods.

Table 1. Analyses in w/o of V_2O_5 used in investigation

Element	Vendor	
	Vanadium Corp.	Union Carbide
Al	.0450	0.0030
C	0.0170	0.0150
Co	----[a]	----
Cr	----	----
Cu	<0.0020	<0.0020
Fe	<0.0030	0.0200
Mg	<0.0020	0.0030
Mn	----	----
N	0.0060	0.0020
Ni	0.0060	0.0040
Si	0.0200	0.0200
Ta	----	----
Ti	----	<0.0020

[a] Element not detected.

As these results indicate, the total impurity levels in both sources of vanadium are about the same. The major impurities in the V_2O_5 from the Vanadium Corporation of America are aluminum and silicon while iron and silicon are the major ones in the oxide obtained from the Union Carbide Corporation.

Carbon

The carbon used in this investigation was grade 48 graphite obtained from the National Carbon Company. It was reported to have a maximum ash content of 0.08 w/o. Laboratory determinations of the ash content never exceeded 0.02 w/o. Sieving this graphite resulted in greater than 99% passing a 200 mesh screen.

Crucible Materials

Y_2O_3 (yttria)

The Y_2O_3 was prepared by calcining yttrium oxalate precipitated from a yttrium-rich fraction in the ion exchange separation of yttrium and rare earths. The purity of this material prepared at the Ames Laboratory was greater than 99% Y_2O_3.

ZrO_2 (zirconia)

This ZrO_2 was prepared from calcined zirconium hydroxide precipitate from a zirconium-rich fraction obtained in a zirconium-hafnium separation plant. This material contained less than 200 ppm hafnium and was greater than 99 w/o ZrO_2. It was obtained from the Carborundum Metals Company.

ZrO_2 (stabilized zirconia)

Zirconium oxide stabilized with lime and designated as Zircoa-B was obtained from the Zirconium Corporation of America. Analysis of this material supplied by the vendor revealed it to contain 93.5 w/o ZrO_2 and HfO_2 and 4.8 w/o CaO. Greater than 99% would pass a 325 mesh screen.

CeO_2 (ceria)

The cerium oxide was prepared by calcining the oxalate of greater than 99% purity. It was obtained from the Rare Earth (Lindsay) Division of the American Potash and Chemical Corporation.

CaO (lime)

The lime was obtained by calcining Fisher Certified ACS Calcium Carbonate obtained from the Fisher Scientific Company. It had a purity greater than 99.74 w/o as $CaCO_3$.

SrO (strontia)

The strontium oxide was obtained by calcining precipitated strontium carbonate obtained from the Fisher Scientific Company. It analyzed greater than 99.1 w/o $SrCO_3$.

MgO (magnesia)

The magnesium oxide used was designated as Magnorite fused magnesia. It was obtained from the Norton Company and had a purity of greater than 96.3%.

Graphite

Grades AGSR and AGSX graphite obtained from the National Carbon Company were used. The purity of the material depended on the diameter of the initial rod and varied from 0.12 w/o to 0.96 w/o ash.

Insulating Materials

Shawinigan Black

The Shawinigan Black used was prepared by the continuous thermal decomposition of acetylene at temperatures above 1500 ^{o}C. It was supplied by Shawinigan Chemicals Limited and reportedly had an ash content of less than 0.04 w/o.

Thermax insulating carbon

Thermax Thermatomic carbon was obtained from the R. T. Vanderbilt Co.

GENERAL THEORETICAL CONSIDERATIONS

The reduction of a metal oxide with carbon can be represented in general terms by the following equation:

$$MeO_z + (x+y)C \rightleftarrows xCO_2 + yCO + Me \qquad (4)$$

where $z = (2x+y)$.

It is to be observed that, by this reaction, both CO_2 and CO are generated by the presence of free carbon. Since CO_2 may react with carbon to form CO by the equation:

$$CO_2(g) + C(s) \rightleftarrows 2CO(g) \qquad (5)$$

consideration should be given to the influence of this reaction on conditions for the oxide reduction. The mole fractions of CO and CO_2 in equilibrium with free graphite as a function of temperature and pressure are represented by Figure 8, which is based on free energy data (19) for the components of this reaction.

At a total pressure of 1 atmosphere, the equilibrium gas phase is composed of essentially all CO_2 at temperatures below 300°C. As the temperature is increased, the proportion of CO in the gas phase tends to increase; at 1100°C, the equilibrium gas phase is nearly all CO. A decrease in the total system pressure to 0.10 atmosphere tends to increase markedly the fraction of CO in the gas phase at all temperatures. Although

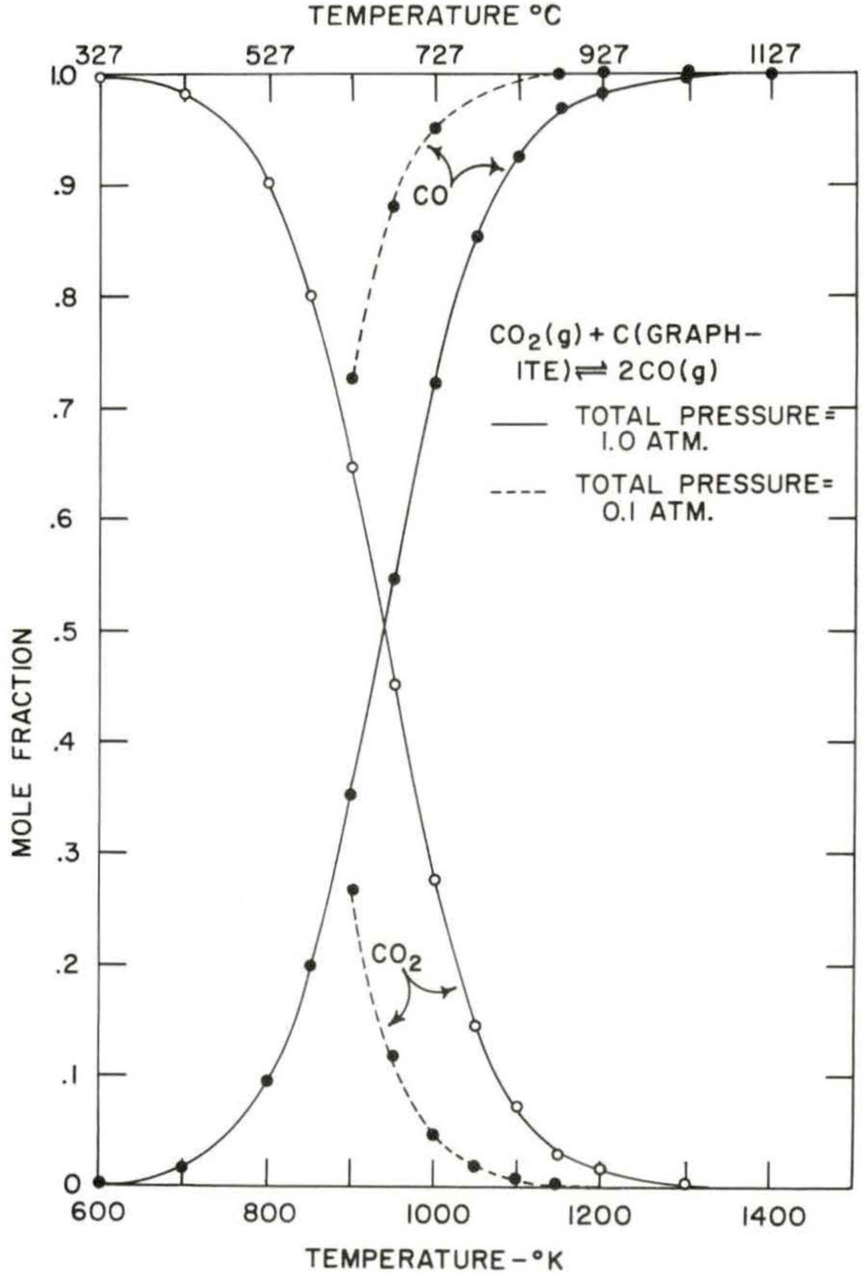


Figure 8. The mole fractions of CO and CO_2 in equilibrium with free graphite as a function of temperature and pressure

equilibrium conditions will not be attained in practice, some consideration must be given to this system in choosing charge materials for the preparation of vanadium metal by the carbon reduction.

Two stable oxides of vanadium can be used, the pentoxide, V_2O_5 or the trioxide, V_2O_3. If the oxide-carbon reaction occurs at well below 900°C, some of the gas is evolved as CO_2. Unless the stoichiometry and conditions of operation are sufficiently reproducible, then, the final metal could contain either an excess of carbon or oxygen due to the potential variability of the CO to CO_2 ratio in this low temperature range. Considering V_2O_5 as the most likely oxide to react to some extent at low temperatures, a general equation for the reaction can be written as follows:

$$V_2O_5 + (x+y)C \rightleftarrows 2V + xCO_2 + yCO \qquad (6)$$

where $(2x+y) = 5$.

If, on the other hand, V_2O_3 is used as the starting oxide, the initial reaction temperature could be high enough so that essentially all of the gas comes off as CO. In this case, the overall reaction could be represented as:

$$V_2O_3 + 3C \rightleftarrows 2V + 3CO \qquad (7)$$

These two overall reactions, as written, appear to be simple and quite basic. However, an analysis of the conditions, if the reaction initiates as written, would show that the first vanadium metal would be formed in the presence of free carbon with temperature conditions suitable for forming vanadium carbide. Therefore, when all residual carbon has been reacted to form vanadium carbide, the remainder of the oxide has to be reduced by carbide instead of free carbon.

A thermodynamic study of the V-C-O system by Worrell and Chipman (20) revealed that a number of intermediate reactions take place which form a variety of stable compounds during the course of the reduction. Table 2 is a summary of the melting points and free energies of formation of the compounds of concern as presented by these authors.

These free energy data can be used to estimate the minimum temperature necessary to obtain metal under a particular pressure by an assumed reduction represented as:

$$V_2C + VO \rightleftharpoons 3V + CO \; . \tag{8}$$

Using the free energy data given in Table 2 and the standard free energy of formation of CO as a function of temperature (20) as given in Equation 9, the standard free energy change

$$\Delta F_T^o = -26{,}760 - 21.0T \tag{9}$$

for the reaction may be represented by Equation 10.

Table 2. Thermodynamic and melting-point data for the stable compounds occurring in the V-C-O system

Compound	Standard free energy of formation calories per mole	Melting point °K
$V_2O_5(s)$	-369,000 + 101.0T	943
$V_2O_5(\ell)$	-347,000 + 77.0T	----
$VO_2(s)$	-166,000 + 36.0T	1818
$VO_2(\ell)$	-150,500 + 28.0T	----
$V_2O_3(s)$	-284,500 + 55.0T	2240
VO(s)	-100,000 + 18.0T	2170
V	----	2161
$V_2C(s)$	-35,200 + 1.0T	2438
$\bar{V}C^a(s)$	-22,200 + 1.5T	2923
$V\bar{C}(s)$	-24,100 + 1.5T	----

[a] The notations $\bar{V}C$ and $V\bar{C}$ denote, respectively, the carbide compositions at the carbon-rich and at the metal-rich boundaries of the homogeneous VC phase.

$$\Delta F_T^o = 108{,}440 - 40.0T = -RT\ln K \qquad (10)$$

The equilibrium constant K for the reaction represented by Equation 10 could be considered as being equal to the partial pressure of the CO gas in atmospheres, if it is assumed that the activities of the other product and reactants are unity. Table 3 summarizes the calculated temperature at four different assumed pressures.

Table 3. Calculated minimum temperature required to obtain vanadium metal by the carbon reduction at various pressures

Pressure (atmospheres)	Temperature °K	°C
10^{-2}	2210	1937
10^{-4}	1870	1597
10^{-6}	1610	1337
10^{-8}	1400	1127

It should be noted that this analysis did not involve any kinetic considerations, that is, rates of chemical reaction which must be taken into account in the development of a feasible process.

Even though calculations indicate, by the reactions as written, that it could be possible to obtain metal using a wide range of conditions, for all practical purposes, an elevated temperature with reduced pressure would be required in order to accelerate the reaction to produce quantities of metal. Furthermore, consideration of conditions that probably prevail for the assumed reaction as represented in Equation 8 would lead to complications not indicated by the simple expression. Vanadium metal, as it is formed, according to Equation 8 would be associated with VO and according to known phase relationships would form a series of V-VO solid solutions. Under these circumstances, the VO activity as well as that of vanadium would vary as the reaction proceeds. Because of these variables, the unit activity assumed in making calculations for the conditions represented in Table 3 are not valid as the reaction proceeds toward completion. Quite likely, as the reaction nears completion, the temperatures required at the specified pressures would be much higher than those listed in Table 3. However, as it was mentioned earlier, molten vanadium presents a containment problem. This difficulty could possibly be obviated by the use of a water-cooled hearth such as those used in arc melting or electron-beam melting or by use of an inert crucible providing such a container can become available. It is obvious that if the temperature during the final stages of a reduction would exceed the melting point of pure vanadium, the melting point of the crucible material should be well above this temperature and preferably greater than 2100°C. Although a number of refractory materials including carbides, sulfides, nitrides, borides and oxides meet this temperature requirement, this investigation was limited to considering certain refractory oxides.

Other considerations may limit the choice of oxide to be used in the preparation of a container for molten vanadium. For example, some refractory oxides exhibit transitions that require other chemical additions for insuring physical stability for service. Others exhibit toxic properties which require special precautions in their handling. If the vanadium metal is to be used in the core of a nuclear reactor, the nuclear properties of the metal of the refractory oxide could be of consequence only in the event that the vanadium becomes contaminated with that metal during the processing. In this use, a high capture cross section for neutrons or the formation of radioactive isotopes by the contaminating metal should also be given consideration.

EXPERIMENTAL

Exploratory Observations

Early exploratory work revealed that when a charge of V_2O_5 and carbon is heated in a graphite crucible under reduced pressure, the initial reaction occurs at a dull red heat. This reaction is quite vigorous and some of the charge may be blown from the crucible. However, the reaction, which is exothermic, soon subsides and by the time the crucible temperature reaches 1000°C gas evolution is essentially nil. The charge at this point consists mainly of V_2O_3 and carbon. Little or no reaction is then noted until the sample reaches a temperature of about 1100°C, and on further heating over a range to approximately 1600°C substantial gas is evolved. If this temperature is maintained for a short period of time, much of the reaction is completed and a sintered metallic product which is a conductor of electricity is formed. If the temperature is then rapidly increased to 1650°C, an increase in the reaction rate is then noted. However, premature melting may occur and reaction between liquid metal and the crucible results in excess carbide formation before the oxide in the metal is completely reacted. See Figure 9. If the charge is maintained at just below this temperature for extended

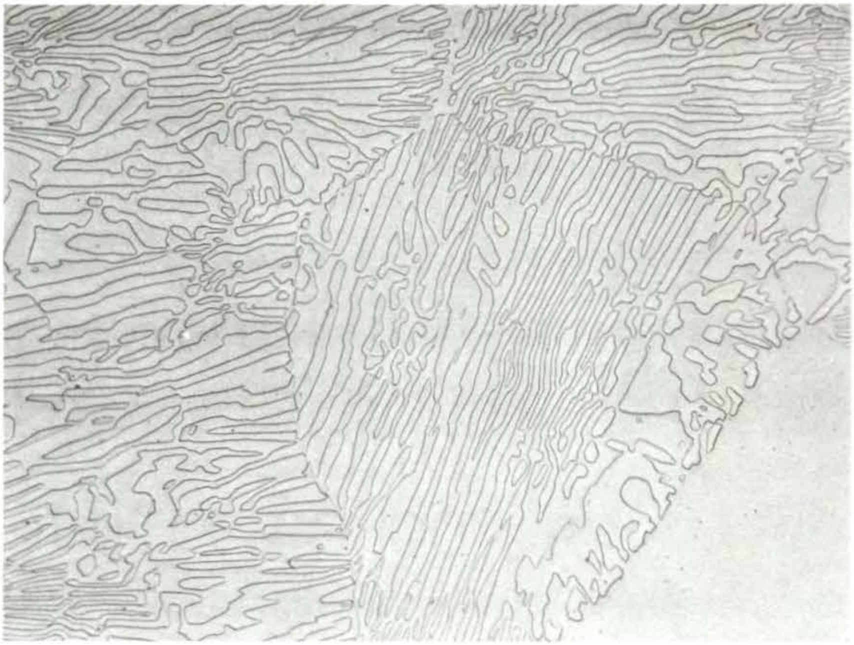


Figure 9. Microstructure of metal produced by reacting a charge of V_2O_5 and carbon under vacuum to the liquid state in a graphite crucible. Contains 4.02 w/o carbon and 1.38 w/o oxygen. Electropolished in $HClO_4$. Etched for 2 minutes with solution containing 5 parts HF, 10 parts H_2SO_4, 10 parts HNO_3 and 50 parts water. 250X

periods of time, the product is still quite impure.

Further exploratory work showed that the complete vacuum reduction of V_2O_5 to metal takes place in roughly three stages or temperature ranges. The primary reaction step which occurs over a range below 950°C appears to be associated with the reduction of V_2O_5 to V_2O_3. The intermediate reaction step which occurs in the range 1200°C to 1650°C and gives a somewhat spongy metallic product containing high oxygen and carbon impurities is possibly the result of a complex series of reactions varying from V_2O_3 with carbon to lower oxides with carbides. The final reaction step takes place readily at temperatures above the melting point of pure vanadium and at a much slower rate just above 1650°C. The predominant reaction at this stage is possibly the reaction between carbon and oxygen impurities in liquid vanadium. Figure 10 is a plot of the cumulative percentage of gas evolved as the temperature is progressively increased during a typical heating of a charge of V_2O_5 and carbon. The quantitative data for such a figure is quite dependent on the heating schedule. However, qualitatively, the gas evolution-temperature curves exhibit the same general shape. Indicated on this plot are general areas in which three stages of the reaction are thought to occur. This

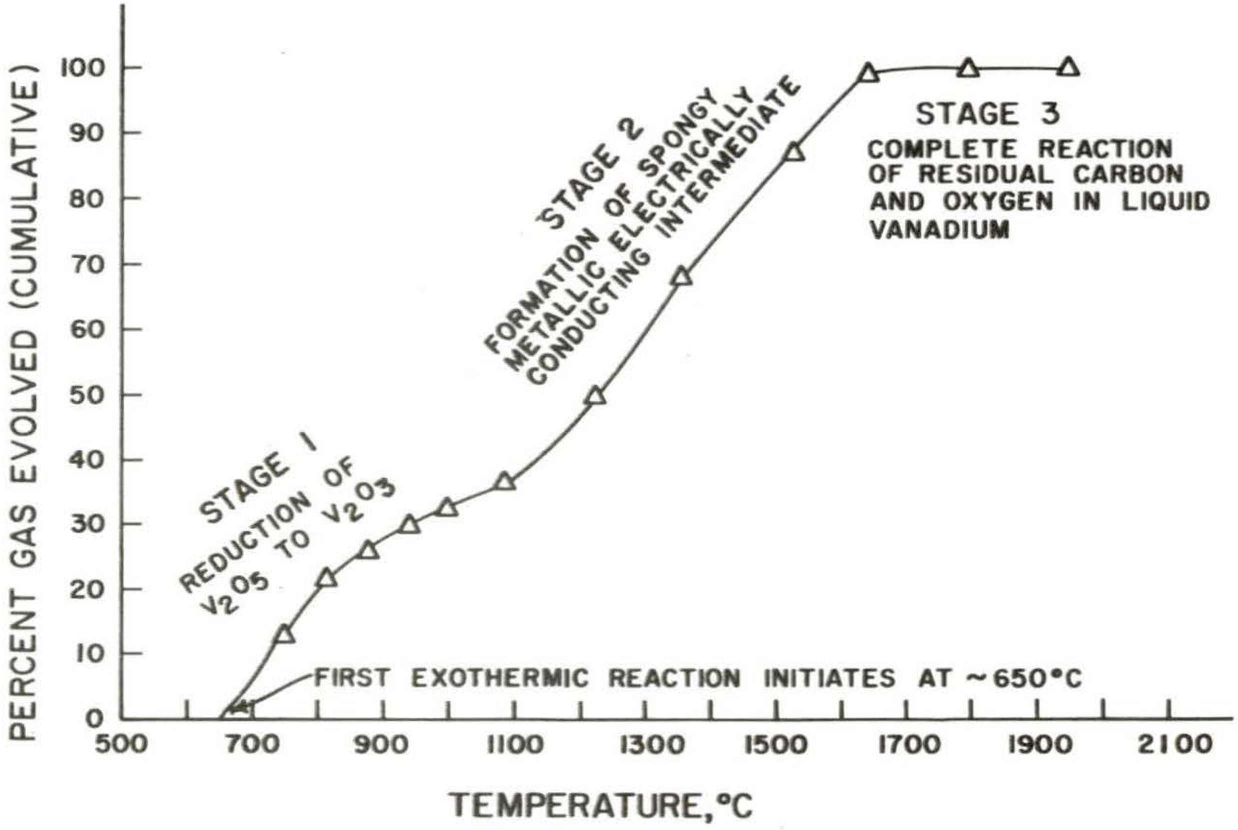


Figure 10. Curve representing the cumulative percentage of gas evolved as the temperature is progressively increased during a typical heating of a charge of V_2O_5 and carbon

type of plot serves only to indicate roughly the degree of reaction to be expected up to a certain temperature.

Discussion of Problems and Possible Solutions

Based on these observations, it is apparent that the preparation of good quality vanadium metal by the carbon reduction of oxide requires that a number of problems associated with a procedure such as that outlined above would have to be bypassed or solved. A means for containing the charge during the vigorous exothermic reaction would be necessary, since any sample loss by blowout, during the course of the reduction, would reduce the overall yield as well as possibly alter the stoichiometry of the charge and thus the quality of the product. Several possible solutions to this blowout behavior exist. The trioxide, V_2O_3, could be substituted for V_2O_5 and essentially eliminate any exothermic reaction at temperatures below $1100^{\circ}C$. A possible disadvantage to this approach, however, is that a separate operation for the reduction of V_2O_5 to V_2O_3 would be required.

Controlled heating of the charge throughout this exothermic reaction is another alternative that warrants some consideration. This might be done by first heating the top of the charge to the reaction temperature and then lowering the hoist-type induction coil in a stepwise fashion until the entire charge has passed through this reaction range. The reaction could thus be made to propagate downward through the cooler portion of the charge and generate gas at possibly a slower rate, reducing the chances of rapid self-heating and sample blowout. Also, pressing the charge into briquettes should reduce the blowout tendency observed with unpressed charges.

A third possibility to eliminate blowout might be to perform this initial phase of the reduction under a gas pressure and then evacuate to complete the process. The gas pressure on the charge should slow down the rate of gas evolution and certainly reduce the tendency to blowout. The simplest method to employ pressure would be to leave the crucible open to the air during this phase of the reduction. However, an inert atmosphere could be employed during this step if air is not satisfactory.

Another alternative and possibly the simplest to employ for containing the charge would be to cover the charge with a porous type lid attached to the crucible. It could be designed to let the product gases escape, yet contain the particles within the crucible.

Another matter of concern in the development of this process for vanadium is the number of moles of carbon required for the reduction of a mole of V_2O_5 to metal. Since the initial reaction of carbon with V_2O_5 occurs at temperatures well below 850°C, undoubtedly a gas mixture of CO_2 and CO is formed. Thus, the number of moles of carbon is less than five. The carbon reduction of the V_2O_3 product from this lower temperature reaction takes place at above 1100°C under vacuum conditions; it should therefore yield essentially CO as the gas phase. Thus, the complete reduction of a mole of V_2O_5 to metal should require at least four, but less than five moles of carbon. Furthermore, since the ratio of the moles of carbon to the moles of V_2O_5 to yield pure metal depends on the conditions under which the sequence of reactions is carried out, especially in the low temperature range, this ratio will need to be determined for the set of operating conditions employed.

Completion of the high temperature reduction to give good quality metal could be theoretically accomplished through either a solid or liquid state reaction. However, certain problems arise in both cases. If the solid state is to be maintained at temperatures below 1650°C (observed melting of the charge) the reaction rate is very slow and, as pointed out above, it appears that impractical extended periods of heating would be required. If a high temperature could be employed, and the solid state maintained, the reaction rate should increase. However, neglecting the effect of oxygen and considering only the vanadium-carbon phase diagram (21) as shown in Figure 11 the temperature of reaction would have to be maintained at below 1650°C until sufficient reaction had occurred to reduce the carbon content to below 0.3 w/o before the temperature could be increased and maintain the solid state. If the reaction can be made to proceed sufficiently with an increase in temperature, then it should be possible to approach the melting point of pure vanadium and maintain the solid state. The effect of oxygen in the ternary system could further complicate this heating program. In order to possibly complete the reduction in the shortest period of time in the solid state by such a means of temperature escalation would require current knowledge of chemical composition during heating. This procedure, if at all workable would be impractical. Although other means for refining the sintered product will be considered, it appears that in order to complete the final carbon reduction in a practical manner by thermal means will require temperatures that yield a liquid product.

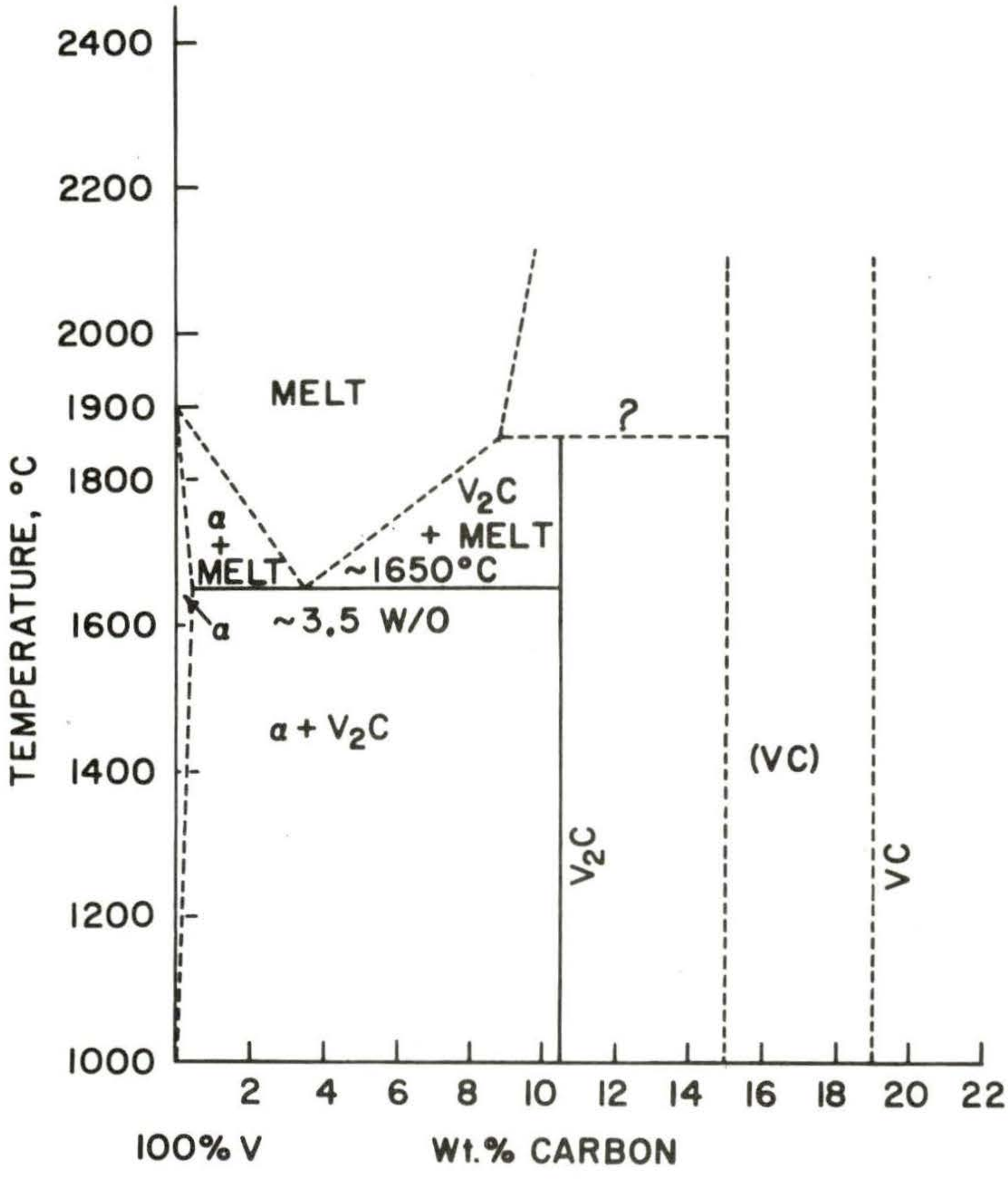


Figure 11. Vanadium-carbon phase diagram after Hansen (21)

Standardized Procedures

A process may be developed on the basis of the results of a number of related experiments in which certain parameters are varied and their effects evaluated with regard to such factors as quality of product, yield, economics and feasibility. During the research and development stages for a process, however, certain established procedures, methods and techniques are frequently employed. In this work on the carbon reduction of vanadium oxide, charge preparation, crucible preparation, V_2O_3 preparation, control and evaluation techniques fall into this category.

Charge preparation

The quantity of each reactant in a charge was weighed to the nearest hundredth of a gram and placed in a suitable container for mixing on a ball mill. When the charge weight was less than 100 grams, an eight ounce jar was adequate. A number of one-half inch diameter alundum grinding stones were placed with the charge to aid in mixing. The length of time a sample was mixed also depended on the charge size; however, instead of mixing a charge a specified period of time, it was observed periodically and mixing continued until it appeared homogeneous.

Crucible preparation

Graphite crucibles were prepared by machining from either AGSR or AGSX Graphite stock. Two different methods were used in preparing the refractory oxide crucibles employed in this study. They were jolt packing and slip casting.

In the jolt packing technique, the refractory oxide is shaped in a graphite mold which consisted of a graphite crucible, mandrel and collar which had been fabricated from graphite stock to yield a finished ceramic crucible of the desired specifications. In the packing operation, enough of the finely ground oxide is placed in the bottom of the mold crucible to yield a base for the mandrel to rest on. The quantity of refractory depends on the thickness of the base, but most of the crucibles used in this study had about a one-eighth inch base and wall. Next, the mandrel is positioned and the oxide added to the annular space between it and the crucible. The collar is then placed around the mandrel at the top of the crucible and the entire assembly placed on a pneumatic jolting table. As the refractory oxide compacts, more is added. This step is repeated until the entire mold is lined with the oxide. With the collar in position, the mandrel is removed leaving a graphite crucible with a lining of compacted oxide. The crucible with the liner is then placed in a graphite heater assembly and heated by induction in a vacuum to the desired temperature. During this step, the ceramic liner sinters and shrinks away from the graphite mold yielding the desired crucible. The fired crucible is sometimes subsequently heated in a muffle furnace to burnout any carbon which may have been picked up during the sintering step.

When ceramic crucibles are prepared by slip casting, it is first necessary to prepare a mold. This is done by pouring a water-plaster of Paris slurry around a smooth graphite mandrel of the desired shape. When the plaster of Paris has partially set, but is still damp, the mandrel is removed. After the mold has sufficiently dried, which required three or four days at room temperature, it is ready for use in slip casting crucibles by the following procedure.

The mold is first lined with α-cellulose. This is done by pouring an aqueous dispersion of this material into the mold and immediately pouring it out. This lines the mold with a paper thin coating which smooths the mold surfaces and helps in releasing the ceramic crucible from the mold.

Next, the crucible is cast by filling the mold with slip which is prepared by suspending very finely ground oxide in a medium such as alcohol or water. As the mold adsorbs the liquid phase, frequent additions of slip are necessary to maintain the level. When the wall thickness of the crucible is assumed adequate, the residual slip is poured out of the mold and the slip cast crucible allowed to air dry in the mold. After about two hours of air drying, enough shrinkage has occurred and enough green strength remains so that the crucible can be readily removed from the mold and placed in a graphite susceptor of a vacuum induction furnace. The drying is then completed under vacuum before the crucible is sintered in the same manner as the jolt packed crucibles.

V_2O_3 preparation (reduction with hydrogen)

The preparation of V_2O_3 from V_2O_5 can be carried out by reducing with hydrogen at temperatures up to about 650°C. In this study, V_2O_3 was prepared by placing V_2O_5 in a quartz boat that was positioned inside a Vycor reaction tube. This tube had a removable Vycor cap which was fitted with an inlet line while the body of the tube had an exit line at the other end. The sample was positioned inside of this tube which was then placed in a split-tube furnace. The inlet line was then connected to a hydrogen supply that was monitored by a flow meter. The exit line was placed in the exhaust port of a fume hood.

After the flow of hydrogen was adjusted to insure a blanket over the oxide, heating was initiated. The V_2O_5 (mp 670°C) was heated slowly to 650°C. By the time this temperature was reached, the V_2O_3 was formed. The furnace and contents were cooled to room temperature with a hydrogen blanket over the sample. The resulting V_2O_3 was then placed in a graphite crucible and heated in vacuum to about 400°C to drive off any adsorbed hydrogen.

Control and evaluation techniques

For each experiment, control data were collected during the reduction and the product was subsequently analyzed. Process evaluation and the course of further experimentation was based on these results. The progress of the reaction was followed by monitoring temperature, cumulative gas evolution, and gas evolution rate.

Temperature measurements were obtained using a Leeds and Northrup optical pyrometer Model 8622-C. Final temperature values were corrected for the effect of the sight glass of the vacuum assembly (Figure 2) by using a pyrometer calibrator. In making this correction, the temperature of a heated tungsten filament was measured with the pyrometer with and without the sight glass interposed. From these two readings, and a transmittancy table, the transmittance of the sight glass was determined and the final temperature obtained.

Gases evolved during the reduction sequence were measured with a wet test meter manufactured by American Meter Controls, Inc. Although this meter had an accuracy of ± 1% at a rate greater than that employed, this degree of accuracy was probably not realized in these small scale experiments. The gas evolution rate was merely relative and was assumed to be indicated by the system pressures which the vacuum pumping system was able to attain. System pressures above one micron were measured with an NRC Type 501 Thermocouple Gauge while pressures below one micron were obtained with an NRC Type 507 Ionization Gauge. They were controlled by an NRC Model 710 Thermocouple-Ionization Gauge Control.

Analysis of the solid products formed in the course of a reduction experiment were based, for the most part, on the results obtained by standard chemical and spectrographic techniques. Oftentimes, however, x-ray diffraction techniques and metallographic examinations were performed to supplement these techniques. Samples were prepared for x-ray analysis by crushing the product finely enough to pass a 325 mesh screen.

These powders were then placed in three-tenths millimeter glass capillary tubes and Debye-Scherrer powder patterns prepared.

Samples for metallographic examination were prepared from metal samples by cutting with an abrasive wheel. The sections to be polished were mounted in bakelite and wet ground using 200, 400 and 600 grit paper. Final surface preparation was carried out by electropolishing in 6% perchloric acid in methanol with the sample as the anode. The solution and sample were maintained at about $-70^{\circ}C$ by a dry ice-acetone bath during the polishing which lasted about 45 seconds using 50 volts. The sample was then ultrasonically cleaned in methanol dried in air and examined metallographically. Any photomicrographs taken were usually at 250 diameters with normal nonpolarized light. To bring out further details, some samples were etched in a solution containing 5 parts HF, 10 parts HNO_3, 10 parts H_2SO_4 and 50 parts water.

General Reduction Sequences

The experimental procedures that were considered on the basis of results of the exploratory studies were limited to a few selected paths that led from oxide to metal. The starting materials in all cases were V_2O_5 and carbon. However, in some cases, vanadium carbide was first prepared and then mixed with oxide to prepare the metal or V_2O_5 was reduced to V_2O_3 which was subsequently employed in the preparation of metal. Regardless of the makeup of the charge, the first heating was always carried out by vacuum induction heating using a graphite susceptor.

One procedure studied consisted of a reduction scheme whereby the complete sequence, oxide to molten metal was effected by continuous heating of the charge in a ceramic crucible that had been placed inside a graphite susceptor. This is considered as a one-step process in which the charge is heated continuously to yield final metal. All other approaches studied consisted of two steps, a primary reduction step to prepare a partially reduced self-conducting sintered product and a refining step. Three variations for refining the sintered product and essentially completing the reaction were of interest. One of these was to transfer this product to a ceramic crucible heater assembly such as shown in Figure 5 in which the sintered metal served as susceptor in self induction heating. The reaction was then essentially completed at higher temperatures yielding liquid metal in a ceramic crucible. Another means employed for treating the sintered product to obtain good quality vanadium metal was to complete the reduction in an electron-beam furnace to yield molten vanadium. A third possibility for converting the sintered metal product to good metal is to employ electrorefining techniques such as described by Lei and co-workers (22).

Reduction Sequences Derived

Single-operation process

In the one-step process, a thoroughly mixed charge composed of V_2O_5 and carbon is first pressed into cylindrical briquettes and placed in a ceramic crucible. This crucible is then placed in an insulated graphite heater assembly within a silica beaker. The heater is lined with a sleeve and base of sheet tantalum or molybdenum to limit any chemical reaction between the graphite heater and ceramic. After the heater lid, with its chimney, is positioned, insulation is packed on top of the lid and around the chimney to complete the heater assembly as shown in Figure 3. This assembly is placed on a silica base and rests within an induction coil. A vacuum chamber around the silica beaker is formed by positioning a silica sleeve around the beaker and through the induction coil onto a neoprene gasket on a water-cooled base. A water-cooled head with sighting window is then placed on the upper end of the silica sleeve and the chamber evacuated. The completed assembly for initiating the heating cycle is shown in Figure 2. When the system pressure is reduced to less than $5x10^{-4}$ mm Hg, heating is started. The hoist-type induction heating coil is first positioned so that the hottest zone of the susceptor is near the top of the charge. Heating proceeds until the top of the charge is at a dull red heat and the reaction is initiated. Following this, the coil is progressively lowered in a stepwise fashion until the charge is symmetrical within the coil. After this initial phase of the reduction has been essentially completed, the power to the induction coil is increased. Further reaction takes place and the sample melts below $1700^{\circ}C$. Heating is continued, however, until a temperature of $1950^{\circ}C$ is attained. This temperature is then maintained and the sample held in the liquid state in the ceramic crucible until the system pressure decreases to less than $5x10^{-4}$ mm Hg, after which the reduction is assumed completed.

When V_2O_3 is used as the starting oxide, the charge is tamped into the ceramic crucible rather than pressing it into briquettes. Three or four 1/16 inch diameter breather holes are then placed the length of the charge to aid in gas release during the reduction sequence. The charge is then placed in the furnace, a vacuum established and the heating performed in the same manner as the finishing phase of the procedure described above.

Double-operation processes

Charge preparation and the heating schedule followed in this approach was essentially the same as that used in the single-operation process up to 1300°C. However, a graphite crucible was used to contain the charge instead of a ceramic crucible. This graphite crucible was fitted with a graphite screw-type lid which had a number of one-sixteenth inch diameter holes drilled in it to let the product gases that may form rapidly during the primary reduction step escape without causing blowout. Instead of heating the charge directly to the molten state, it is maintained in the double-operation process at between 1300°C and 1600°C until a substantial portion of the reaction is completed as determined from gas evolution data. After the sample is cooled, it is removed from the graphite crucible and further reacted and refined by melting by either self-induction or electron-beam heating.

When self-induction heating is employed, the sintered metallic sponge is first finely ground. The resulting powder is then pressed into the shape of a cylinder and placed in a ceramic crucible. The charge and crucible are then placed in a ceramic crucible furnace assembly as shown in Figure 5. A ceramic lid with a chimney is then placed on the outer crucible and further insulation added around the top in the form of oxide powder. The same type of vacuum chamber is employed here as used in the single-operation process. After the system pressure is decreased to less than $1x10^{-4}$ mm Hg, heating is started.

Due to the low self-induction coupling of the small charge sizes employed in this experimental work, it is necessary to use the 25 KW RF generator as the power supply. Negligible reaction occurs until the sample exceeds the maximum temperature obtained during the intermediate heating step. As the sample temperature reaches about 1700°C, melting occurs. Heating continues, however, until the liquid reaches about 2000°C. This temperature is maintained until the system pressure decreases to about $5x10^{-5}$ mm Hg, after which the reaction is assumed to be essentially completed. After the product has cooled it is removed and samples taken for chemical analysis.

When electron-beam melting is used, the intermediate metallic product is first placed in the melting chamber of the 9KVA electron-beam furnace as shown in Figure 6 and the chamber is then evacuated. When the pressure is reduced to 7×10^{-6} mm Hg, the sample is melted on the water-cooled hearth. When the mass is completely molten, it is held in the liquid state for about two minutes. At this point, the sample is then allowed to cool, the resulting button is flipped and melted a second time. The pressure in the melting chamber is usually less than 5×10^{-6} mm Hg at the conclusion of the second two minute melting step. Portions of the resulting metal buttons are then analyzed chemically.

RESULTS AND DISCUSSION

Crucible Material Selection

In an effort to find a refractory oxide that would be suitable for containing liquid vanadium up to 2000°C, a number of criteria were considered. Two conditions which a potential material had to meet in order that it be given further consideration were a melting point greater than 2200°C and a free energy of formation of at least 60 kilocalories per gram atom of oxygen at 2000°K which is about the value of free energy of formation for vanadium monoxide. Table 4 lists the melting point and free energy data of oxides that meet these two

Table 4. Refractory oxides suitable for containing liquid vanadium based on melting point and free energy of formation

Oxide	Melting point (23) °C	$F^{o}_{2000^{o}K}$ (24) kcal/gm mole oxygen
MgO	2800	-77
CeO_2	2600	-85
SrO	2415	-87
ZrO_2	2677	-87
HfO_2	2770	-88
UO_2	2860	-88
Sc_2O_3	2400	-92
BeO	2550	-96
Y_2O_3	2458	-98
Sm_2O_3	2350	-99
CaO	2630	-99
ThO_2	3220	-101
La_2O_3	2305	-101

preliminary conditions. It should be emphasized that the free energy values used for this table are for conditions (especially pressure) that will not prevail under the operating conditions proposed in this investigation of the carbon reduction of vanadium oxide.

Other considerations which further limited the number of these materials to be evaluated dealt with such factors as nuclear properties, toxicity and availability. Since throium-232 can be converted to fissile uranium-233 by neutron absorption, it was decided that even though ThO_2 might serve as a crucible material for the experimental studies, the possibility of thorium contamination of vanadium for large scale use in nuclear reactors might require special considerations. On the basis of such possible complications, ThO_2 was tentatively set aside for future tests in case an otherwise suitable crucible material could not be found. UO_2 as a possible crucible material was eliminated for a similar reason. BeO was bypassed because of toxicity problems associated with beryllium. La_2O_3 was rejected because of the special handling problems that would be required due to its affinity for CO_2 and moisture in the air. Finally, Sc_2O_3, HfO_2, and Sm_2O_3 were tentatively disregarded primarily because of their scarcity. The suitability of each of the remaining oxides (CaO, SrO, MgO, CeO_2, ZrO_2 and Y_2O_3) as crucible materials for containing liquid vanadium was then tested experimentally.

After each of these materials was fabricated into a crucible by jolt-packing, a piece of vanadium metal was placed in each of them. Each crucible was placed in a graphite susceptor and heated in vacuum by induction. To prevent any reaction between the crucible and graphite susceptor, a sheet of tantalum or molybdenum was interposed. A temperature of $2000^{\circ}C$ was maintained for about 10 minutes unless failure of the crucible was noted. After the heating was stopped and the crucible allowed to cool, it was examined. Although the oxides of calcium, magnesium, and strontium had suitable melting temperatures, they were unstable under the conditions of the tests and reacted significantly with the vanadium metal. The cerium dioxide (CeO_2) crucible appeared to be severely attacked by the vanadium. This was probably due to the formation of some Ce_2O_3, which melts at about $1700^{\circ}C$, (25) through the reduction of the CeO_2 by vanadium. The ZrO_2 crucible was wetted by the vanadium although the degree of wetting appeared that it might be controllable. Of these six crucibles tested, only the ones prepared from Y_2O_3 appeared to be essentially inert to molten vanadium. Spectrographic analysis of the vanadium metal following this melting revealed it to contain less than 40 ppm yttrium.

Even though yttria was satisfactory as a material for containing liquid vanadium, further tests were conducted to determine if the degree of wetting of the ZrO_2 could be controlled to make it a suitable crucible material. This was prompted by its relative abundance and low cost compared to Y_2O_3. Pure ZrO_2 exhibits a phase transition at about 1000°C and unless it is suitably stabilized with another material crucible failures could result when heated through this transition temperature. CaO is commonly used for stabilizing zirconia and was used in the test crucible. In an effort to improve zirconia's resistance to liquid vanadium both CeO_2 and Y_2O_3 were tested as stabilizing agents.

Stabilization with CeO_2 appeared to increase the crucible's resistance to wetting somewhat; however, crucible failures resulted in all cases when temperatures up to 2000°C were maintained for more than a few minutes. The Y_2O_3-ZrO_2 crucible exhibited similar failures and would react with the graphite susceptor at temperatures around 1800°C unless it was adequately shielded.

Since it was felt that possibly a more dense ZrO_2 crucible could sufficiently withstand the wetting tendency of the more porous jolt packed crucibles, crucibles prepared by slip casting were prepared and evaluated. This was done by mixing a sample of lime stabilized zirconia in an aqueous solution containing 1 w/o polyvinyl alcohol for 12 hours on a ball mill. Prior to casting, the pH of this dispersion was adjusted to between 1.5 and 2 with concentrated hydrochloric acid. After the crucible was cast, it was allowed to dry for several hours in air followed by sintering in vacuum to $1700^{\circ}C$ by induction heating. Although this method resulted in very dense ZrO_2 crucibles, subsequent testing revealed that they too were unsuitable for containing liquid vanadium metal. Based on these results, it was felt that of the six oxides tested, Y_2O_3 appeared to be the most suitable material for use as a melting crucible in studying the carbon reduction of vanadium oxide.

Y_2O_3 Crucible Preparation

Y_2O_3 crucibles prepared by jolt-packing proved to be the easiest to fabricate. Since the yttria used in this study was obtained in form of flakes, it was first necessary to grind the yttria to a fine powder. This was done by dry grinding a batch of about 300 grams of the Y_2O_3 with 250 to 300 three-eighths inch diameter steel balls in a one-liter porcelain ball jar. Some iron pickup from the steel balls occurred during this ball milling operation but since it did not appear to be detrimental to the finished crucible, no attempts were made to remove it. After the oxide was packed in a graphite mold, as previously described, it was sintered in a vacuum at temperatures up to 1600°C. This was done by heating the crucible at an average rate of ten degrees centigrade per minute until this temperature was attained. This heating schedule allowed the crucible to shrink at a slow enough rate that little distortion and no cracking resulted. Figure 12 is a photograph of Y_2O_3 crucibles prepared by jolt-packing.

Yttria crucibles prepared by slip casting proved more difficult and required some developmental work for satisfactory results. At the outset of this study, water was used as the dispersion medium; however, all of the crucibles prepared from this aqueous medium cracked on drying. Apparently, the Y_2O_3 became somewhat hydrolyzed which led to these failures. After a number of organic dispersion mediums were tested, absolute methanol was selected based on the quality of the crucible produced. Before it was used, however, it was treated with size 3-A molecular sieves to eliminate the pos-

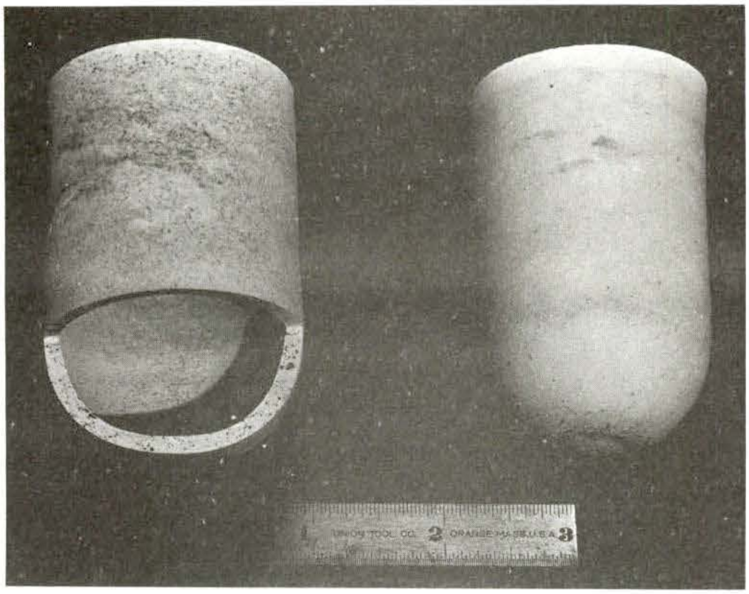


Figure 12. Jolt packed yttria crucibles. Sectioned crucible on left shows wall thickness

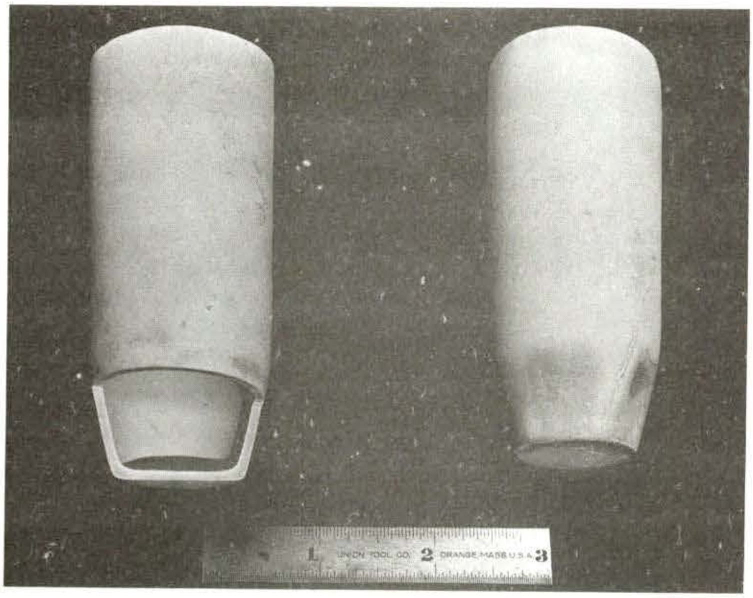


Figure 13. Slip cast yttria crucibles. Sectioned crucible on left shows wall thickness

sibility of any moisture.

The slip was prepared by grinding about 300 grams Y_2O_3 in 250 ml treated absolute methanol with about 300 of the steel balls for a number of hours in a one-liter ceramic ball jar. Iron contamination of the slip was more noticeable than the dry ground yttria, as evidenced by the color change of the yttria from white to grey-yellow; however, it appeared to have little effect on the quality of the crucible.

After the mixing step was completed, crucibles were cast as previously described employing the α cellulose in plaster of Paris mold. The cast crucibles usually released from the mold within six hours and maintained their green strength for about 24 hours. If the green crucible was not transferred into the induction furnace for heating during this period, the chances of breaking it during the transfer step was greatly enhanced. Essentially the same heating schedule was used for the slip cast crucibles as was described for the jolt packed crucibles. Figure 13 is a photograph of Y_2O_3 crucibles prepared by slip casting.

First Double-Operation Process - Sinter Plus Electron-Beam Melting

Due to the lack of a known crucible material for containing liquid vanadium, when this investigation was initiated, the first reduction sequence studied was a double-operation process wherein the charge of oxide and carbon were partially reduced in a graphite crucible and the vanadium intermediate further reacted and refined by electron-beam melting. In an effort to determine how many moles of carbon would be required to reduce a mole of V_2O_5, three charges were prepared which contained 4.0, 4.5 and 5.0 moles of carbon respectively. In order to reduce the blowout effect during the first exothermic reaction, each of these charges was given a primary heating in air to about $1000^{\circ}C$. This was then followed by continuing the heating under vacuum to about $1450^{\circ}C$. Even though the gas evolution rate was substantial after two hours of heating at this temperature, the reaction was stopped and the sample allowed to cool. After samples were taken for chemical analyses, the resulting intermediate products were electron-beam melted and resampled for analysis. Table 5 summarizes the results obtained.

Although this series of experiments yielded metal of

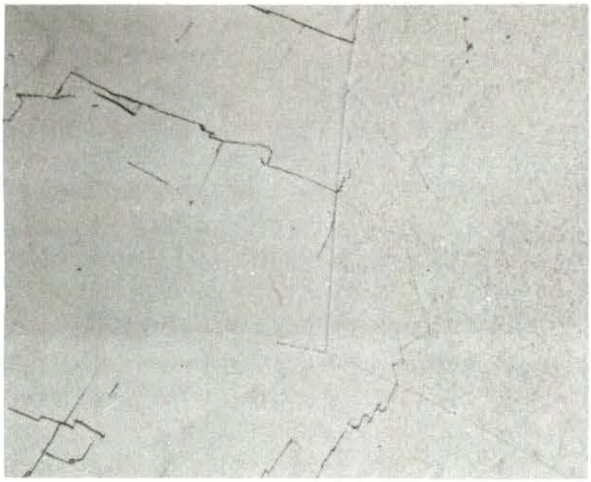
Table 5. Analyses of sintered intermediate products before and after EM melting

Sample number	Carbon to V_2O_5 mole ratio	Product analyzed	Product analysis in weight percent			Calculated stoichiometric mole ratio
			carbon	oxygen	nitrogen	
1-33	4.0	intermediate	6.27	4.18	0.050	3.72
1-33A	4.5	"	7.17	2.24	0.048	3.99
1-33B	5.0	"	12.38	1.80	0.053	4.06
1-33EB	4.0	EB melted	0.13	0.77	0.052	3.96
1-33AEB	4.5	"	3.91	0.057	0.050	4.17
1-33BEB	5.0	"	9.88	0.032	0.053	4.16

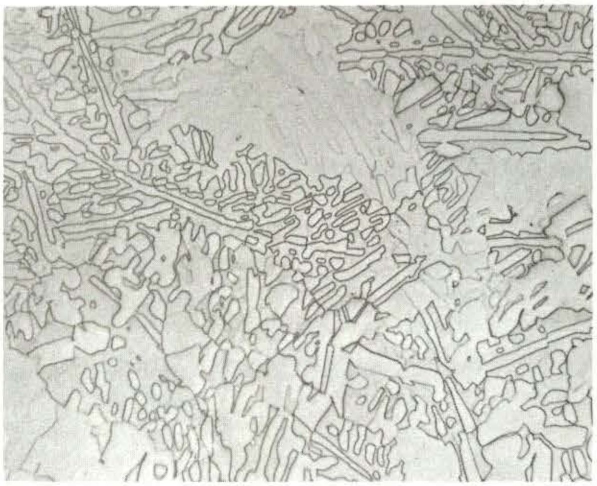
unsuitable quality, calculations based on the analytical results shown in Table 5 suggested that the number of moles of carbon required to reduce a mole of V_2O_5 completely to metal by the procedure used was about 4.0. Some indication of the resulting metal's purity is seen by referring to the photomicrographs of the electron beam-melted products both before and after an annealing treatment shown in Figure 14. One observation based on these results which served as a guide in planning future experiments and helped to evolve a portion of the standardized reduction sequences was the increased nitrogen content (500 ppm) noted in the intermediate product over that in the starting oxide (50 ppm). This would be of little consequence providing it was removed by the subsequent EB melting. As these results indicated, however, no decrease in nitrogen content occurred while there is some indication of a slight increase in nitrogen during EB melting. These findings were in agreement with a study by Anable (26), in 1967, who reported that electron-beam melting was ineffective for removing nitrogen from vanadium.

In another study on the ductility of vanadium metal, Lincoln and co-workers (27) concluded that the sum of the carbon, oxygen and nitrogen concentrations must be less than

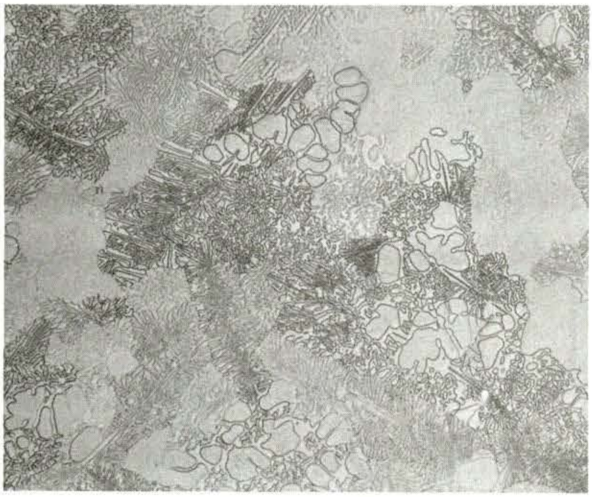
Figure 14. Microstructures of JKM-1-33EB, JKM-1-33AEB and JKM-1-33BEB before and after a 1500°C annealing treatment. JKM-1-33EB contains 0.130 w/o carbon and 0.770 w/o oxygen; JKM-1-33AEB contains 3.91 w/o carbon and 0.057 w/o oxygen and JKM-1-33BEB contains 9.88 w/o carbon and 0.032 w/o oxygen. All three samples contain about 0.050 w/o nitrogen. Electropolished in $HClO_4$. Etched for two minutes in HF-H_2SO_4-HNO_3-H_2O solution. 250X



JKM-1-33EB

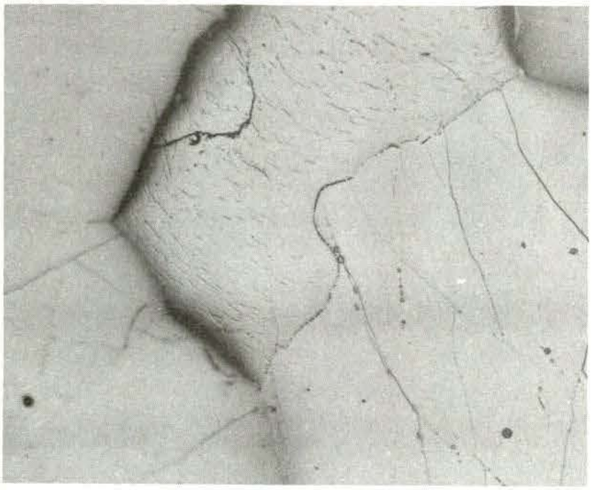


JKM-1-33EB Annealed

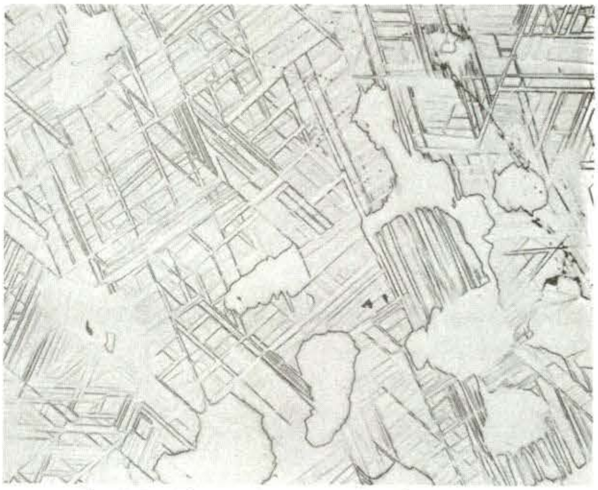


JKM-1-33AEB

JKM-1-33AEB Annealed



JKM-1-33BEB



JKM-1-33BEB Annealed

2600 ppm to yield ductile vanadium metal. In an effort to prevent the pickup of nitrogen during the preparation of the intermediate product, the procedure for the primary heating step was altered to permit heating the charge under vacuum conditions instead of in air. Since the entire reduction sequence was to be carried out under vacuum, it was felt that the mole ratio for stoichiometry would be slightly greater than 4.0 due to the fact that more of the oxygen would come off as CO.

Electron-beam melting of the vanadium intermediates of Table 5 proved quite difficult. This was due to the fact that the primary heating step was terminated before enough of the reaction was completed (sum of the carbon and oxygen content was between 9 and 14 w/o). When these samples were heated by the electron beam, enough gas was evolved to cause the melter to loose vacuum and malfunction. Three or four attempts were needed before a sample could be adequately melted. Later tests revealed that charges heated to about 1575°C and maintained at this temperature until the system pressure decreased to less than one-half micron produced a vanadium intermediate that readily melted in the electron beam. Analysis of the intermediates prepared in this manner usually contained less than a total of one percent carbon and oxygen.

A series of tests were then made to determine more nearly the number of moles of carbon to completely reduce a mole of V_2O_5 using this double-operation process. A number of charges ranging in the initial carbon to V_2O_5 ratio from 4.10 to 4.20 were then partially reduced at about 1600°C and then electron beam melted. Table 6 summarizes the analytical results obtained on three of these electron beam-melted samples.

Table 6. Analyses of EB melted sintered intermediate products

Sample number	Carbon to V_2O_5 mole ratio	Product analysis in weight percent carbon	oxygen	nitrogen	Calculated stoichiometric mole ratio
1-215EB	4.10	0.0494	1.112	0.0048	4.16
1-202EB	4.15	0.0311	0.7445	0.0050	4.19
1-230EB	4.20	0.0666	0.0669	0.0040	4.19

From these data, it appears that the final product purity is highly dependent on this mole ratio. Even though calculations based on these data revealed that the number of moles of carbon required to completely reduce a mole of V_2O_5 was about 4.19, the analytical data of Table 6 show that the residual carbon plus oxygen are such that the 4.20 moles of carbon can give vanadium of purity well within the 2600 ppm limit concluded by Lincoln et al. (27) as necessary for ductile metal. Subsequent testing revealed that metal prepared in this double-operation process employing charges based on Equation 11 did yield ductile metal as evidenced by the fact

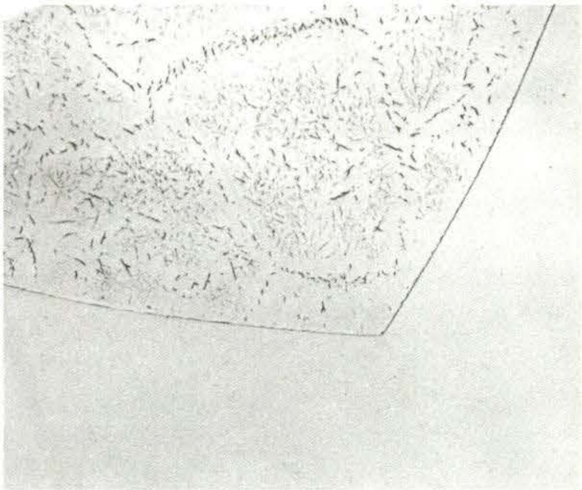
$$V_2O_5 + 4.20C \rightleftharpoons 2V + 0.8CO + 3.4CO \qquad (11)$$

that it could be reduced in thickness more than 90% by cold rolling with negligible edge cracking. Figure 15 shows two photomicrographs of sample 1-230EB of Table 6. One micrograph shows the metal in the as EB melted form, while the other one reveals the structure following a subsequent 1500°C annealing treatment.

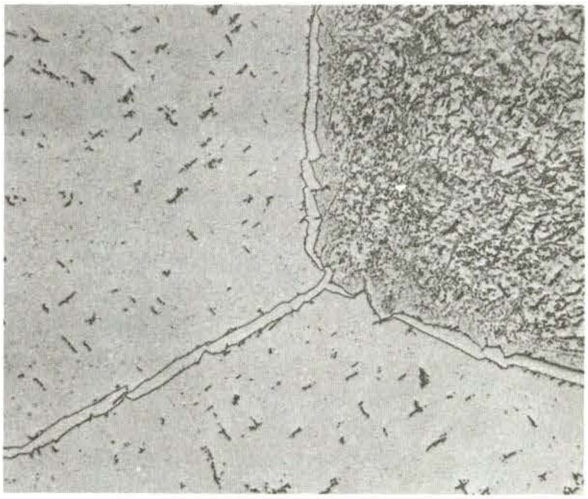
Single-Operation Process

Soon after the study of the previously described double-operation process was underway, other tests being conducted revealed that yttria (Y_2O_3) could serve as a relatively inert container for liquid vanadium metal at temperatures up to 2000°C and possibly higher. Based on these findings, investigations began on a single-operation process wherein the oxide would be reduced to the liquid metal without interruption of the heating.

Since the yttria crucible was to be heated in a graphite



A. As prepared. Can be reduced by cold-rolling with minor edge cracking



B. The above after annealing at 1500°C. Carbide in grain boundaries. Cracks on cold rolling

Figure 15. Microstructures of JKM-1-230 EB (vanadium metal) before and after a 1500°C annealing treatment. Electropolished in $HClO_4$. Etched for two minutes in HF-H_2SO_4-HNO_3-H_2O solution. 250X

susceptor, the first series of tests conducted were set up to determine the stability of the yttria crucible inside the graphite susceptor when heated to various temperatures up to 2100°C. The results obtained, with the yttria crucible resting on a zirconia disc indicated little or no chemical reaction between the susceptor and yttria at temperatures up to 1600°C. Some indication of reaction was noted, however, at temperatures above 1700°C while appreciable reaction of the yttria with the graphite occurred above 2000°C. Even though the yttria and graphite were not in direct contact with each other, some yttrium carbide was found on the walls of the susceptor and a decrease in wall thickness of the yttria crucible was quite evident. At this temperature, it is possible that carbon vapor reacts with the Y_2O_3 to form a more volatile yttrium species such as a lower oxide, which then contacts the graphite to form carbide. Subsequent tests revealed that when the Y_2O_3 crucible is shielded from the graphite heater with sheet tantalum or molybdenum, deterioration of the crucible is reduced to within tolerable limits.

Since this approach employed somewhat different conditions than the sintering plus electron-beam melting procedure, a series of tests were initially conducted in an effort to determine the carbon to V_2O_5 mole ratio for this single-operation process.

This was accomplished by first reducing a series of charges of varying composition to the liquid state in yttria crucibles at temperatures up to 1750°C in vacuum. Table 7 summarizes the results obtained on three typical reductions.

Table 7. Analysis of metal produced in single operation process at 1750°C

Sample number	Carbon to V_2O_5 mole ratio	Product analysis in weight percent carbon	oxygen	nitrogen	Calculated stoichiometric mole ratio
1-56	4.10	0.144	0.713	0.0048	4.13
1-59	4.20	1.39	0.389	0.0040	4.10
1-61	4.30	1.95	0.103	0.0050	4.14

As was expected, these analytical results revealed that relatively impure metal had been formed by the reduction at 1750°C. On the basis of this series of tests however, it appeared that the number of moles of carbon required to reduce a mole of V_2O_5 by this means was about 4.12. A later series of similar tests revealed that this value was more nearly 4.08. The general overall equation representing the reaction by this process would then be:

$$V_2O_5 + 4.08C \rightleftarrows 2V + 0.82CO_2 + 3.36CO. \qquad (12)$$

Due to the high concentrations of carbon and oxygen in the metal prepared at 1750°C, it appeared that higher temperatures possibly above the melting point of pure liquid vanadium metal would have to be employed in an effort to obtain quality metal. In a subsequent series of reductions, charges prepared using 4.08 moles of carbon per mole of V_2O_5 were reduced at temperatures up to 2000°C. Chemical analyses on the resulting metals revealed that they were all less than 600 ppm oxygen, while the carbon content was always greater than 2500 ppm. Obviously, the vapor pressure of the carbon from the graphite susceptor is such at these temperatures as to contribute significant amounts of carbon to the charge. Finishing temperatures below 2000°C reduced the carbon vapor pressure from the susceptor, but the increased time for completing the reaction would not make this single-operation process, as designed, practical.

Subsequent electron-beam melting of the vanadium product formed during the above reductions at temperatures up to 1750°C yielded ductile metal based on its rollability and its total interstitial impurity content of less than 2600 ppm. However, since this approach required a yttria crucible and yielded metal of substantially the same quality as the previously described double-operation process, it appeared that vanadium metal preparation based on such a procedure would be quite limited in application.

Alternate Double-Operation Process - Sinter Plus Self-Induction Heating

In the double-operation process described earlier, the charge was heated by induction in a graphite crucible under vacuum conditions to a temperature at which the charge is incompletely reacted and an impure sintered metallic product is obtained. This intermediate product is subsequently melted in an electron-beam furnace to further the reaction and yield ductile vanadium metal.

Furthermore, it was shown that Y_2O_3 was inert to liquid vanadium at temperatures up to 2100^oC. These two observations coupled with the known electrical conductivity of the vanadium intermediate pointed to the possibility of producing ductile metal by self-induction heating of the intermediate under vacuum in a yttria crucible. In connection with the development of a means for preparing the metal by self-induction heating, tests were first conducted to determine the lowest suitable temperature for preparing the electrically conducting vanadium intermediate. This was done by heating, in a graphite crucible under vacuum, a number of charges with the same carbon to V_2O_5 mole ratios to temperatures in the range from 1200°C to 1600°C. Each of these temperatures was maintained until a marked decrease in the reaction rate occurred. Samples prepared by such heating at 1200°C usually contained a total of about 16 w/o carbon and oxygen. As the holding temperature was increased, the carbon and oxygen decreased; the intermediates produced at 1600°C usually contained a total of about 4 w/o carbon and oxygen. The sintered product from the various treatments were crushed and pressed into right circular cylinders. A rough indication of their conductivities was then made with a volt-ohm meter. It was found that a relatively good conducting product could be formed by reacting the charge at a temperature as low as 1200°C. However, the time required to complete most of the reaction at this low temperature made this method unfavorable. The time necessary to reach the decrease in reaction rate in the preparation of the intermediate became less and less as the holding temperature increased. A suitably conducting product could be formed in a convenient period of time by carrying out the reaction at 1300°C or higher.

Data on subsequent reductions by self-heating some vanadium intermediate products are shown in Table 8. These data reveal that about 4.20 moles of carbon per mole of V_2O_5 in the starting charge is required to completely reduce the oxide to metal. This was the same mole ratio as was obtained in the sinter plus electron-beam melting procedure. Since the conditions under which the intermediate products were formed and since no carbon was employed in the environment during the final heating in either case, a mole ratio near 4.20 was more or less expected. Furthermore, metal prepared by this alternate double-operation process has been analyzed to contain as little as 200 ppm carbon and 300 ppm oxygen.

Table 8. Analyses of metal produced by the self-induction heating of vanadium intermediate products to 2000°C

Sample number	Carbon to V_2O_5 mole ratio	Product analysis in weight percent			Calculated stoichiometric mole ratio
		carbon	oxygen	nitrogen	
2-208	4.18	0.0100	0.2875	0.0050	4.19
2-209	4.19	0.0160	0.1675	0.0088	4.20
2-210	4.20	0.0770	0.0300	0.0046	4.20
2-212	4.20	0.0115	0.0980	0.0050	4.20

Since this operation, as presently developed, does not include pouring the liquid metal from the yttria crucible, an objectionable feature is encountered. The removal of the solidified vanadium metal product from the yttria crucible invariably results in damage to the crucible. Even though the Y_2O_3 can be reclaimed from the damaged crucible, it is necessary to regrind the crucible parts in order to fabricate another crucible. A separate crucible is therefore required for each reduction when the metal is permitted to solidify in the crucible.

In an effort to reduce the amount of yttria required to prepare the self-induction heater assembly shown in Figure 5, an assembly was prepared wherein the lid and outer crucible were fabricated from stabilized zirconia. Unstabilized zirconia powder was then used to insulate this outer crucible from the fused silica beaker. It was then demonstrated that the substitution of less expensive zirconia for yttria in this assembly, except for the inner crucible, gave an assembly that was satisfactory for self-induction heating of the vanadium intermediate to the liquid state and completion of the reduction.

V_2O_3 Preparation and Reduction

The preparation of V_2O_3, for subsequent reduction to metal, by the carbon reduction of V_2O_5 was investigated to determine if this method was practical. Based on previous results obtained during the reduction of V_2O_5 to metal, it was believed that about 1.20 moles of carbon would be required to yield stoichiometric V_2O_3. If this were the case, the overall general reaction could be represented as:

$$V_2O_5 + 1.20C \rightleftharpoons V_2O_3 + 0.8CO_2 + 0.4CO. \qquad (13)$$

A series of charges containing V_2O_5 and carbon in mole ratios varying from 1.14 to 1.20 in 0.01 mole increments were initially prepared. These samples were then reduced in vacuum to 1300°C. Analysis of the resulting products revealed that the charge containing 1.20 moles of carbon yielded a product which was analyzed to be $V_2O_{3.03}$ with a residual carbon content of about 35 ppm. The other oxide products prepared with the lesser amounts of carbon in the initial charge all contained greater than 3.03 moles of oxygen.

Tests conducted on the reduction of V_2O_3 to metal were limited to double-operation processes. The general overall reaction for the complete reduction of V_2O_3, based on the results obtained, can be written as:

$$V_2O_3 + 3C \rightleftarrows 2V + 3CO. \qquad (14)$$

The metal produced using this approach was of essentially the same quality as for a charge containing V_2O_5 even though a separate processing step, the reduction of V_2O_5 to V_2O_3 is required. The low temperature exothermic reaction exhibited with charges containing V_2O_5 is eliminated in processing the charge containing V_2O_3. This coupled with a small gain in vanadium content per unit volume of V_2O_3 and carbon charge might warrant employing this technique in larger scale operations.

VC and V_2C Preparation

The quantity of metal realized per reduction can be increased if the oxide is reduced with a vanadium carbide instead of with pure carbon. Two carbides of vanadium, VC and V_2C were of interest in this part of the investigation. It was found that both VC and V_2C can be readily formed by the reactions of either V_2O_5 or V_2O_3 with carbon. This was accomplished by heating such charges in a graphite crucible under vacuum conditions at temperatures up to 1850°C. In order to produce a carbide that was essentially free of oxygen, it was necessary to hold the charge at 1850°C for about two hours. The system pressure following this time at temperature was usually less than two microns. The general overall equations which represent the formation of VC and V_2C from either V_2O_5 or V_2O_3 can be represented as:

$$V_2O_5 + 6.20C \rightleftarrows 2VC + 0.8CO_2 + 3.4CO \qquad (15)$$

$$V_2O_5 + 5.20C \rightleftarrows V_2C + 0.8CO_2 + 3.4CO \qquad (16)$$

$$V_2O_3 + 5.0C \rightleftarrows 2VC + 3CO \qquad (17)$$

and

$$V_2O_3 + 4.0C \rightleftarrows V_2C + 3CO\ . \qquad (18)$$

Exploratory work conducted on preparing vanadium metal by reducing V_2O_5 with these carbides revealed that substantially less than five moles of carbide are required to completely reduce a mole of V_2O_5 to metal while about three moles of carbide are required to reduce a mole of V_2O_3 to metal.

SUMMARY AND CONCLUSIONS

The carbon reduction of vanadium oxides has been successfully employed to yield ductile vanadium metal on a laboratory scale. This was accomplished by either of two double-operation processes. The first step or operation in each process was to prepare an electrically conducting vanadium intermediate by partially reducing a charge of either V_2O_5 or V_2O_3 with carbon in a graphite crucible under vacuum at temperatures between 1300 and 1600°C. The refining step consisted of either electron-beam melting this product to complete the reaction or to refine it by self-induction heating at temperatures up to 2000°C in a ceramic crucible. Yttria (Y_2O_3) was found to be essentially inert to liquid vanadium metal at temperatures up to 2100°C and was selected as the crucible material in this investigation.

A problem of containing the charge was encountered when V_2O_5 was used as the starting oxide since the first reaction with carbon at about 650°C is quite exothermic. Several methods of controlling this initial reaction were investigated. Controlled heating of the charge and the employment of a crucible with breather holes worked satisfactorily. It was found necessary to exclude nitrogen during all phases of the heating sequence when low nitrogen in the final metal was desired, since nitrogen could not be removed by electron-beam melting.

The reduction of V_2O_3 with carbon exhibits no blowout problem; however, an additional processing step is required to prepare this oxide. Two methods of preparing the trioxide from V_2O_5 were used. They were the carbon reduction in vacuum and the hydrogen reduction. The general overall equation describing the carbon reduction under the conditions employed can be represented as:

$$V_2O_5 + 1.20C \rightleftarrows V_2O_3 + 0.8CO_2 + 0.4CO \ . \tag{19}$$

Although this chemical reaction is the same as for the initial step in the overall reduction to metal, it takes place here in the presence of stoichiometric carbon only. Thus, this reaction is decidedly less vigorous.

Ductile vanadium metal has been prepared by the carbon reduction of either V_2O_5 or V_2O_3 using both double-operation processes. This metal contains a total carbon, oxygen and nitrogen concentration of less than 1400 ppm. When V_2O_3 is used as the starting oxide, the overall general reaction can be represented by Equation 20, while Equation 21 represents

$$V_2O_3 + 3C \rightleftarrows 2V + 3CO \tag{20}$$

the overall general reaction when V_2O_5 is used as the starting oxide.

$$V_2O_5 + 4.2C \rightleftarrows 2V + 0.8CO_2 + 3.4CO \qquad (21)$$

A single-operation process wherein the charge of vanadium oxide and carbon was heated continuously in a Y_2O_3 crucible to 2000°C in a graphite susceptor yielded liquid metal that was contaminated with carbon. By lowering the final temperature to 1750°C, contamination was substantially reduced, but incomplete reaction of the charge occurred. Electron-beam melting of this impure product yielded ductile metal, however, this becomes a double-operation process which has no advantages over those double-operation processes pointed out above.

VC and V_2C were also prepared by the carbon reduction of vanadium oxides in the presence of controlled excesses of carbon. Holding temperatures of 1850°C for periods of up to two hours were required for essentially completing the reactions. These carbides were also used to reduce the oxides, but this phase of research only reached the exploratory stages.

RECOMMENDATIONS FOR FURTHER STUDY

During the course of scientific investigations new ideas and interesting exploratory results that are not of immediate concern will often develop. Since these ideas and results may have a minor bearing on the main objectives of the investigation, they usually do not warrant full consideration at the time. During this study on the carbon reduction of vanadium oxides, such developments included the following items.

1. Some exploratory work was conducted wherein V_2O_5 and Al_2O_3 were co-reduced with carbon. Enough carbon was added to the charge to completely reduce the V_2O_5 to metal and to reduce the Al_2O_3 to possibly Al_2O_2. It was hoped that the excess oxygen afforded by the aluminum oxide would reduce any residual carbon to essentially zero. Then, the suboxide of aluminum could be volatilized out in the electron-beam furnace or by self-induction heating. Exploratory tests on this variation yielded encouraging results and should be investigated further.

2. Other exploratory tests revealed that the addition of certain fluorides to the intermediate products had an effect on the impurity levels in the resulting metal. Samples of metal prepared from an intermediate product that were treated

with fluoride were found to contain substantially less oxygen than metal prepared from the same untreated intermediate product. This behavior difference warrants further study.

3. In this connection, spectrographic analyses of the resulting metal following the reduction of the vanadium intermediates that were treated with these fluorides also exhibited substantial decreases in the silicon content over that in the starting oxide. The effect, if any, that these fluorides have in reducing the silicon content should also be established.

4. The co-reduction of mixed oxides using one of the processes developed during the course of this study should also be investigated as a means for producing certain vanadium alloys.

5. Based on the substantial increase in vanadium yield per unit volume of charge, the carbide reduction of vanadium oxides should be studied further.

6. Since the major investigation was carried out on a scale that yielded between 50 and 100 grams of metal per reduction, consideration should also be given to the determination of any variations that might be encountered in the processing conditions as larger charges are employed.

7. The yttria crucible, as pointed out earlier, usually

becomes damaged when the liquid vanadium metal is allowed to solidify in it. The development of a method to drain or pour the liquid product from the yttria crucible would, therefore, be advantageous and would contribute to the success of a large-scale operation.

8. Electrorefining the vanadium intermediate product as a method of purification should be explored.

9. The possibility of using or developing other crucible materials for containing liquid vanadium metal leaves room for further investigation.

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