1951

Preparation of vanadium metal

John Reed Long
Iowa State College

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UMI®
PREPARATION OF VANADIUM METAL

by

John Reed Long

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College

1951
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I. INTRODUCTION

In what might be called the age of rare metals, vanadium is one of the last to be made quantitatively available. Impetus for its preparation has been given by the Atomic Energy Commission's interest in the metal, while metallurgical techniques acquired through development of other new metals have made its production feasible. Its high melting point, ease of fabrication, good ductility, and other desirable physical properties, in combination with a low capture cross section for fission neutrons, make vanadium an excellent structural material for fast reactors (62).

For fission neutrons the capture cross section of most of the elements below an atomic weight of 100 has been shown to decrease linearly with decreasing atomic weight, while above this value the neutron capture of the elements remains roughly constant (22). The most promising elements of lower atomic weights possessing high-melting and high-strength characteristics are to be found in the fourth period. Vanadium, with an absorption cross section of about 2.2 millibarns for effective energy neutrons of 1 m.e.v., has the lowest cross section of any metal in the first transition series (62). The ductility of vanadium is such that the pure metal can easily be formed into bars, sheet, wire and rods with existing
techniques. Moreover, with an elastic modulus-density ratio practically equivalent to that for steel (28) and a melting point exceeding 1700°C., vanadium is uniquely suited for use in nuclear structures.

Attention to vanadium as a new structural metal alone encourages development of new and simpler methods for its production. Its possible use in nuclear reactors imposes additional requirements of high purity and good ductility. An acceptable process should be readily amenable to expansion in productive capacity and should be evolved with a view towards economy of operation.

The present investigation was undertaken to produce pure massive ductile vanadium by processes more economical than those currently in use. Contemporary investigators have been concentrating on reductions from a pentoxide of chemically pure quality. Because of the large price differential between technical and chemically-pure grades of starting material, it was hoped that a process utilizing the former might be uncovered. Moreover, experience with other metals at the Ames Laboratory has brought forward the possibility of reduction to the metal from other compounds, notably the fluoride. Therefore, prior to the reduction studies, research on the preparation of various intermediate vanadium compounds
is necessary because of their unavailability. The use of the bomb reduction method allows for ample latitude in experimental techniques and affords a convenient means for possible development on a larger scale.
II. REVIEW OF LITERATURE

In 1801 del Rio (71), a mineralogy professor at the School of Mines in Mexico City, examined a brown lead ore from Zimapán and decided that it contained a new metal, similar to chromium and uranium. He named it erythronium, meaning red, after the red color of its salts when treated with acids. Later, however, he became doubtful of his discovery and decided that he had a basic lead chromate. This conclusion was also reached a few years later by Collet-Descotils, and all work on erythronium was abandoned. But in 1831 Sefstrom (60), a Swedish chemist at the School of Mines at Fahlun, discovered in an iron ore from Smaland a new element which he called vanadium, after the Scandinavian goddess of love and beauty, Vanadis. That same year Wohler (71) proved erythronium and vanadium to be identical. The controversy over the rightful credit for the element's discovery is still being waged (65), although Sefstrom is generally acknowledged as the discoverer, since he was the first to give definite proof of its existence.

Berzelius (1), experimenting in 1831 with Sefstrom's material, was the first to attempt the preparation of the metal. By heating a volatile chloride, which was actually an oxychloride, in an atmosphere of ammonia, he thought he obtained vanadium powder. What he probably prepared, as was
later shown (55), was the nitride and not metallic vanadium.
By exploding vanadic acid with potassium or by reacting the
pentoxide with hydrogen, Berzelius produced only a mixture
of the lower oxides (1,55). That same year, Johnson (25),
heating vanadic acid with carbon, was likewise unsuccessful,
as was SAFARIK in 1858 (58) in passing vanadyl chloride vapors
and hydrogen through a hot tube.

The first to produce fairly pure metal (95 per cent)
was Roscoe (55) in 1869 by the hydrogen reduction of the
dichloride to a vanadium powder. However, the process was
long and difficult and yielded only a few grams of vanadium.
Roscoe also obtained vanadium by reducing the chloride with
sodium at a red heat in a hydrogen atmosphere. The product,
after it had been washed in water, was 91 per cent metal.
However, his endeavors to produce the metal by hydrogen
reduction of the nitride or trioxide, by sodium reduction of
vanadium oxytrichloride or trioxide, and by magnesium reduc­
tion of the trioxide, all met with failure. Setterberg (61)
in 1882, using Roscoe's sodium reduction of the chloride, was
able to improve the yield to 98.7 per cent, but like Schicht
(59) two years previously, was unable to obtain the metal by
the electrolysis of an aqueous solution of a series of
vanadium salts. The compounds were merely reduced.

With his electric furnace Moissan (42,43) (1893-6)
attempted the reduction of the pentoxide with carbon but
succeeded only in preparing a vanadium carbide; reduction of the pentoxide with aluminum resulted in a vanadium-aluminum alloy. Helouis (20), however, could only produce a lower oxide by aluminum reduction of the pentoxide. In 1898 Goldschmidt (17), employing his alumino-thermic process, claimed to have obtained chemically pure vanadium, but Hittorf (18) showed this to be a vanadium hemioxide. Difficulty with aluminum reductions was also experienced by Koppel and Kaufmann (30), whose regulus analyzed only 79 per cent vanadium. Their results, using a carbon or a calcium carbide reductant, were not much better. Prandtl and Bleyer (52), however, succeeded in preparing 95 per cent vanadium by carrying out their aluminum reductions in a calcium fluoride well instead of a magnesium crucible. They believed the other 5 per cent to be oxygen, present in the form of a lower oxide, which escaped further reduction by alloying itself with the metallic vanadium. The substitution of vanadium trioxide for the pentoxide gave no better metal; and the replacement of vanadium trisulfide for \( V_2O_5 \) gave no reaction at all (53). Yet, by the aluminum reduction of unfused, dry and ammonia-free \( V_2O_5 \), Vogel and Tammann (67) were able to prepare a regulus which was 99 per cent vanadium. Unfortunately, this purity was not reproducible.

Later researches with alumino-thermic reductions have brought about only minor improvements in the process and only
meager increases in the purity of the metal. Wittig (73) maintained the yield is increased some 14 per cent by a preliminary treatment of the vanadium compound before reduction by heating with an ammonium salt. He attributed this to the formation of vanadium nitrides. Oya (47) repeatedly obtained metal analyzing 98.5 per cent vanadium by substituting sodium carbonate for a portion of the aluminum and introducing a potassium chlorate and barium peroxide booster. Recently, Merle (41) has claimed that a refined vanadium powder of unspecified purity can be prepared by carrying out the thermite reaction in a centrifuge, to which a selected purifying molten slag is introduced.

Cowper-Coles (9) in 1899 claimed to have prepared a brilliant metallic deposit of vanadium by the electrolysis of an aqueous solution of vanadium pentoxide and sodium hydroxide, to which hydrochloric acid was later added. The anode was of carbon, the cathode of platinum. Borchers (4) could not verify Cowper-Coles statements, but Gin (16) reports to have obtained a limited deposit by this method. Gin also tried two modifications: the electrolysis of vanadium oxide dissolved in a molten bath of vanadium tetrafluoride and calcium fluoride, using a lead cathode; and the electrolysis of vanadium oxide dissolved in a solution of ferrous fluoride in calcium fluoride, using a carbon cathode. With the former, metallic vanadium could not be obtained directly, since the lead must be eliminated from the alloy by volatilization in
the electric furnace; and with the latter, the vanadium was tapped with great difficulty and invariably was contaminated with iron. Fisher (13), in an exhaustive study on the electrolysis of vanadium salts, was totally unsuccessful in depositing metallic vanadium. He found that the Cowper-Coles method gave only a cathodic deposit of platinum hydride, which he believed Cowper-Coles and Gin mistook for vanadium.

Using mischmetal, Weiss and Aichel (72) in 1904 obtained metallic vanadium from the pentoxide. The reaction, initiated by a booster charge of barium dioxide, potassium chlorate, and aluminum, proceeded very rapidly and produced a silvery regulus, quite hard but fairly pure. With the same reductant, Muthmann and co-workers (46) claim to have attained a purity of 99.7 per cent vanadium, although their metal was as brittle as glass and partially bronze colored.

It was not until 1905 that vanadium was found to be ductile. By employing a unique method of thermal dissociation, von Bolton (3) produced metallic vanadium which was able to absorb the blows of a hammer. He compressed a plastic mass of vanadium pentoxide and paraffin into bars and heated them under vacuum by an electric current. In the process, the pentoxide was carbonized to the trioxide, which was subsequently separated into its components by dissociation. The small samples of vanadium he obtained showed a
melting point of 1680°C. Ruff and Martin (56), using a similar process, obtained 95 to 97 per cent 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. The trioxide was used instead of the pentoxide, since the latter is more readily fusible and is therefore more easily passed into the slag. Similar attempts to reduce the trioxide with aluminum and a small portion of carbon, with vanadium carbide, and with carbon directly, gave no more satisfactory results. By plotting the melting points of specimens with varying amounts of oxygen or carbon and extrapolating to the pure metal, it was concluded that vanadium has a melting point of 1715°C.

Prandtl and Manz (53), in the reduction of vanadium trichloride with sodium, obtained neither a better metal than their predecessors, Roscoe or Setterberg, nor a more vanadium-rich product than with alumino-thermic reaction. Billy (2) prepared what he regarded to be pure vanadium by passing the vapour of the chloride over sodium hydride at about 450°C. and extracting the sodium chloride formed with acid and water. Edson and McIntosh (11) were able to deposit free vanadium upon a glowing platinum wire filament by heating vanadyl chloride vapors in an atmosphere of hydrogen or in a vacuum. The silvery gray coating of
vanadium, for which no analysis was given, was obtained only on a small scale. Further experimental work on preparation of vanadium from its chloride was performed by Hunter and Jones (23) in 1923. They reduced vanadium trichloride with sodium in a sealed iron bomb but produced only vanadium powder, and that of 95 per cent purity.

The use of calcium as a reducing agent for vanadium compounds was first tried by Prandtl and Bleyer (51) in 1909. Although the oxide was reduced vigorously, the metal remained in isolated particles, owing to the absence of a fusible slag. They found that a mixture of 3 atoms of calcium and 2 atoms of aluminum worked much better, yielding a crystalline slag and a homogeneous regulus. The vanadium thus prepared was a bright steel-gray metal, capable of taking a high polish, but was indicated to be quite hard since it scratched quartz; and the best samples contained only 94.5 per cent vanadium. That same year Kuzel and Wedekind (33) patented a process for the production of pure vanadium by reduction of the pentoxide with calcium alone. The product was declared to be a powder, but the purity was not stated. A patent of a similar nature was secured by Cachemaille (7) for the extraction of vanadium metal from its oxide by means of calcium. The reaction was carried on in a closed iron vessel lined with lime, which was heated to 800°C. for several hours. In addition to a 50 per cent excess of
reductant, a halide of an alkaline earth, or alkali metal, was employed as a flux. The fineness of the metal powder obtained was regulated by the time of heating and the proportions of the mixture.

Definite proof of the ductility of vanadium was established by Marden and Rich (38) in 1927. These investigators found that the metal beads, obtained by the reduction of vanadium pentoxide with calcium, could be cold rolled. To obtain a lower melting slag, calcium chloride was added in an equal proportion with the calcium; for the cleaning up of residual air and moisture, a small piece of sodium or potassium was placed on top of the charge. A typical charge consisted of 175 grams of vanadium pentoxide and 300 grams each of finely milled calcium and calcium chloride. The reductant was thus 56 per cent in excess of the theoretically required amount. The reaction, which was carried out in a bare steel bomb, may be represented as follows:

\[ V_2O_5 + 5Ca + 5CaCl_2 \rightarrow 2V + 5CaO \cdot CaCl_2 \]

A wire-wound resistance furnace was used to heat the bomb to around 900°C. for one hour. After cooling, the charge was dug out with a cold chisel and leached in a copious quantity of water. The vanadium beads, varying in size from a steel pinhead to 3/8 of an inch in diameter, were further washed in dilute hydrochloric acid, water, alcohol
and ether and finally dried in a vacuum. The purity of the metal was the highest thus far attained - 99.8 per cent vanadium with 0.2 per cent iron and 0.05 per cent silicon. The pellets were easily worked into short lengths of wire, from which various physical and mechanical properties of the pure metal were determined. This work marked a great advance in the metallurgy of vanadium, but according to Marden, they could not do it again (28).

Modifications of Roscoe's earlier work on hydrogen reductions of vanadium compounds were actuated by Wartenberg et al. (70) in 1923 and Doring and Geiter (10) in 1934. The former were successful in reducing vanadium trioxide to the metal by employing hydrogen at four atmospheres pressure and heating to 1770°C. in an electric resistance furnace. The purity of the hard, shiny, reguline drop of vanadium formed is not given. The latter were able to obtain 99.9 per cent vanadium, as a fine, gray powder, by passing hydrogen over vanadium trichloride in a platinum tube. This increased vanadium content may be attributed to the higher purity of the reactants, although the reaction time remained at 80 hours, and the yield was 2 grams of powder from 7 grams of the trichloride.

In 1934, Van Arkel (66) found that vanadium, prepared by the decomposition of the iodide on a hot metal wire, was even more ductile than the metal prepared by Marden and Rich.
Because dissociation takes place at a temperature below the melting point of the metal, the embrittling impurities, such as oxygen and nitrogen, are not as easily acquired as when the metal is melted. A fairly pure metal was first obtained by reducing vanadium trichloride with sodium in an iron tube. This "crude" metal powder was then mixed with iodine crystals and heated to 900°C in an evacuated quartz flask, fitted with tungsten electrodes and heating wires. The vanadium diiodide formed volatilized and was decomposed by a glowing tungsten wire on which the pure vanadium was deposited. The metal analyzed 99.5 per cent vanadium and about 0.5 per cent iron. Although the deposited vanadium was easily contaminated with iron and other metals of volatile iodides, it was virtually free of oxides, nitrides, carbon and carbides. With prior separation of other metal impurities, this method might be well suited for the preparation of vanadium of the highest purity. However, the process has not been developed for use on anything but a small scale because of the difficulty of sealing the electrodes to the quartz and the excessively high currents required as the deposit accumulates.

Van Arkel also produced ductile vanadium of less pure quality by a similar process. Vanadium tetrachloride and hydrogen were passed into a flask containing two tungsten electrodes, between which a thin tungsten wire was stretched. The wire was heated to 800 - 1000°C to cause the reduction
of the chloride by the hydrogen on the wire surface. The deposit was an impure and brittle vanadium consisting of a solid solution of hydrogen in the metal. By subsequent heating in a vacuum the hydrogen was removed and a ductile metal specimen analyzing 99 per cent vanadium was obtained. However, if the hydrogen had only traces of nitrogen, the metal was contaminated with nitride. The drawbacks of this method are the difficulty of preparing a pure tetrachloride and the large loss of this tetrachloride that is reduced only to the trichloride.

Magnesium reduction of the various chlorides of vanadium was accomplished by Morette (44). By passing the tetrachloride vapor with a carrier gas of purified hydrogen over heated magnesium filings, vanadium, 99.3 per cent pure, was obtained as a grayish powder. The reaction, carried out in a magnesia boat in an electric furnace, required two and a half hours at 700°C. The di- and trichloride deposited with the powdered metal were later removed by washing with water. By mixing the dichloride with half its weight of magnesium and reacting in an argon or hydrogen atmosphere under the same conditions as before, vanadium of 98.9 to 99.5 per cent purity was again obtained as a dull, gray powder. No mention is made of the consolidation of either product into massive metal.
Morette also tried reducing the vanadium oxides with carbon monoxide and carbon (45). Action of carbon monoxide on the pentoxide proceeded no further than the trioxide at temperatures up to 1200°C. Using sugar charcoal on the tri- and pentoxides, a metal was obtained, but it was highly contaminated with carbides; and the vanadium content was never greater than 85 per cent. The reaction was not completed below a temperature of 1700°C., even though a large excess of reductant was used. Later, Kroll and Schlechton (32) made a thorough investigation of the reduction of vanadium oxide with carbon in a vacuum and concluded that this method was not practical. CP. grade vanadium pentoxide was briquetted with minus 100 mesh graphite and heated in an induction vacuum furnace. The reaction was initiated at 650°C., but a final temperature of 1550°C. at a pressure of 2 microns was required for complete reduction. Above that temperature, melting occurred, causing a violent reaction of the metal with the beryllia crucible. After completion of a run, the briquettes were crushed, rebriquetted, and reheated to allow for complete reaction. Even so, no better than 94 per cent vanadium was secured. Carbon analyzed about one per cent, with the remainder oxygen.

In an earlier paper Kroll (31) described the preparation of workable vanadium by a modified procedure of the Marden and Rich method. A briquetted mixture of vanadium pentoxide
and calcium, when reduced under argon in a steel bomb lined with calcium chloride, produced vanadium pellets the size of peas, which were malleable but which could not be further agglomerated through sintering. Remelting was not considered because of the reaction between crucible lining and metal. However, suitable vanadium powder was prepared by a double reduction process, wherein a charge of vanadium pentoxide, calcium and a mixture of calcium and barium chloride yielded, upon heating, an impure metallic powder. This powder in turn was again mixed and heated with more reductant and flux to produce vanadium, in fine particles, capable of being pressed into slugs. After sintering of the slugs at 1400°C. in a vacuum by means of an induction furnace, the fused mass was cold forged and rolled into sheets. Hardness readings measured up to 360 Brinell, after the metal was rolled to ten times its initial length.

Meerson et al. (40), also interested in winning a powdered product, reacted vanadium trioxide with calcium hydride to obtain fine crystalline grains, in which vanadium, plus hydrogen, amounted to better than 99 per cent. The hydride and oxide were heated to 1100°C. for one hour in an electric furnace under hydrogen, whereupon the powder, after cooling, was freed of lime by washing with dilute hydrochloric acid. The 90 per cent hydride reductant employed in 50 per cent excess yielded a vanadium with one or two per cent hydrogen content.
Vanadium produced from its fluoride has been given only scant attention. Marden (37) patented a process in 1922 for the aluminum reduction of the vanadium fluoride or potassium fluovanadate. The reaction mass was heated in an electric furnace in a vacuum, or in an inert atmosphere, first to effect reduction to the metal, and then to distill out the fluoride of aluminum or of aluminum and potassium. The spongy mass remaining was then further heated to sinter it into a white, coherent metal. Recently, Emeleus and Gutmann (12) attempted to prepare the vanadium difluoride from the trifluoride by reduction with hydrogen at 500°C., but only the metal was formed. No other details are given.

During the progress of this investigation there have been three important papers published on the preparation of ductile vanadium of a high purity. McKechnie and Seybolt (39) of the Knolls Atomic Power Laboratory described the preparation of massive vanadium from its pentoxide by the employment of an iodine booster with a calcium reductant. The formation of calcium iodide not only liberates additional heat sufficient to yield a solid regulus but also lowers the melting point of the slag, thus aiding in separating the dross from the biscuit. Metal, capable of being cold rolled to thin foil from the as-reduced state, analyzed 99.0 - 99.6 per cent vanadium. The reduction was carried out in a 4 inch diameter steel bomb, 11 inches high and 3/8 of an inch wall thickness, with welded bottom and copper-gasketed, flanged
cover, bolted in place. Magnesia liners holding a 1.5 liter charge were slipped inside the bomb. The reaction was initiated by heating to 700°C. by means of an induction coil, powered by a 50-kw vacuum tube oscillator, with a frequency of about 220 kilocycles. Firing time averaged about 12 minutes. With an optimum charge of 300 g. CP. V₂O₅, 552 g. Ca and 150 g. I₂ yields of 74 per cent, or 125 g., were obtained. It was found that 60 per cent excess calcium was required for ductile metal in good yields. Vickers hardness numbers ranged from 110 to 150 for the ductile vanadium, depending on the content of oxygen, nitrogen, and hydrogen. Wet oxygen treatment of the vanadium pentoxide at 400°C. for 18 hours was beneficial in the lowering of the oxide's nitrogen content and was believed to be a contributing factor in obtaining soft metal. Chemical analysis of the regulus is given in Table I for comparison with other investigators. No physical properties other than hardness were given for this metal. Although several pounds of high purity ductile vanadium have been produced, the Knolls Laboratory is not in a position to supply enough metal for an experimental program (62). Moreover, since the reactants employed are of the highest purity, the cost of vanadium metal by this process would undoubtedly be high.

These experimenters also attempted the reproduction of the Marden and Rich procedure and obtained ductile pea size
Table I
Analysis of Ductile Vanadium

<table>
<thead>
<tr>
<th>Element</th>
<th>Marden &amp; Rich %</th>
<th>McKechnie &amp; Seybolt %</th>
<th>Gregory et al. %</th>
<th>Kinzel %</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>99.8 - 99.3</td>
<td>99.6 - 99.0</td>
<td>99.8 - 99.7</td>
<td>99.9 - 99.8</td>
</tr>
<tr>
<td>Fe</td>
<td>0.20 - 0.24</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.05 - 0.06</td>
<td>0.001 - 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.20 - 0.29</td>
<td>0.05</td>
<td>0.03 - 0.07</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.011 - 0.023</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>0.017 - 0.029</td>
<td>0.1 - 0.25</td>
<td>0.05 - 0.12</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>0.006 - 0.016</td>
<td>0.01 - 0.015</td>
<td>0.02 - 0.04</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.002 - 0.005</td>
<td>0.001 - 0.004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
beads of a high vanadium content. However, the benefits ascribed to the use of calcium chloride could not be observed, and neither the mass nor the yield of the product could compare with metal produced with an iodine booster. Efforts to further lower the melting point of the calcium oxide and calcium iodide slag by the addition of aluminum metal or aluminum oxide resulted in a uniformly brittle metal, due to aluminum contamination.

Gregory and co-workers (19) at Westinghouse report the preparation of fine powdered vanadium, adaptable to the formation of mass metal by the techniques of powder metallurgy. By reduction of the trioxide of vanadium with calcium and calcium chloride, the temperature of reaction was maintained below the melting point of the metal to yield a uniformly fine powder. The trioxide was obtained by hydrogen reduction of the pentoxide at 600°C. The charge, in the proportion of 1 mol. V_2O_3 to 6 mols Ca and 1 mol CaCl_2, was reacted in an iron cup lined with a refractory oxide under argon. The charged container, enclosed in a Vycor-glass system, was heated by means of high frequency coils at approximately 1000°C. for one hour. Powder recovery, after leaching with 50 per cent acetic acid, washing with water, and vacuum drying at 50°C., amounted to 80 per cent of theoretical. Unless stabilized by heating in a vacuum to 400°C., vanadium powder was likely to take on a greenish hue, indicating some possible
reaction with air at room temperature. Even stabilized powder, however, possessed the tendency to become activated and ignite on exposure to air; therefore, it was desirable to fabricate to a massive product as soon as possible.

The formation of solid metal was accomplished by first pressing the powder in steel dies at 15 - 20 t.s.i., followed by sintering in a vacuum for several hours at 1400 - 1500°C. The sintered ingots were able to be rolled to about 50 per cent of their cross sectional area without annealing. Between passes, gradually decreasing from a 25 to a 10 per cent reduction in area, the metal was heated to 600°C. in argon. Vickers hardness numbers approached 350 when the material was fully cold worked, but the metal could be completely annealed at 850°C. for one hour in a vacuum to give a Vickers number of 230. With a protective iron sheath, other ingots were hot rolled and forged at temperatures around 1000°C.

Comparison of the chemical analyses of the Westinghouse metal with that from Knolls (Table I) reveals in the former a high oxygen content which is reflected by the higher hardness values listed. The high carbon content reported by McKechnie and Seybolt is unaccounted for, although both started with CP oxide and purified calcium. As small amounts of dissolved gases have a pronounced effect on the physical properties of vanadium, the values for hardness, tensile strength and per cent elongation that have been reported by Gregory do not represent the properties of gas-free metal.
Vanadium has been proclaimed a new article of commerce in a paper by A. B. Kinzel (28) of the Electro Metallurgical Division of Union Carbide and Carbon Corporation. Ductile metal, 99.8 per cent pure, is said to be available in limited quantities in the form of ingots, bars, foil and chips. Kinzel does not describe the actual method of production but implies that it is similar to the method of McKechnie and Seybolt, wherein CP vanadium pentoxide is reduced by metallic calcium in a pressure bomb. The recovery of the vanadium as a solid crystalline mass is claimed to be better than 90 per cent. Fabrication of either the massive vanadium or the argon-arc-melted ingot is initiated by heating to a temperature of 2000 to 2100°F. Sheathing of the metal, generally with 1/8 inch thick stainless steel, is necessary if a protective atmosphere is not provided. Hot working could then be carried on at temperatures of between 1475 and 2100°F., although the metal does not appreciably work harden if rolled at lower temperatures. For sheet rolling it is customary to hot work down to 1/4 inch thickness, whereupon the plate may be cold rolled to the final article, following an intermediate annealing at 1650°F. for one hour under inert gas or vacuum. It is suggested that the hardness of the annealed metal to be cold rolled be less than Rockwell B-85, since total reductions of 85 per cent may increase the hardness to around Rockwell B-95, at which point edge cracking usually
occurs. This vanadium machines well, can be bent, stamped and pressed, and is easily welded with argon shielding and a Heliarc torch. Overall hardness values for Electromet's vanadium varies between Rockwell B-75 and C-29, depending on the amount of cold working and the content of oxygen, nitrogen and carbon. Analysis in Table I indicates an oxygen content intermediate between the softer metal from the Knolls Laboratory and less ductile Westinghouse vanadium.

The presence of small amounts of dissolved gases in metallic vanadium influence to a marked degree the mechanical and physical properties of the metal. Reaction of vanadium with oxygen and nitrogen is rapid at elevated temperatures, and both the oxide and nitride phases are soluble in the metal itself. X-ray photographs of the metal powder indicate, too, that oxygen may form a solid solution in vanadium up to about $V_0 0.4$ (48). Hydrogen is also readily absorbed by vanadium. The principal effect of these gaseous impurities is to increase the hardness and the brittleness of the metal. Without prior hot working it has not been possible to cold roll vanadium containing more than about 0.07 per cent oxygen. A good correlation has been shown to exist between the oxygen content of vanadium and its Vickers hardness number (29). As an oxygen content of only 0.3 per cent by weight is equivalent to almost 1 atomic per cent of foreign atoms, the influence of this gas can more readily be realized. Since nitrogen and
hydrogen diffuse through vanadium at a much slower rate (62),
they are not as dangerous a contaminant as oxygen. Although
other non-metallic and metallic impurities may alter certain
characteristics of vanadium, their effect on ductility, as
compared with that of the dissolved gases, is not so pro-
nounced. Moreover, if the atomic weight of the foreign
elements in the metal is less than that of vanadium, they
are not likely to effect adversely the fast neutron absorption
of the metal.

The formidable array of serious efforts and the mediocre
results generally obtained have made it clear that the prepara-
tion of pure ductile vanadium in massive form has presented
numerous difficulties and that the production of the metal
in any appreciable quantity has been an arduous task. The
reduction of vanadium chloride by ammonia has furnished only
a nitride, and reactions with potassium or sodium reductants
have never been completely successful. The action of carbon
on vanadium oxide provided an incomplete reduction product
contaminative with carbides, while with aluminum, the vanadium
regulus produced invariably contains the embrittling reductant.
All attempts to obtain vanadium by the electrolysis of an
aqueous solution have failed. Metal produced by fused salt
electrolysis either has been contaminated with impurities
or alloyed with the cathode.
Of the methods listed by Pearson (48) for the preparation of a malleable vanadium, the hot-wire decomposition of the iodide and the hydrogen reduction of the chlorides have proved to be time consuming for production beyond small scale operations. Greater possibilities for expansion are afforded by the calcium reduction of the pentoxide. This method has proven a reliable source of metal of sufficient purity and ductility to be satisfactory for nuclear purposes. Metal prepared at the Knolls Laboratory has been of excellent quality, but due to the emphasis on more pressing developments, the vanadium program there has been sharply curtailed. The Westinghouse metal is not directly produced in massive form, and the small quantities prepared have been sufficient only for their own research. The availability of high-purity vanadium in quantity has recently been announced by Electromet's Research Laboratory; the controllable limits of hardness, though, are fairly high. Although the available processes for preparing vanadium could supply certain requirements in the Atomic Energy Commission's program, it is desirable to investigate the possibility of developing new or improved processes for the preparation of large quantities of ductile vanadium of satisfactory purity, which can be produced with minimum cost.
High purity and good ductility are fundamental requisites of metallic vanadium for use in nuclear reactors. The formation of a reduction product in massive form, adaptability to a larger scale of operations, and attention to the economics involved are considerations desirable of incorporation in an acceptable process. These are factors which have not been fully regarded in previously proposed procedures, but which have been salient considerations in guiding this investigation. Due heed must also be taken of the hazards to health in the materials employed and in the processes involved.

Reduction to a massive product does not necessitate subsequent operations, such as pressing and sintering, prior to metal fabrication, as does a product in powdered form. To obtain massive metal, sufficient heat must be provided to bring the reaction products to a molten condition. This is best accomplished by the employment of a strongly exothermic reaction between the reductant and compound to be reduced, although additional heat is usually necessary to reach the temperatures required for fusion of the high melting metals. This supplementary heat may be provided by a secondary reaction of a booster reagent with excess reductant. In addition, the booster reaction may be useful in lowering the melting point of the slag or the metal, thus effecting better separation of phases. Inert additives are sometimes helpful in
this respect without supplying auxiliary heat, although differences in density and immiscibility of phases largely determine the degree of separation of the reaction products. For the setting off of both primary and secondary reactions, the application of heat from an external source is generally required.

While the free energy change of reaction determines the feasibility of a proposed reduction, and as such, the choice of materials for the reduction charge, the extent of the enthalpy change of reaction is a good measure of the likelihood of the reaction products reaching the molten state. Although the use of a calcium reductant with vanadium pentoxide has been shown to yield a satisfactory metal, reductions from other compounds of vanadium offer favorable possibilities for the formation of massive metal. Such suitable starting materials for reduction, which are not likely to introduce alloying impurities that may embrittle the metal or reduce its purity, include the lower oxides, fluorides, double fluorides, chlorides and sulfides of vanadium. By the proper selection of a thermal booster or fluxing agent, it is possible to obtain a solid regulus from a variety of starting materials, supplying varying heats of evolution upon reduction. A slightly exothermic reaction between the compound of the metal to be prepared and the reducing agent would therefore require a powerful booster reaction, while
a strong primary reaction may not necessitate the use of auxiliary heat or might even require a diluent to increase the heat capacity. A few of the reagents appropriate for use as boosters are potassium chlorate, sulfur and iodine. Of these, only the last is known to have been employed in vanadium reductions. The addition of an alloying agent may contribute to the aggregation of the reduced product or increase the yield of massive metal by lowering the melting point of the metallic phase. Recovery of the desired metal from the massive alloy may be accomplished in subsequent operations. The use of other additives, as a salt of the alloying agent, may serve the dual role of lowering the melting point of the metal and of supplying additional heat. The many untried combinations afforded in the reduction charge thus offer attractive possibilities for experimentation.

The closed bomb method is readily adaptable to expansion of operations. While the technique allows experimental reductions yielding less than a quarter of a pound of vanadium metal, existing facilities permit expansion on a scale 50 times this figure. In similar reduction processes, an expansion in productive capacity reduces the proportionate heat losses and provides an increase in product yield. Another advantage of this reduction method is the exclusion of the bomb's contents from contact at elevated temperatures with any atmosphere other than its own evolution. Since the
solid charge is tightly packed in a refractory liner before closing, there is little chance of contamination with embrittling gases from the atmosphere upon reduction. The refractory liner aids in reducing heat losses from the reaction mass as well as in preventing interaction between the reduction materials and the bomb itself. A more detailed treatment of the bomb reduction technique may be found elsewhere (68).

The economic aspects of vanadium preparation by the bomb reduction method must be considered in any development on an expanded scale. From a free energy standpoint, the choice of reductants for metallic vanadium is principally limited to the alkali and alkaline earth metals, hydrogen, magnesium, beryllium, aluminum, silicon and carbon. While alloying of an embrittling reductant with the desired metal excludes the last three, and the unsuitability of a gaseous component in a sealed bomb prohibits the use of hydrogen reductions, economic factors generally restrict the remaining reducing agents to sodium, magnesium and calcium. The cost of booster reagents may likewise be an important factor. Although molar quantities of iodine and sulfur boosters furnish almost the same heat of reaction with calcium metal, the cost of iodine, due to its higher molecular weight and higher price, is several hundred times that of sulfur supplying an equivalent amount of heat. Moreover, from among the
various grades of purity of commercially available vanadium pentoxide, there exists a large price differential. This price differential may not be justified for the reduction purposes intended; however, only chemically pure grades have been utilized by current experimenters. By recourse to vanadium compounds furnishing higher heats of reaction upon reduction than the pentoxide, the savings in increased metal yields and in booster reagents may offset the cost of reactants and labor involved in their preparation.

Vanadium is generally regarded as a poisonous element. If inhaled in the form of oxides in dust or fumes, vanadium's physiological effects in the more extreme cases consist of a dry cough, acute bronchitis, sore throat, palpitations, fatigue, eye sores, kidney disturbances, and in some cases, a rash on the extremities (63). The resulting complications often terminate fatally. However, there is no evidence of a cumulative effect from vanadium ingestion or of tubercular complications, and neither gastro-intestinal nor central nervous system injuries have been observed (64). A dose of 100 milligrams of vanadium pentoxide must be regarded as toxic (54). The treatment employed should follow the usual pattern of removal from exposure and attendance of an experienced doctor; specific care is needed for each of the symptoms displayed. Thorough ventilation and the use of respirators are generally adequate protective measures, although these precautions are not necessary if the material is larger than 40 mesh.
Certain precautions must also be exercised with the bomb reduction method. The generation of extreme pressures at elevated temperatures by the formation of gaseous products eliminates the use of hydrides, nitrates, ammonium salts and hydrated compounds as starting materials. Reactants which are hydroscopic must be kept under controlled atmospheres, since the absorption of a few per cent water may cause explosive pressures upon heating in a sealed vessel. The products of the booster reaction may dissociate into gaseous components due to the temperatures reached with the primary reduction, a circumstance which cautions the use of a magnesium reductant with a sulfur booster. Excessive temperatures attained by too great a heat of reaction can break down the liner insulation and weaken the bomb walls sufficiently to be perilous. For this reason the more powerful boosters, such as the chlorates and sulfates, must be used with care. Attention to the hazards involved in the handling of hydrogen fluoride, hydrogen sulfide and hydrogen reactants employed in the preparation of various intermediate vanadium compounds must also be given.
At present, the compounds of vanadium commercially available are limited to ferrovanadium, vanadyl dichloride and vanadium pentoxide. Since the separation of vanadium from iron in ferrovanadium is a difficult task, and since economic factors eliminate consideration of vanadyl dichloride, the selection of a starting material for development of a reduction process is reduced to vanadium pentoxide.

Vanadium pentoxide can be obtained from a number of suppliers in several grades of purity and in various physical forms, depending on the conditions under which it is prepared. The air-dried form of technical grade pentoxide generally contains between 83 and 85 per cent \( V_2O_5 \), with sodium being the major contaminant. Since the material shows an appreciable weight loss upon ignition, it is not suited for direct reduction to metal. However, the particle size of this red oxide may be closely controlled when dried, usually between 20 and 40 mesh. As such, it is well suited for the preparation of intermediates, since it is free of dust particles hazardous to health, yet sufficiently fine to promote rapid reaction. The fused form of technical grade vanadium pentoxide has a higher \( V_2O_5 \) content, usually around 89 to 92 per cent, because of the loss of volatile matter upon fusion. This material is black, crystalline, and generally supplied in large chunks, which require a reduction in size for subsequent reactions.
Chemically pure vanadium pentoxide generally has a purity of greater than 99 per cent \( V_2O_5 \). In the last stage of its purification, the vanadium is present as an ammonium vanadate, and unless it is thoroughly roasted, the resulting pentoxide may contain appreciable quantities of nitrogen. After grinding, the purified material is marketed as a very fine powder. Properly calcined vanadium pentoxide is yellow to orange in color. A comparison of the analyses and cost of technical grade and chemically pure vanadium pentoxide from the Vanadium Corporation of America is given in Table II. The price differential between the two grades of purity is seen to be appreciable. A CP. grade of vanadium pentoxide of 99.50 per cent purity is offered by the Electro Metallurgical Division of Union Carbide and Carbon Corporation for $5.35 per pound of contained vanadium.

Some purification of technical grade material was accomplished by suspension of the pentoxide in an aqueous solution of reagent grade ammonium chloride. Because of the corrosive nature of the ammonium chloride, the purification step was carried out in a 12 liter monel bucket heated on an electric hot plate; an electric stirrer was employed to keep the solids in motion. Five hundred grams of oxide were thus treated in one batch. The resulting ammonium vanadate was filtered on size 3 Buchner funnels and heated in 12-inch diameter evaporating dishes in a large electric muffle to
Table II

Analysis of Vanadium Pentoxide

<table>
<thead>
<tr>
<th></th>
<th>Tech. Air Dried Vanadium Pentoxide</th>
<th>Tech. Fused Vanadium Pentoxide</th>
<th>CP. Vanadium Pentoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2O_5$</td>
<td>84.15$^a$</td>
<td>89.25$^a$</td>
<td>99.94$^b$</td>
</tr>
<tr>
<td>Na$^b$</td>
<td>3.82</td>
<td>4.33</td>
<td>trace</td>
</tr>
<tr>
<td>Ca$^b$</td>
<td>0.05</td>
<td>0.13</td>
<td>trace</td>
</tr>
<tr>
<td>Si$^b$</td>
<td>0.07</td>
<td>0.15</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe$^b$</td>
<td>0.08</td>
<td>0.13</td>
<td>0.005</td>
</tr>
<tr>
<td>S$^b$</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.001</td>
<td>0.002</td>
<td>none</td>
</tr>
<tr>
<td>Ignition loss$^a$</td>
<td>8.98</td>
<td>0.36</td>
<td>none</td>
</tr>
<tr>
<td>Cost$^c$</td>
<td>$2.14</td>
<td>$2.14</td>
<td>$12.48</td>
</tr>
</tbody>
</table>

$^a$ Ames Laboratory
$^b$ Vanadium Corporation of America
$^c$ 1950 prices per pound of contained vanadium
eliminate ammonia and form a vanadium oxide of higher purity. A rough comparison of all the various grades of vanadium pentoxide was then made from the approximate concentrations of impurities as determined by general qualitative spectrographic analyses.

Besides the pentoxide, the compounds of vanadium offering promising possibilities for reduction to the metal include vanadium trioxide, vanadium trifluoride, vanadium trisulfide and potassium fluovanadate. A reduction of the pentoxide from the five valent to the three valent state is first necessary for the preparation of any of these compounds.

Vanadium trioxide was easily prepared by the hydrogen reduction of the pentoxide at an elevated temperature. Besides its disposition in bomb reduction charges, vanadium trioxide served as a convenient starting material for the formation of other trivalent vanadium salts. The red pentoxide was reduced through the blue tetraoxide to the black trioxide in a four tray monel reactor. This reactor, also serving for hydrofluorinations, is pictured in Figure 1 and diagrammed in Figure 3. High purity cylinder hydrogen from the Balback Company was passed through an S shaped monel preheater pipe and then introduced into the lower rear of the reactor. After sweeping over the bottom tray, the reducing and reaction gases ascended and passed in the reverse direction over the second-from-bottom tray. The flow was
Figure 1 - Hydrogen Reduction and Hydrofluorination Assembly.

Figure 2 - Bomb Reduction Furnace and Sealed Bomb after Firing.
Figure 3 - Hydrogen Reduction and Hydrofluorination Assembly.
continued in a like manner over the remaining two trays, and the exit reaction gases condensed in a water-cooled condenser. The monel trays, measuring 36 inches long, 6 inches wide and one and one-half inches deep, had an individual capacity of 1500 grams of vanadium pentoxide, or a total capacity for the furnace of 6 kilograms. The trays slid into compartments inside the monel shell, which was supported by an angle iron cradle. The reactor door, a copper gasketed monel plate, was held in place by 8 one-half inch diameter bolts. Heat was furnished by an H shaped horizontal gas burner, the crossbar of the H running parallel to the length of the furnace. The entire assembly was enclosed in brickwork and covered with a hood for exhaustion of the combustion gases. A Brown three-point recording and controlling potentiometer was used to regulate the furnace temperature.

Vanadium trifluoride was obtained by low temperature hydrofluorination of vanadium trioxide, followed by drying of the partially hydrated product at a higher temperature in a hydrogen fluoride atmosphere. The same furnace (Figures 1 and 3) was used for hydrofluorinations as was used for hydrogen reductions. Connection of the anhydrous hydrogen fluoride cylinder, obtained from the Pennsylvania Salt Company, with the one-half inch monel line was made through a monel sylphon bellows. Gas flow was facilitated by the circulation of hot water over the cylinder. The water
temperature was regulated by electrical immersion heaters in the reservoir below the cylinder, and the heated water was recirculated to the ring spray atop the cylinder by means of a small centrifugal immersion pump.

A monel orifice and kerosene filled fluorothene manometer inserted in the inlet line to the furnace indicated the gas flow rate. Passage of hydrogen fluoride through the reactor followed the course of the hydrogen flow. Condensation of hydrogen fluoride in the inlet and outlet lines was prevented by running steam lines parallel to the inlet and outlet lines and enclosing both within a magnesia jacket. After passage of the exit furnace gases through the water-cooled condenser, any excess hydrogen fluoride was neutralized in a sodium carbonate bath. Subsequent to the initial hydrofluorination and drying steps, the green lumps of vanadium trifluoride were ground to 65 mesh in an 8-inch diameter Wiley mill, and the hygroscopic powder was redried as before.

The preparation of vanadium trifluoride from solution was effected in 3 liter capacity fluorothene beakers. Vanadium trioxide was dissolved in 48 per cent hydrofluoric acid, and the solution was filtered through improvised fluorothene funnels. Upon evaporation of the green filtrate to dryness at low heat on a hot plate, the trihydrated vanadium fluoride was removed from the beakers, powdered, and transferred to the hydrofluorinating unit for final drying.
Potassium fluovanadate was precipitated from the above filtered solution of vanadium trifluoride by the addition of reagent grade potassium fluoride. Decantation of the supernatant liquid from the fluorothene beakers was followed by filtering, pulverizing and drying of the green potassium fluovanadate in the apparatus previously described for vanadium trifluoride.

Vanadium trisulfide was produced by the solid-gas reaction between vanadium trioxide and hydrogen sulfide. To attain the temperatures required for satisfactory conversion, the quartz reaction vessel was heated by a 5.5 kilowatt electric resistance furnace. The open-end heating chamber of the cylindrical furnace measured 5 inches in diameter and 24 inches in length. Inside the 4-inch diameter tubular quartz shell, 35 inches long, was inserted a semicylindrical quartz boat, 24 inches long. The boat capacity was approximately 1000 grams of vanadium trioxide. Circular cut refractory bricks were then inserted to insulate from the heat the asbestos gasketed rubber stoppers used to seal the quartz shell. Pyrex tubes inserted through the one-holed number 15 stoppers allowed flow through the system. Rubber tubing connected the hydrogen sulfide cylinder, obtained from Matheson Chemical Company, with the apparatus. The bubbling of the exit reaction gases through a sodium carbonate solution absorbed any unreacted hydrogen sulfide.
Reductions of vanadium compounds to the metal were made almost entirely with a calcium reductant. Metallic calcium, prepared by aluminum reduction of calcium oxide and obtained from Dominion Magnesium Ltd., was redistilled at the Ames Laboratory. A typical analysis of high purity calcium is shown in Table III. Before use, the redistilled product was ground sufficiently to pass a 10 mesh screen and was stored under argon. A few experimental reductions were attempted with a magnesium reducing agent. This metal was procured from the New England Lime Company.

A booster reagent, the reaction of which with metallic reductant was highly exothermic, was generally a required addition to vanadium reduction charges in the obtaining of a massive product. The thermal boosters usually employed were sublimed sulfur or iodine. In addition to their heat

<table>
<thead>
<tr>
<th>Element</th>
<th>p.p.m.</th>
<th>Element</th>
<th>p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10</td>
<td>Mg</td>
<td>400</td>
</tr>
<tr>
<td>C</td>
<td>250</td>
<td>Mn</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Fe</td>
<td>17</td>
<td>N</td>
<td>11</td>
</tr>
<tr>
<td>K</td>
<td>&lt;50</td>
<td>Na</td>
<td>&lt;50</td>
</tr>
</tbody>
</table>
effects, the resulting iodide and sulfide were useful in lowering the melting point of the slag. Both were available in extremely pure form. Reagent grade of potassium chlorate was occasionally used mainly for auxiliary heat to obtain the products of the reaction in the liquid state and thus effect separation of the metal phase. In addition, the small amount of chloride from this booster contributed some to the fluxing action of the slag. Experimental reductions using potassium chlorate have to be made with caution because of the extreme heat of reaction of this compound with calcium metal.

Closed bombs of standard wrought iron pipe, with a 3/8 inch thick disk welded on the bottom and a malleable iron pipe cap threaded on the top, were used for carrying out the reduction process. The two and one-half inch bomb of 0.203 inches wall thickness and 12.5 inches high was rated at a pressure of 125 pounds per square inch. The bomb was lined with a refractory material to prevent too rapid loss of heat from the reaction mass, as well as to keep the bomb wall at a safe temperature below its softening point. The liner also served to prevent reaction of the reduced metal with the iron bomb. Either presintered or jolt packed liners of magnesium oxide, calcium oxide or electrically fused dolomitic oxide were employed. With the presintered liners, Magnorite grains were used to adjust the liner height and to fill the void between liner and bomb wall. The effective charge volume of a two and one-half inch bomb with liner was
Figure 4 - Charged Reduction Bomb.
approximately 600 cubic centimeters or 37 cubic inches. The bomb cap was also packed with the same refractory as the liner, and the threads were coated with a high temperature pipe seal. After the charge was loaded in the bomb, the cap was screwed in place. A charged reduction bomb is illustrated in Figure 4.

Firing of the charged bomb took place in the gas-fired furnace pictured in Figure 2. The drum walls were insulated from the 12-inch diameter steel liner with exploded granular mica. Heat was supplied by a ring burner fitted with a gas-jet air intake. An auxiliary air blower was required, however, for adequate combustion. Combustion gases were exhausted through the hood atop the furnace. The temperature of the furnace was regulated through a Wheeloo capacitrol, which operated the solenoid valve controlling the main gas supply. The charged bomb was suspended in the heated furnace from a metal loop on the bomb's cap. The temperature of the bomb wall was measured with a Wheeloo potentiometer connected to a thermocouple inserted in the well at the side of the bomb. At the time of firing of the reaction, a sudden and marked increase in the rate of temperature rise was noted.
V. METHOD OF PROCEDURE

With vanadium pentoxide available as a starting material, it is possible to examine various promising modifications of existing reduction methods for vanadium metal preparation. The use of certain technical grades of vanadium compounds may be permissible for the ultimate purpose intended. Although the purity of the vanadium compound to be reduced determines to a large extent the purity of the metal itself, there are nevertheless some of these impurities, like calcium, which are known to concentrate in the reduction slag and others, as zinc, which are capable of being distilled from the metal product. Some distribution between metal and slag can also be expected for the remaining contaminants. Since non-embrittling impurities of lower fission-neutron capture and thus of lower atomic weight may be permissible, the possibility of the utilization for nuclear purposes of metal produced from the lower grade starting material is worthy of inquiry.

As it was not known whether the quantity of sodium, present in technical grade vanadium oxide as an alkali vanadate, would even allow reduction to metal or whether, if reduction were possible, there would be a high contamination of sodium in the metal product, methods of purification were investigated which would greatly reduce the content of sodium and possibly
of other contaminants in the starting material. Certainly the price differential between technical and chemically-pure grades of oxide was sufficient to justify the investigation of a purification stage.

Of course, the corrosion characteristics of vanadium, in addition to its physical and nuclear properties, are largely influenced by the impurities incorporated with the metal. The effects of specific contaminants in this respect have not been evaluated. However, in the absence of accurate data on the maximum limits of individual contaminants for a high purity ductile vanadium, it appeared advisable to proceed in the development of the reduction process using the most economical materials available and to resort to higher grades of starting material or further purification methods if later demanded.

Reduction to metal from vanadium compounds other than the pentoxide offers good potentialities for the development of a suitable process. Possible increased metal yields together with savings in reductant or booster reagent are items which have already been mentioned. Furthermore, with oxygen a prime embrittling agent in metallic vanadium (39), a reduction in the ratio of oxygen to vanadium in the compound to be reduced or the elimination of oxygen altogether from the starting material might contribute to a more ductile product.

The compounds which generally lend themselves to bomb reduction methods are the halides, oxides and sulfides; these
compounds must be in the solid and anhydrous state at ordinary temperatures and their reaction product with reducing agent reasonably stable at elevated temperatures. Their use must also justify their cost of preparation. The chlorides, bromides and iodides of vanadium are extremely hygroscopic, deliquescing in air to liquid pools in a short time. Because it is difficult to be assured of their being completely dry before use, they are not as desirable to employ in a closed vessel as non-hygroscopic compounds. Of the remaining vanadium compounds, the trivalent form appears to offer the most promise for application in reduction charges. In this oxidation state, these compounds are solid to reasonable temperatures and can be prepared in apparatus at hand. Tetra- and pentavalent compounds, other than the oxides, are either liquid at ordinary temperatures or readily volatilized at slightly elevated temperatures. Except for the oxides, these compounds generally are prepared from the trivalent state. Divalent compounds, while solid to a high temperature, usually require preparation temperatures in excess of $1200^\circ$C., thus necessitating special equipment. They too are generally prepared from the trivalent state. However, for trial in experimental reductions of these suitable intermediates from various grades of purity, their preparation is first required.
A. Preparation of Vanadium Intermediates

Commercially available, chemically-pure vanadium pentoxide may be obtained in suitable form for immediate metal reduction or for preparation of other intermediates. The appreciable content of volatile matter in air-dried, technical grade vanadium pentoxide made this form of the compound unsuitable for direct reduction to metal without prior ignition. Technical grade vanadium pentoxide in the fused form was furnished in a partially crushed condition, rendering additional size reduction necessary for further operation. On moist days, however, moisture pick-up by this oxide in the grinding operation was sometimes sufficient to require a further drying step before use in bomb reduction charges. Therefore, where vanadium compounds of a technical grade of purity could be employed, the air-dried form was utilized for intermediate preparations and the fused form, after grinding and drying, for direct reduction to the metal.

Purification of technical grade material was attempted by dissolution of the impurities in an ammonium chloride bath in a manner similar to that employed by Frick (14). Five-hundred gram batches of the insoluble vanadium oxide were suspended in 5 liters of a 10 per cent aqueous solution of ammonium chloride. The reaction between chloride and oxide required about 15 minutes at 70°C. under constant stirring. The solid reaction product, containing a
substantial proportion of ammonium vanadate was filtered from
the solution and washed several times with distilled water.
The separated product was then resubjected to a fresh ammonium
chloride bath for further production of the vanadate. After
again filtering and washing, the ammonium vanadate was roasted
at 400°C. to a purified yellow pentoxide. Satisfactory
elimination of ammonia was accomplished with 17 hours heating.

The simplest method of preparing vanadium in the tri-
valent state was by hydrogen reduction of the pentoxide at
an elevated temperature. The reaction is represented by the
equation

\[ \text{V}_2\text{O}_5 + 2\text{H}_2 = \text{V}_2\text{O}_3 + 2\text{H}_2\text{O}. \]

Preliminary trials with various temperature and time com-
binations indicated that at least a temperature of 400°C. was
required for the reaction to start. Reaction at 500°C. for
eight hours yielded a product containing appreciable quanti-
ties of the tetraoxide, while at 600°C. for the same period
of time, conversion to the trioxide was essentially complete.
Reaction time at 700°C. was reduced to approximately four
hours. Trials above this temperature were not made, since
the upper temperature limit of the furnace employed was
about 725°C. The progress of the reaction was followed by
collecting the condensed steam of the exit gases. The loss
in weight by solid reaction material was also a good indication of the completeness of conversion.

For larger scale runs, the trays were filled with the pentoxide to a depth of one and one-half inches and the increase in tray weight recorded. The four tray monel reaction chamber, illustrated in Figure 3, had a total capacity of 6 kilograms of vanadium pentoxide. Upon loading and closing of the chamber, the gas burners were ignited. At a temperature of 400°C, the flow of hydrogen was started, and a flow rate averaging 12 cubic feet per hour maintained throughout the run. The reactor was held at a temperature of 700°C, for a period of 10 hours to insure complete reaction and loss in any volatile matter. This allowed at optimum temperature a flow of hydrogen 100 per cent in excess of that theoretically required. Since the auto-ignition temperature of hydrogen is around 575°C., all connections to the monel unit inside the brickwork had been welded to decrease the possibility of any gas leakage. After cooling, the product was again weighed, transferred to polyethylene bags, and stored under an argon atmosphere. The resulting trioxide was thus used in direct reductions to the metal or in further preparation of the other intermediates.

Vanadium trifluoride had been prepared by Petersen (49) by dissolving vanadium trioxide in an aqueous solution of hydrofluoric acid and evaporating to dryness. Initial attempts
at trifluoride preparation were made following this procedure. Fifty grams of the trioxide were dissolved in 150 milliliters of 48 per cent hydrofluoric acid and 150 milliliters of distilled water added. This proportion of acid to oxide was approximately 100 per cent in excess of that theoretically required. Solution was completed by heating at 100°C. on a hot plate. After filtering of the solution, the green filtrate was evaporated to dryness at 150°C. in about 6 hours. The trihydrated trifluoride was ground with mortar and pestle and then dried to the anhydrous state under hydrogen fluoride. This was accomplished in four hours at 300°C.

The anhydrous preparation of vanadium trifluoride from vanadium trioxide and ammonium bifluoride was unsatisfactory. Reaction to ammonium fluovanadate required a temperature of several hundred degrees, at which point a good portion of the vanadium was volatilized as yellow vanadyl trifluoride. Unless protected from the air while the ammonium fluoride was driven off, the ammonium fluovanadate reverted to the oxide instead of the trifluoride; if driven off under vacuum, the ammonium fluoride both corroded and plugged the evacuating equipment.

Reasonably successful was the preparation of vanadium trifluoride by the anhydrous hydrofluorination of vanadium trioxide. Since the reaction would form a hydrated trifluoride at temperatures below 130°C., first trial runs were made at varying temperatures from 150°C. to 600°C. In all
of these cases very little fluoride was formed. After one such run, however, the charge which was left in the cooled furnace overnight without flushing out the residual hydrogen fluoride gave a product that had the bright green color of the hydrated trifluoride. Further trials produced a satisfactory trifluoride by reaction under hydrogen fluoride at room temperature for 8 hours, followed by dehydration under hydrogen fluoride at 300°C. for 8 hours. The assumed equation for the reaction was

\[ V_2O_3 + 6HF \rightarrow 2VF_3 \cdot 3H_2O \rightarrow 2VF_3 + 3H_2O \]

Drying under nitrogen was unsatisfactory, as the trioxide had a tendency to hydrolyze to the oxide.

In larger scale runs the monel unit (Figure 3) was charged with 4 kilograms of vanadium trioxide previously prepared from either chemically-pure or air-dried technical grade pentoxide. A hydrogen fluoride flow rate of roughly one pound per hour was maintained for eight hours. Over 100 per cent excess hydrogen fluoride was thus passed over the trioxide while at room temperature. The furnace was not opened prior to drying since a nitrogen purge was insufficient to remove condensed hydrogen fluoride, and the escaping gas was corrosive on the furnace door bolts and the hood. The partially hydrated vanadium trifluoride was then dried at 300°C. for eight hours under hydrogen fluoride.
maintained at the previous flow rate. Upon cooling to 100°C., the furnace was flushed out with dry nitrogen. The caked trifluoride necessitated a grinding operation and if done in a moist atmosphere, redrying of the hygroscopic trifluoride under hydrogen fluoride for several hours was required. Caking of the once-dried trifluoride did not reoccur. Dry and powdered vanadium trifluoride was kept in polyethylene bags under argon.

Subsequent to this work, Mackey and Johnson (36) reported the preparation of vanadium trifluoride by a similar method. Anhydrous hydrogen fluoride was passed over vanadium tri-oxide in a rotary tube furnace cooled to 10°C. by a dry ice bath, and the hydrated trifluoride was dried at 500°C. under a flow of hydrogen fluoride. Good results with 5 pound batches were indicated.

Potassium fluovanadate, \( \text{K}_2\text{VF}_5 \), was prepared following the method employed by Powers (50). An aqueous solution of vanadium trifluoride was made by dissolving 500 grams of technical vanadium trioxide in 1.5 liters of 48 per cent hydrofluoric acid. After standing, the solution was filtered or decanted from any undissolved matter, and to the clear solution was slowly added a concentrated solution of potassium fluoride. When the precipitate of potassium fluovanadate monohydrate ceased to form, the equivalent of 1500 grams of dihydrated potassium fluoride had been added.
Upon settling, the supernatant liquid was decanted off, and
the precipitate was further separated from solution by filtra-
tion and washing. The green, pasty mass was then dried at
300°C. for 24 hours in the hydrofluorination unit under a
slow stream of hydrogen fluoride. Two kilograms thus pre-
pared were ground with mortar and pestle in a dry box before
being used in the reduction process.

Among the methods described for the preparation of
vanadium sulfide in either the di- or trivalent state, the
most convenient appeared to be the action at elevated tem-
peratures of hydrogen sulfide on vanadium trioxide to form
the trisulfide (26) and of sulfur on vanadium pentoxide to
form the disulfide (15). Only the former was successful.
Faithful repetition of the Gerasimov and Tschunikhina pro-
cedure for the latter, whereby three portions of vanadium
pentoxide and one portion of sulfur were heated three hours
at 400°C. in a closed quartz vessel under a stream of carbon
dioxide, gave only a mixture of lower vanadium oxides. To
remove any unreacted sulfur, the temperature was raised to
500°C. after suitable reaction time. Larger sulfur ratios
and longer reaction periods gave no better results.

Vanadium trisulfide preparation by reaction of hydrogen
sulfide on vanadium trioxide presented little difficulty.
The reaction is represented as follows:

\[ V_2O_3 + 3H_2S = V_2S_3 + 3H_2O \]
The quartz boat, filled to a depth of two inches, held about one kilogram of technical vanadium trioxide. After the reaction vessel was loaded and sealed, the flow of hydrogen sulfide was started at about the rate of 10 liters per hour and the apparatus brought up to 850°C. Reaction at this temperature under a hood was carried on for 24 hours, allowing a gas flow 65 per cent in excess of theoretical. Trouble with plugging of the outlet tube with small amounts of sulfur was averted by using a one-half inch diameter tube. Upon cooling to 100°C, the reaction chamber was flushed with argon. The black product was slightly caked but could be broken up easily.

B. Reduction of Vanadium Compounds

Reduction of vanadium compounds to massive metal was deemed possible, provided that free energy considerations were satisfactory for reaction to occur and that sufficient heat was liberated for fusion to take place. The more promising vanadium intermediates having been prepared, attention was directed to their reduction by the bomb reduction process.

The reaction charge consisted of a mixture of the vanadium compound, the reductant and, when required, a booster reagent. Usually, equal amounts of contained vanadium were employed in the reduction mixtures to allow easy
comparison among intermediates of charges and yields. The weighings were done in air, and the components transferred to a mixing bottle previously flushed with argon, for thorough tumbling of the reaction mixture.

The iron bombs were prepared for receiving the reduction charge by lining with a refractory material. These liners were either of the presintered or the jolt packed type. The presintered liners were slipped into the bomb to rest on a layer of magnorite, and any space between the liner and walls of the bomb were filled with Magnorite grains. The jolt-packed liners were formed by first packing a half-inch layer of powdered refractory in the bottom of the bomb by means of a hydraulic jolter. The liner walls were then formed by jolting more refractory around a carbon mandrel. To reduce the possibility of contamination of the reaction products with air entrapped in the bomb, the bomb assembly was flushed with argon several minutes before loading. The charge was added in several small stages and compressed with an iron mandrel between stages. Powdered refractory was packed above the charge to a level even with the top of the liner, and the same material was used to fill the bomb cap. After the threads of the bomb were coated with pipe cement, the cap was screwed tightly on the bomb.

To set off the reduction charge, the assembled bomb (Figure 4) was placed in a gas-fired furnace heated to
700-800°C. The unit is pictured in Figure 2. A thermocouple was inserted in the well at the side of the bomb, and the bomb was suspended in the furnace by a hooked metal rod. The course of the reaction was followed by measuring the temperature of the outside of the bomb. The reaction generally fired five minutes after the bomb was placed in the furnace, as indicated by a marked increase in temperature resulting from the exothermic reaction. The outside temperature of the bomb wall usually registered near 600°C. when the reaction was initiated and reached a peak of 900°C. and occasionally 1000°C. several minutes later. After the maximum temperature was reached, the bomb was removed from the furnace and allowed to cool in air to room temperature.

When cool, the cap was unscrewed from the bomb, and the liner and reaction products were knocked out with a hammer and cold chisel. The metal regulus was separated from the slag and washed, first in distilled water and then in dilute hydrochloric acid. For total metal recovery, the slag was dissolved in dilute hydrochloric acid and the clear liquid decanted from any metal powder. The bomb and cap were cleaned by filling with water to loosen any adhering slag or liner material and allowed to dry in air.

The reduction of CP. vanadium pentoxide with calcium metal, using an iodine booster, was known to yield massive vanadium (39). The equation representing the reaction is:
\[ V_2O_5 + 5Ca = 2V + 5CaO. \]

From published data (21,27,34), the free energy change, \( \Delta G \), and the enthalpy change, \( \Delta H \), for this reaction at 1000\(^\circ\)K. was calculated to be -300 kcal. and -340 kcal., respectively, per gram mole of \( V_2O_5 \). Reproductions of the McKechnie and Seybolt charge, wherein iodine was employed to furnish additional heat, were made, using chemically-pure vanadium pentoxide from Vancoram and Electromet. On the scale of a two and one-half inch bomb, the charge consisted of 160 grams vanadium pentoxide, 300 grams calcium and 80 grams iodine. With the molar heat of reaction of iodine with calcium at 1000\(^\circ\)K. about -141 kcal. (27,34), the reaction of this proportion of thermal booster with excess reductant furnished an additional -50 kcal., for a total heat of reaction at furnace temperature of -390 kcal. per gram mole of vanadium pentoxide. From this computed thermodynamic data in combination with the time of firing, temperatures of the bomb wall, metal yields and hardness values from the experimental runs, various modifications in the reduction procedure were attempted.

Substitution of sulfur for iodine as a booster material was very successful. At 1000\(^\circ\)K., the computed molar heat of reaction between sulfur and calcium was -114 kcal. (27,34), thus requiring an additional 25 mole per cent sulfur to furnish the theoretical heat equivalent of iodine. The initial reduction with a sulfur booster was made, supplying the calculated amount of heat equal to that with an iodine booster,
but the presence of scattered beads of metal in the slag indicated more heat was necessary for aggregation into a solid regulus. However, yields comparable to those from iodine-booster reductions were secured with a charge of 160 grams vanadium pentoxide, 300 grams calcium and 20 grams sulfur. The molar ratio of booster to contained vanadium was therefore 0.35 for sulfur reductions and 0.18 for iodine reductions, both types of charge employing 50-60 per cent excess reductant.

The use of fused technical grade vanadium pentoxide in the reduction charge was subsequently investigated. Reductions with an iodine booster, although giving evidence of having properly fired, yielded no appreciable quantity of massive metal. The use of iodine to pentoxide molar ratios up to 1.25 were equally unsuccessful. Reductions with a sulfur booster, however, produced good yields of massive metal. A charge containing 180 grams technical vanadium pentoxide, 312 grams calcium and 20 grams sulfur proved to be the most satisfactory. Since the \( \text{V}_2\text{O}_5 \) content of the technical grade oxide was roughly 89 per cent, or 160 grams, the product yield could be directly compared with those from chemically-pure oxide. Combinations of sulfur and iodine boosters were also tried in the reduction of technical grade pentoxide, and although an improvement over reductions with an iodine booster, the results were
never as promising as with sulfur alone. The use of potassium chlorate as a thermal booster, furnishing about -468 kcal per mole with calcium at 298°C. (34), gave acceptable metal yields, but the reguli were always extremely hard. A ratio of 0.09 moles potassium chlorate per mole of contained vanadium was employed.

On preliminary reductions of the technical grade pentoxide a few of the metal biscuits were undercoated with a fused black crust. This material was not dissolved from the regulus when washed in hydrochloric acid and increased considerably the hardness of the metal. Since this occurrence was not consistent, it was not thought to be caused by impurities in the oxide. With the possibility of the black coating being unreduced vanadium oxide, a layer of 5 grams of calcium reductant was first placed in the bottom of the bomb before the charge was loaded. Further difficulty was not encountered.

Further modifications in the reduction of technical grade pentoxide besides the substitution of a variety of boosters in varying proportions were investigated. The effect on hardness of the variation in excess calcium was studied. A magnesium reducing agent was not considered when using a sulfur booster because of the dissociation of magnesium sulfide at elevated temperatures. A number of refractory liner materials—dolomitic oxide, magnesium oxide
and calcium oxide—were tested with a constant reduction mixture. The amount of oxygen picked up by the regulus from the liners was roughly indicated by the hardness values of the as-reduced metal.

With the replacement of vanadium trioxide for vanadium pentoxide, the use of less calcium as reductant was expected. For the reaction,

\[ V_2O_3 + 3Ca = 2V + 3CaO, \]

the calculated free energy change at 1000°C, -113 kcal. per mole of trioxide (21, 27, 34) indicated that reduction was plausible. However, with a molar heat of reaction at this temperature of only -128 kcal., the larger amount of thermal booster required for the formation of massive metal made necessary an increased quantity of calcium for the booster reaction. The theoretical molar enthalpy difference of 212 kcal. between the two oxide reactions indicated that a ratio of 1.3 moles sulfur for each mole of contained vanadium would probably be required. However, this charge ratio was able to be lowered to 0.90 without materially reducing the yield of the biscuit metal. By the use of technical grade vanadium trioxide containing 87 per cent \( V_2O_3 \), a typical charge consisted of 150 grams technical trioxide, 256 grams calcium and 50 grams sulfur.
Because of the highly exothermic heat of reaction of vanadium trifluoride with calcium, a secondary reaction supplying auxiliary heat was not required with the higher purity material. At $1000^\circ$K., the enthalpy change for the reaction

$$2\text{VF}_3 + 3\text{Ca} \rightarrow 2\text{V} + 3\text{CaF}_2$$

was calculated to be $-371$ kcal. and the free energy change $-371$ kcal. (5,21,27). The optimum charge, using trifluoride from either purified or chemically-pure pentoxide, was 216 grams vanadium trifluoride and 192 grams calcium. With trifluoride from technical grade pentoxide, a 5 gram addition of sulfur on the above scale was needed to fuse the reduced product.

The increased yield and large evolution of heat accompanying the formation of a fluoride slag suggested the possibility of obtaining a massive product with a magnesium reductant. From published data (5,27,34), the free energy change for the reaction

$$2\text{VF}_3 + 3\text{Mg} \rightarrow 2\text{V} + 3\text{MgF}_2$$

was computed to be $-279$ kcal. at $1000^\circ$K., and the enthalpy change at $1000^\circ$K., $-298$ kcal. In attempts to form massive metal by this reaction, varying amounts of potassium chlorate as thermal booster were added to the reduction charge. Because the results on preliminary reductions of trifluoride
from CP. pentoxide were not promising, use of a magnesium reducing agent was suspended.

The reduction of potassium fluovanadate was tested by using 60 per cent excess calcium without a booster reaction. Although the time-temperature measurements upon heating of the bomb gave evidence of the charge having fired, no massive metal was produced. Upon washing of the reaction products with water, it became evident that a good portion of the reducing power of the calcium had been spent in obtaining elemental potassium. Because of the increased requirement of calcium and the explosive nature of the slag, further plans for reduction of potassium fluovanadate were abandoned.

Since sulfur had been used successfully as a booster reagent in calcium reductions of the oxides and fluoride of vanadium, the reduction of vanadium sulfide was attempted. The trisulfide had been prepared from technical grade starting materials. Its reduction with calcium is represented by the following equation:

\[ V_2S_3 + 3Ca \rightarrow 2V + 3CaS. \]

The heat of formation of vanadium sulfide was not known, but by comparison with elements in the same group as vanadium, it was approximated. The heat of reaction of the trisulfide with calcium was then calculated and found to approach that
of the trifluoride with calcium. Preliminary reductions were therefore made without a booster charge. Although it was possible to obtain massive metal without a booster reaction, the yield was increased considerably by the addition of small amounts of sulfur. A charge containing 198 grams technical vanadium trisulfide, 323 grams calcium and 20 grams sulfur gave the best yield of metal on this scale of operation.

Reduction of the trioxide and pentoxide on a larger scale was investigated. The bombs employed were 4 inches in diameter and 14 inches long and were similar in construction to the two and one-half inch diameter bomb. The jolt-packed liners were made from dolomitic oxide. The same relative proportions of reactants were retained in the charge as had been used with the smaller bombs. The larger bomb permitted a 3.5-fold increase in the size of charge employed.

C. Methods of Analyses

Compounds of vanadium were analyzed for their major constituents to determine the amount of contained vanadium and the degree of conversion to the compound to be reduced. Analyses of the reduced metal were performed to ascertain the vanadium content and the extent of impurity contamination. Chemical methods alone were employed, since standards for
the quantitative spectrographic analyses were not set up and the facilities for vacuum fusion analyses were only in the process of construction.

Analysis for vanadium in vanadium compounds, such as the fluoride, sulfide and oxide, were made by the ferrous sulfate titration method. A 0.5-1 gram sample was dissolved in a mixture of concentrated nitric and 48 per cent hydrofluoric acids. Ten milliliters of concentrated sulfuric acid were added, and the solution was fumed on a hot plate for 20 minutes in order to remove the fluoride ions. After this solution had been transferred to a volumetric flask and diluted to volume with redistilled water, aliquots were removed, brought to a 5 molar solution with 10 molar sulfuric acid, and diluted to a 100 milliliter volume. After cooling, the aliquots were titrated with ferrous sulfate in 5 molar sulfuric acid from a blue to an olive green color by use of a ferroin indicator.

Determinations of fluorine in vanadium trifluoride were made using the method of Warf and Cline (69), wherein the fluoride was pyrohydrolyzed to vanadium oxide and hydrogen fluoride, and the condensed acid titrated as in regular acid-base determinations. A sample of 0.5-1 grams weighed in a platinum boat was placed into the furnace, heated to 1000°C. Steam generated from distilled water was passed through the enclosed apparatus and over the boat for a period of three minutes. Hydrogen fluoride and excess steam were condensed
in a platinum condenser and collected in a silver dish containing 5 milliliters of distilled water. The distillate was titrated with standard sodium hydroxide, using phenolphthalein as an indicator.

The sulfur content of vanadium trisulfide was determined by the micropearl tube method (24), whereby the sulfur dioxide produced upon roasting of the sulfide was converted to sulfuric acid by the contact process and the resulting acid titrated with standard base. Beyond the combustion chamber of the quartz tube apparatus were placed two platinum catalyst stars, and to the catalyst section was attached a receiving finger with a quartz spiral, which had been covered with a 5 per cent hydrogen peroxide solution. A micro torsion balance was used to weigh out a 5-8 milligram sample, which was then transferred to a porcelain micro combustion boat. After the boat had been placed in the combustion chamber and the apparatus connected to an oxygen supply, oxygen was allowed to pass over the sample at the rate of 5 cc. per minute. The combustion boat was gradually heated to 850°C. with a long burner, while the contact stars were separately heated to 500°C. The sample was oxidized to vanadium pentoxide, and sulfur was driven off as sulfur dioxide and some sulfur trioxide. After passing the platinum stars, some 95 per cent of the sulfur dioxide had been converted to the trioxide. Absorption of the oxides of sulfur
and complete conversion to sulfuric acid was accomplished by the hydrogen peroxide solution. Upon completion of the reaction, the receiving finger was removed and rinsed five times with 3 milliliter portions of boiled, distilled water. The acid was titrated with 0.01 N sodium hydroxide to a pH of 4.5, with a methyl purple indicator being used for the neutral gray end point.

Analysis for vanadium in the reduced metal was made by the oxidation method employed by Marden and Rich (38). A 0.5-1 gram sample was dissolved slowly in concentrated nitric acid in a weighed porcelain crucible. The sample was evaporated to dryness at about 90°C. and then ignited at 800°C. for several hours. From the increase in sample weight, the content of vanadium was calculated.

The Kjeldahl method was used to analyze for nitrogen in vanadium metal. The metal was put into solution by dissolving a 0.2 gram sample in 48 per cent hydrofluoric acid. After adding 10 milliliters of concentrated sulfuric acid, the sample was fumed on a hot plate to a volume of about 10 milliliters. With redistilled water, the solution was first diluted to about 50 milliliters, and then following transference to a 100 milliliter volumetric flask, diluted to volume. An aliquot was pipetted into the distillation flask, to which 15 milliliters of 50 per cent sodium hydroxide were introduced; to the receiving flask and vapor trap were
added 10 milliliters of boric acid and methyl purple indicator. Steam was passed through the vanadium solution until 50 milliliters of the distillate had been collected. After the trap and condenser had been rinsed with redistilled water, the distillate was titrated with 0.01 N hydrochloric acid to a neutral gray end point. Calculations of the nitrogen content were made after corrections for the indicator and reagent blank were made. For the determination of nitrogen in vanadium pentoxide, a 1-2 gram oxide sample was dissolved in 30 milliliters of 50 per cent sodium hydroxide, and, after the solution was transferred to the distillation flask, the normal procedure was followed.

Silicon in metallic vanadium was determined colorimetrically following a procedure modified from those of Case (8) and Bunting (6). A 0.5-1 gram sample of the metal was dissolved in a fluorathene beaker by concentrated nitric acid. Added to this were one-half milliliter of 24 per cent hydrofluoric acid and 40 milliliters of a saturated solution of boric acid. The resulting solution was diluted with redistilled water, heated for one-half hour at low heat and cooled. More redistilled water was added to an appropriate volume, from which three aliquot portions were removed with plastic pipettes to plastic beakers. To the second and third aliquots were added 4 milliliters of 10 per cent molybdic acid reagent, and the pH was adjusted to 1.2-1.3 with a special ammonia solution. After standing, all three aliquots
were treated with 4 milliliters of 20 per cent tartaric acid plus one milliliter of a reducing agent of sodium bisulfite and 1-amino-2-naphthol-4-sulfonic acid. Fifty micrograms of silicon as sodium silicate were also added to the second aliquot. Upon standing for 20 minutes, the blue solutions were transferred to cuvettes, and the absorbancies were determined at 815 m\(\mu\) in a Beckman spectrophotometer. The first aliquot served as a blank, with the second acting as a check on silicon recovery. Comparison of the absorbancy of the third aliquot with a previously prepared standard curve gave the silicon content.

The determination of carbon in vanadium metal was made with a carbon combustion furnace and absorption train. Ignition of a one-gram sample of vanadium turnings or foil in an alundum boat was accomplished in 45 minutes at 1900°F. under an oxygen flow of 0.5 cubic feet per minute. From the increase in weight of the sodium hydroxide and magnesium perchlorate absorption tubes, the carbon content of the sample was computed.

Calcium in vanadium was determined as the oxalate after extraction of the vanadium from the dissolved metal (57). A one-gram sample was dissolved in concentrated nitric acid and evaporated to dryness several times with hydrochloric acid. The vanadium chloride was again dissolved in 10 per cent hydrochloric acid and transferred to
a separatory funnel, and 15 milliliters of 5 per cent cupferron solution were added to precipitate the vanadium as the cupferride. After shaking, the cupferride was extracted with 50 milliliters of chloroform. The precipitation and extraction were repeated until the vanadium was completely removed. The aqueous phase was withdrawn and repeatedly evaporated to dryness, with nitric and hydrochloric acid being used to destroy any residual organic matter. The residue was dissolved in 20 milliliters of distilled water plus a few drops of hydrochloric acid. The solution was made acid to methyl red with acetic acid and heated to boiling. One to three milliliters of 0.5 N ammonium oxalate were added, and the precipitated calcium oxalate was allowed to settle. After filtering and washing, the precipitate was dissolved with 10% sulfuric acid. Upon heating to 65°C., this solution was titrated with 0.01 N potassium permanganate.

Oxygen and hydrogen in metals are normally determined by vacuum fusion techniques, but since the facilities required were only in the process of construction, analyses for these gases were not made. The hardness of a metal can sometimes be used as an indication of its oxygen content. A correlation of Vickers hardness numbers and weight per cent oxygen in vanadium has been made by the Knolls Laboratory (29). This relationship is reproduced in Figure 5, to which a conversion scale of Rockwell B hardness numbers has been added.
Figure 5 - Correlation of the Oxygen Content of Vanadium Metal with its Hardness Number (29).
by the writer from hardness measurements made on vanadium with both types of hardness testers. A rough measure of the amount of oxygen in vanadium was therefore ascertained from the metal's hardness value and the accompanying graph.
VI. EXPERIMENTAL RESULTS

A. Preparation of Vanadium Compounds

It was possible to obtain some purification of technical grade, air-dried vanadium pentoxide by suspension of this material in an ammonium chloride bath, followed by heating the solid reaction product to eliminate ammonia and re-form the pentoxide. The vanadium content was thus increased from 47.2 per cent to 56.4 per cent, corresponding to an increase in $V_2O_5$ content from 84.1 per cent to 98.8 per cent. However, the nitrogen content was also increased—from 0.001 per cent in the lower purity red pentoxide to 0.005 per cent in the purified yellow pentoxide. The approximate concentration of other impurities was obtained from general qualitative spectrographic analyses of the oxides. A comparison of these results indicated that, while the amount of sodium present in the oxide had been greatly decreased, there was no noticeable removal of other contaminants. A slight increase in the copper and nickel content was noted, which apparently had been introduced from the monel reactor; but this contamination could be avoided by the use of a glass-lined vessel.

This low-cost purification step, using the lower purity oxide, was initially attempted before it was known whether reduction to metal was possible from technical grade vanadium.
materials. As purification of the technical grade oxide was later found to be unnecessary for the preparation of ductile metal, material purified in this manner was tested in only a few reductions. However, since calcium was found to reduce the sodium compound contained in the technical grade material to elemental sodium, the saving in reductant might justify the purification step on an expanded scale.

Vanadium trioxide was prepared by high temperature reduction of vanadium pentoxide with hydrogen. Both the decreased weight and the color of the oxide after reaction served as a measure of the degree of conversion. Vanadium pentoxide completely reduced to the trivalent state was black in color, while the appearance of a bluish hue on the reaction product indicated the presence of the tetraoxide. The loss in weight expected with high purity pentoxide was the theoretical difference in weight between the trivalent and pentavalent states; an additional loss in weight resulted in reduction of technical grade pentoxide in the air-dried form because of the accompanying ignition loss. At the elevated temperature required for the reaction, some scaling of the monel unit occurred. While most of the scale could be removed manually, more complete removal was accomplished by repeated passes of the trioxide over a magnetic separator. Some reduced iron was also removed in this manner.
No analyses for vanadium were made on the trioxide from either purified or chemically-pure pentoxide because weight losses indicated satisfactory conversion. Also, most of this material was utilized for the preparation of other intermediates which were to be analyzed for vanadium. Analysis for vanadium was made on the trioxide from technical grade pentoxide, since the weight loss or prolonged reduction of this material did not approach the calculated, theoretical weight loss plus ignition loss. The vanadium content of the technical vanadium trioxide averaged by analyses about 57.9 per cent, while the calculated value was 61 per cent. It is possible that the sodium present in the pentoxide is associated with vanadium as a sodium vanadate, which is not reduced by hydrogen under the conditions employed.

A small amount of vanadium trifluoride was prepared from solution by dissolving vanadium trioxide in hydrofluoric acid and evaporating the solution to dryness. This method of preparation was not too satisfactory, since the hydrated trifluoride had a tendency to hydrolyze during the final drying, even in an atmosphere of hydrogen fluoride. Moreover, even on a small scale, the process necessitated the evaporation of a considerable quantity of acid. The highest fluorine to vanadium molar ratio obtained for the dried
product was only 2.67. Chemically-pure oxide has been used in the preparation of the trifluoride by this process.

The fluorine to vanadium molar ratios averaged slightly higher for the trifluoride prepared by the reaction of anhydrous hydrogen fluoride on vanadium trioxide. For dried vanadium trifluoride made from the higher purity oxides, this ratio averaged about 2.88, while for the product obtained from technical grade oxide, the ratio was 2.96. Possible reaction of the sodium contaminant with hydrogen fluoride might account for the higher fluorine to vanadium ratio for the trifluoride prepared from technical grade oxide. The total vanadium plus fluorine content for the former material was 94.5 per cent and for the latter product, 88.7 per cent. No satisfactory method for the analyses for water was found. Heating of a sample, previously dried at 300°C. for 24 hours under hydrogen fluoride, for an additional 24 hours at 200°C. in a stream of nitrogen showed a weight loss of 3 to 5 per cent. However, the formation of a yellow condensate in the outlet tube and the decrease in the fluorine to vanadium ratio of the original sample indicated that volatilization of an oxyfluoride was probably taking place. However, no difficulty in the bomb reduction process was encountered with vanadium trifluoride dried at 300°C. for 24 hours under a flow of hydrogen fluoride.
Potassium fluovanadate was analyzed only for vanadium. The vanadium content found was 20.5 per cent; the calculated vanadium content of $K_2VF_5$ is 22.7 per cent.

Vanadium trisulfide had been prepared only from technical grade starting material. The product, obtained by the solid-gas reaction between technical vanadium trioxide and hydrogen sulfide, analyzed 45.6 per cent vanadium and 35.9 per cent sulfur. This analysis corresponds to the sulfur to vanadium molar ratio of 1.25. The remaining impurities, of which a good portion is sodium, are possibly associated with vanadium as vanadates or vanadyl compounds. Any vanadium oxide not in the trivalent state at the start of the reaction was reduced to this valency state by the hydrogen sulfide, with an accompanying deposition of sulfur in the outlet tube. Although the black, lustrous trisulfide did not exhibit the hygroscopic tendencies of the trifluoride, it too was stored under an argon atmosphere.

B. Reduction of Vanadium Compounds

Reproductions on a smaller scale of the McKechnie and Seybolt reductions (39), wherein chemically-pure vanadium pentoxide was employed with a calcium reducing agent and an iodine booster, gave percentage yields of vanadium metal comparable with their results. Reproducible yields of 80-85 per cent, or about 75 grams of metal, were obtained from
vanadium pentoxide from either Vancoram or Electromet. The hardness values for the as-reduced metal produced from pentoxide furnished by the former supplier averaged about 130 Vickers. Metal produced from the oxide supplied by the latter gave slightly higher hardness values, averaging 140 Vickers. Rockwell B hardness numbers corresponding to these Vickers values are about 66 and 71, respectively. Metal prepared by this procedure was malleable when hammered.

The substitution of a sulfur booster for iodine in the above reduction charge gave approximately the same yields of metal as previously. The regulus also could be hammered without fracture. Average Rockwell B hardness values on the metal biscuits ranged from 65 to 75. Charges using both types of boosters included a 50-60 per cent excess of calcium. Thus, metal produced with a 20 gram sulfur booster compared favorably in yield and ductility with that obtained with 80 grams of iodine. On an expanded scale, with the utilization of chemically-pure vanadium pentoxide, the replacement of sulfur for iodine would represent an appreciable saving in cost of the booster material, considering the price differential between the two.

Reductions of fused technical grade vanadium pentoxide were most successful when a sulfur booster was employed. Metal yields of 70-75 per cent were lower than obtained with CP oxide, and the Rockwell B hardness values of 75-85 were
slightly higher. The metal biscuits had the same shiny appearance and shape as before. After a satisfactory booster ratio had been established, the effect of excess calcium on the hardness and yield of biscuit metal was investigated. The results of these reductions, using a constant booster charge and sintered dolomitic oxide liners, are shown in Table IV. Excess calcium is calculated as the amount in excess of that required for the booster reaction and for the reduction of the contained vanadium oxide. The data obtained indicates that higher yields and softer metal are more likely to be obtained when at least 50 per cent excess calcium is employed in the reduction charge with the pentoxide.

Replacement of dolomitic oxide liners with magnesium oxide liners, using a constant reaction mixture, increased the hardness of the as-reduced metal about 5 numbers on the Rockwell B scale. The use of calcium oxide liners gave metal with hardness values comparable with those obtained using dolomitic oxide liners. As the previously sintered liners were preferable to the jolt packed type, because of the ease of handling, and as dolomitic oxide liners did not have the tendency to warp when sintered as did the calcium oxide liners, almost all subsequent reductions were made employing the presintered type with a dolomitic oxide refractory.

The use of an iodine booster in varying proportions with technical grade vanadium pentoxide never afforded yields of
Table IV
Yield and Hardness of Vanadium Reguli Reduced with a Constant Booster Ratio from Technical Grade Vanadium Pentoxide and Trioxide Using Sintered Dolomitic Oxide Liners.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Compound Reduced</th>
<th>Molar Ratio S</th>
<th>Per Cent to Contained V</th>
<th>Excess Ca</th>
<th>Per Cent</th>
<th>Rockwell B Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-130</td>
<td>tech. $V_2O_5$</td>
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<td>51</td>
<td>95</td>
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<td>2-129</td>
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<td>35</td>
<td>60</td>
<td>92</td>
<td></td>
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<tr>
<td>2-128</td>
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<tr>
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<tr>
<td>2-134</td>
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<td>55</td>
<td>73</td>
<td>75</td>
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<tr>
<td>2-136</td>
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<td>65</td>
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<td>85</td>
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<tr>
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<td>70</td>
<td>82</td>
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<tr>
<td>2-224</td>
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<td>77</td>
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<td>2-221</td>
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<td>70</td>
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<tr>
<td>2-220</td>
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<td>65</td>
<td>77</td>
<td>75</td>
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<tr>
<td>2-155</td>
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<td>75</td>
<td>75</td>
<td>71</td>
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</tr>
<tr>
<td>2-159</td>
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<td>75</td>
<td>80</td>
<td>69</td>
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<tr>
<td>2-171</td>
<td>tech. $V_2O_3$</td>
<td>0.92</td>
<td>75</td>
<td>81</td>
<td>85</td>
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<td>75</td>
<td>74</td>
<td>64</td>
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</tr>
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<td>2-212</td>
<td>tech. $V_2O_3$</td>
<td>0.92</td>
<td>75</td>
<td>71</td>
<td>67</td>
<td></td>
</tr>
</tbody>
</table>
massive metal greater than 12 per cent. Various combinations of iodine with sulfur, while increasing the metal yield up to 60 per cent, always gave an extremely brittle product with hardness values well over Rockwell B 100. A potassium chlorate booster gave yields up to 45 per cent, but these hardness values also ran above Rockwell B 100.

It was noticed, when removing the reaction products from a bomb originally charged with a technical grade vanadium compound, that a pyrophoric component had volatilized through the refractory above the charge. Apparently the calcium reductant was also reducing the sodium contaminant to its elemental form. However, its presence in this form did not cause undue difficulty, as the quantity of sodium contained in technical grade material was not large.

A calcium reductant and sulfur booster were also successful in reducing technical grade vanadium trioxide to massive metal. A typical vanadium button reduced from technical vanadium trioxide is pictured in Figure 6. The reguli generally weighed between 60 and 70 grams, or 70 to 80 per cent of the theoretical yield of vanadium. The slightly higher yields over those obtained with technical grade pentoxide were probably due to a higher reaction temperature promoted by the booster reaction. Although identical charges did not always produce metal of equal hardness, the Rockwell B values generally ranged between 65 and 75. Representative
metal yields and their hardness values are given in Table IV. Reduction to massive metal of chemically pure vanadium tri-oxide, using calcium reducing agent and sulfur booster, was also demonstrated.

Table V

Purity of Ductile Vanadium Metal
Reduced from Technical Vanadium Trioxide

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>99.5</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.07</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.15</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Chemical analysis of an as-reduced regulus of vanadium metal prepared from technical grade vanadium trioxide is shown in Table V. The average Rockwell B hardness value for this sample was 65. The comparatively high nitrogen content could not be adequately explained, since a portion of this biscuit was able to be 90 per cent cold rolled without annealing. The oxygen content for this sample was approximated to be about 0.04, as determined from the correlation of oxygen content with hardness number shown in Figure 5.
Reduction of vanadium trifluoride with calcium increased the yield of vanadium noticeably. Consistently high yields, ranging from 85 to 90 per cent, were obtained with chemically-pure, purified and technical grade trifluoride. Since a booster reaction was not required with the higher purity fluoride, and only a small booster reaction was necessary for the fluoride of lower purity, the increased yields represented a significant decrease in the amount of reductant required for the preparation of a given quantity of vanadium. However, the metal was considerably harder than that produced from the oxide, with Rockwell B hardness numbers ranging from 85 to 95. Because of the consistent lack of ductility in the metal prepared from the fluoride, attention was directed to the production of vanadium from other compounds.

Magnesium reduction of vanadium trifluoride, using a potassium chlorate thermal booster, did not produce massive vanadium. The proportion of potassium chlorate booster was successively increased until a temperature was reached which sufficiently weakened the bomb wall to allow the internal pressure to bulge the metal bomb. The reduction products were always in the powdered form.

Massive metal could be obtained from technical grade vanadium trisulfide by the use of a calcium reductant without a booster reaction. The yields, however, were never more than 50 per cent. By the introduction of a booster reaction
with sulfur, the yields were increased. With molar ratios of sulfur to contained vanadium equivalent to those in pentoxide reductions, buttons weighing about 65 grams, or 70 per cent yields, were obtained. Metal hardness values were regularly above Rockwell B 85. The metal buttons did not possess the shiny, metallic appearance or the solid form of the metal from oxide or fluoride reductions, but were dull gray in color and excessively pitted. No analyses for this metal were made.

An estimate of material costs for the preparation of vanadium metal by calcium reduction from various vanadium compounds, based on vanadium pentoxide as a starting material, is given in Table VI. The quantity of reagents employed for the preparation of intermediate vanadium compounds was taken as 100 per cent in excess of that theoretically required for complete conversion. The charge compositions and metal yields are based on average reductions in two and one-half inch diameter bombs. Prices quoted, except for calcium, are from 1950 price lists. The price of redistilled calcium from the Ames Laboratory was estimated at $2.50 per pound. Vanadium prices are from the Vanadium Corporation of America.

Table VI indicates that the replacement of sulfur for iodine as a booster reagent in the reduction of chemically pure vanadium pentoxide represents a slight decrease in the
### Table VI

Material Costs for the Preparation of Vanadium Metal

<table>
<thead>
<tr>
<th></th>
<th>Reduction from CP. V(_2)O(_5)</th>
<th>Reduction from CP. V(_2)O(_3)</th>
<th>Reduction from Fused Tech. V(_2)O(_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantity lbs./lb.</td>
<td>Unit Cost $/lb.</td>
<td>Total Cost</td>
</tr>
<tr>
<td>Contained V in V(_2)O(_5)</td>
<td>1.21</td>
<td>12.48</td>
<td>15.10</td>
</tr>
<tr>
<td>Ca</td>
<td>4.12</td>
<td>2.50</td>
<td>10.30</td>
</tr>
<tr>
<td>I(_2)</td>
<td>1.20</td>
<td>2.55</td>
<td>3.06</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>$28.16</td>
<td></td>
</tr>
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</table>
Table VI (Continued)

<table>
<thead>
<tr>
<th></th>
<th>Reduction from Tech. V₂O₃</th>
<th>Reduction from Tech. V₂S₃</th>
<th>Reduction from Tech. VF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantity</td>
<td>Unit</td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>lbs./lb.</td>
<td>Cost</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.10</td>
<td>4.50</td>
<td>0.45</td>
</tr>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contained V in V₂O₅</td>
<td>1.24</td>
<td>2.14</td>
<td>2.65</td>
</tr>
<tr>
<td>Ca</td>
<td>3.55</td>
<td>2.50</td>
<td>8.86</td>
</tr>
<tr>
<td>S</td>
<td>0.70</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>$11.98</td>
</tr>
</tbody>
</table>
cost of materials for the preparation of vanadium metal; while the substitution of technical grade vanadium compounds for those of higher purity affords an appreciable saving in materials cost. Although material costs for the preparation and reduction of the trifluoride and trisulfide of vanadium are lower than those for the oxides, the labor costs involved in the trifluoride and trisulfide preparations would undoubtedly offset any saving in cost.

Since softer metal had been obtained from oxide reductions, several reductions of technical grade vanadium trioxide and pentoxide were made in larger sized bombs to test the applicability of the process on a larger scale. With the utilization of a four-inch diameter bomb, the yields of metal from the pentoxide were about 230 grams of vanadium, or 73 per cent of theoretical, while metal buttons weighing approximately 240 grams, for a yield of 80 per cent, were obtained from the trioxide. Hardness values of the biscuit metal from both charges were about Rockwell B 75. Although higher yields of metal were anticipated, the absence of such an increase may be attributed to the use of the more porous jolt packed liner. Employment of this type of liner, however, introduces a possible further economy for consideration in vanadium preparation. As the size of the bomb is increased further, the smaller ratios of surface area to volume and the proportionately less heat losses would be favorable for increased yields of vanadium.
C. Metal Studies

The as-reduced vanadium buttons were sectioned and polished before hardness readings were taken. Although the buttons could be cut with silicon carbide or aluminum oxide cut-off wheels, faster results were obtained by using a reciprocating power driven saw. The samples were mechanically ground and polished by the usual metallographic techniques.

Massive vanadium was remelted by arc-melting the metal in a helium atmosphere and a water-cooled copper crucible; tungsten tip electrodes and a getter of zirconium metal were employed. An increase in metal hardness of 10 to 15 points on the Rockwell B scale was noted after arc-melting. An equivalent decrease in hardness value was accomplished by annealing of the arc-melted vanadium for four hours at 900°C. at a pressure below 0.01 microns.

Figure 6 shows a typical vanadium regulus reduced from technical grade vanadium trioxide with a sulfur booster, and vanadium sheet cold rolled to 0.010 inches from an arc-melted and annealed regulus prepared from the same material. A micrograph of the arc-melted and annealed sample before rolling is shown in Figure 7. Samples were etched in a glycerin solution containing 5 per cent hydrofluoric acid and 10 per cent nitric acid.
Figure 6 - Vanadium Regulus and Rolled Sheet.

Figure 7 - Structure of Arc-Melted and Annealed Vanadium; 250 X.

Figure 8 - Structure of 90% Cold Rolled Vanadium from an As-Reduced Button; 100 X.
The density of arc-melted vanadium prepared from technical grade vanadium trioxide was measured at 6.12 grams per cubic centimeter. This figure compares favorably with the value given by Kinzel (28).

As-reduced buttons from oxide reductions also could be directly cold rolled to thin sheets without annealing. However, the quality of this sheet was not very good because of the lack of regular geometry in the starting material. A micrograph of the cold rolled material from technical grade trioxide is shown in Figure 8.
VII. CONCLUSIONS

1. A method has been developed for the preparation of small amounts of high purity massive vanadium by reductions of vanadium pentoxide, vanadium trioxide, vanadium trifluoride and vanadium trisulfide with calcium.

2. The use of a sulfur booster reagent in the reaction charge made possible the successful reduction to massive metal of technical grade vanadium compounds as well as those of higher purity.

3. Metal obtained by reduction of vanadium trifluoride gave the highest yields of biscuit metal; the softest metal was obtained from vanadium trioxide reductions with a sulfur booster. The more ductile reguli were capable of being cold worked to thin sheets of vanadium.

4. The preparation of vanadium metal from technical grade vanadium compounds was shown to represent an appreciable saving in cost in comparison with reductions made from chemically-pure vanadium compounds.

5. The bomb reduction method was demonstrated to be applicable for the preparation of massive vanadium on a larger scale.
Vanadium metal in the massive form was prepared by calcium reductions of vanadium pentoxide, vanadium trioxide, vanadium trifluoride and vanadium trisulfide. The exothermic chemical reduction was carried out in closed iron bombs lined with dolomitic oxide refractory. A secondary reaction between a sulfur booster reagent and excess reductant furnished auxiliary heat and gave a product capable of lowering the melting point of the slag. This allowed better agglomeration of the metallic phase. On the scale investigated, metal thus reduced collected in a solid regulus weighing about 70 grams. Some of the metal produced was ductile, and could be cold rolled to thin sheets.

From vanadium pentoxide, available commercially in the chemically-pure and technical grade forms, other vanadium compounds utilized in the reduction process were prepared. Vanadium pentoxide was reduced to vanadium trioxide with hydrogen at 700°C. Vanadium trifluoride was prepared by passing anhydrous hydrogen fluoride over vanadium trioxide at room temperature, followed by drying of the hydrated trifluoride at 300°C, in an atmosphere of hydrogen fluoride. Vanadium trioxide was converted to vanadium trisulfide by reaction with hydrogen sulfide at 800°C.
The reduction charge, containing the compound to be reduced, the reductant and the booster reagent, was thoroughly mixed and packed in the refractory-lined metal bomb. After the bomb was capped, the reaction was initiated by heating the bomb assembly in a gas-fired furnace. The course of the reaction was followed by measuring the temperature of the outside of the bomb. After the reaction had fired and the bomb had cooled, the reaction products were removed with a chisel and leached in water and dilute acid. The regulus recovered generally contained 75-80 per cent of the vanadium and was indicated to be of high purity.

The use of sulfur in the reaction charge made possible the successful reduction to massive metal of technical grade vanadium compounds as well as those of higher purity. Reductions from technical grade compounds were shown to represent an appreciable saving in cost in comparison with reductions made from chemically-pure vanadium compounds. A large excess in calcium gave best results from the standpoint of recovery and hardness of metal. Of the lower purity vanadium compounds reduced, the trifluoride furnished the highest biscuit yields, while the trioxide supplied the softest metal. Only metal obtained from the oxides was found to be ductile. A typical trioxide reduction charge for a two and one-half inch diameter bomb contained 150 grams of technical grade vanadium trioxide, 256 grams of calcium and
50 grams of sulfur. The practical use of larger bombs with larger charges was demonstrated.
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X. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. H. A. Wilhelm for his suggestions and encouragement throughout the progress of this investigation. The capable assistance of the members of the metallurgy groups in the fabrication of the metal and the cooperative aid of those in the analytical section in performing chemical analyses are gratefully acknowledged. The author is indebted to the Ames Laboratory of the Atomic Energy Commission for the funds and the facilities made available for this research.