Reduction of niobium pentoxide by carbon

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Reduction of niobium pentoxide by carbon

Abstract
The investigations of the reduction of niobium pentoxide by carbon showed that niobium metal could be prepared by a direct reduction. High temperatures in the region of 2000°C but below the melting point of niobium and dynamic vacuum of one micron or less were the principal experimental conditions employed throughout the course of this study. The reaction, which followed very closely the stoichiometry of the equation \( \text{Nb}_2\text{O}_5 + 5\text{C} \rightarrow 2\text{Nb} + 5\text{CO} \), began at a temperature near 1200°C and was nearly completed at 1600°C. The data indicated that it might be possible to allow reduction to take place at approximately 1800°C. After the reaction is completed at this temperature, raising of the temperature of the reaction material to nearly 2000°C might eliminate residual oxygen as a result of volatilization of a lower oxide of niobium.

Disciplines
Metallurgy
REDUCTION OF NIOBIUM PENTOXIDE BY CARBON

By
Ernest Roger Stevens
H. A. Wilhelm

February 1961

Ames Laboratory
Iowa State University
Ames, Iowa
F. H. Spedding, Director, Ames Laboratory.

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Ernest Roger Stevens
H. A. Wilhelm

February, 1961

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### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>6</td>
</tr>
<tr>
<td>A. Materials</td>
<td>6</td>
</tr>
<tr>
<td>B. Preparation of the Charge</td>
<td>8</td>
</tr>
<tr>
<td>C. Reduction</td>
<td>9</td>
</tr>
<tr>
<td>D. Examination of the Metal Product</td>
<td>12</td>
</tr>
<tr>
<td>E. Analytical Methods</td>
<td>14</td>
</tr>
<tr>
<td>III. RESULTS AND DISCUSSIONS</td>
<td>16</td>
</tr>
<tr>
<td>IV. BIBLIOGRAPHY</td>
<td>40</td>
</tr>
</tbody>
</table>
REDUCTION OF NIOBIUM PENTOXIDE BY CARBON*

by

Ernest Roger Stevens and H. A. Wilhelm

ABSTRACT

The investigations of the reduction of niobium pentoxide by carbon showed that niobium metal could be prepared by a direct reduction. High temperatures in the region of 2000°C but below the melting point of niobium and dynamic vacuum of one micron or less were the principal experimental conditions employed throughout the course of this study. The reaction, which followed very closely the stoichiometry of the equation

\[ \text{Nb}_2\text{O}_5 + 5\text{C} \longrightarrow 2\text{Nb} + 5\text{CO}, \]

began at a temperature near 1200°C and was nearly completed at 1600°C. The data indicated that it might be possible to allow reduction to take place at approximately 1800°C. After the reaction is completed at this temperature, raising of the temperature of the reaction material to nearly 2000°C might eliminate residual oxygen as a result of volatilization of a lower oxide of niobium.

*This report is based on an M.S. thesis by Ernest Roger Stevens, submitted February, 1961, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
If, then a larger scale preparation could be derived from this work, such a process would eliminate various intermediate steps in the usual industrial production of niobium metal. A simple direct reduction below the melting point of niobium and subsequent arc melting of the metal to give a massive, good quality product might prove to be an economical process for the production of niobium.
I. INTRODUCTION

A demand for greater efficiency in the production of power has created considerable interest in the development of materials with superior properties at elevated temperatures. The thermodynamic efficiency of a heat engine is a function only of the two temperature levels involved and is directly related to the difference between the higher and the lower operating temperatures. Since there is little to be gained by lowering this lower temperature, increasing the efficiency is essentially dependent on raising the higher operating temperature. Present materials are being used at their upper temperature limits and, therefore, they are inadequate for use at the proposed operating temperatures. As a result, a number of the less common refractory metals, their compounds and their alloys, are being investigated in an effort to develop satisfactory materials for use at higher temperatures. A study on a method for the preparation of niobium, which is one of these refractory metals, is the subject of this report.

Niobium metal has much to offer for possible applications in the field of high temperature technology. Niobium melts at 2468°C (1) and has good strength at high temperatures. Although it has poor resistance to oxidation above a few hundred degrees Centigrade, progress is being made to overcome this unsatisfactory property. Niobium can be protected from air oxidation by cladding, and it is believed
that it can also be protected by developing a more resistant surface. Considerable effort is being expended in the development of alloys of niobium to improve the corrosion resistance of the metal. The mechanical properties of niobium are affected by very small additions of interstitial impurities such as carbon, oxygen, hydrogen and nitrogen, and for this reason hot working of the metal in air is generally avoided. Since niobium can be easily cold worked, fabrication is usually carried at or near room temperature. Niobium has a thermal neutron capture cross-section of 1.1 barns which, in combination with its high temperature strength, favors its use in components of some reactors for nuclear power. The combination of high temperature strength and medium density makes the metal potentially useful as a structural material in the aircraft industry. The increasing demand for niobium metal has led to the renewed interest in the development of the methods for its preparation. The specific purpose of this work was to investigate the preparation of niobium by the direct reduction of the pentoxide by carbon.

The relatively high cost of good quality niobium has been a factor in limiting its use. The cost has been due, in part, to a number of processing steps in the usual commercial production of the metal by the carbide reduction of niobium pentoxide. At present, niobium is produced in commercial quantities by a method which was developed by
Balke (2). This method is based on the fact that when a mixture of niobium pentoxide and niobium carbide is heated in a vacuum, carbon monoxide is evolved and niobium metal is produced. The carbide is first made by heating high purity niobium pentoxide with carbon in an inert atmosphere. After analyzing the carbide for its carbon content, it is mixed with the pentoxide in proportion corresponding to

\[ \text{Nb}_2\text{O}_5 + 5\text{NbC} \rightarrow 7\text{Nb} + 5\text{CO} \]  

and the mixture is compacted under a pressure of 50 tons per square inch. These compacts are supported within a graphite resistor tube of a vacuum furnace and heated above 1600°C where the reaction proceeds. The vacuum is employed to remove the carbon monoxide gas and thus promote the reaction. As a result of this heating, the compacts become metallic and porous. They are removed from the furnace and converted into powder by a ball mill. The powder is pressed into bars which are then heated in a vacuum by their resistance to an electrical current. This heating, which generally reaches a higher temperature, reduces the gas content to a low value. The bars, which now are sintered metal and still porous, are compacted by working with a heavy hammer. The wrought metal is heated again in a vacuum by self resistance. During this last heating, the pores seal and the resulting solid metal bars are then ready for fabrication into desired shapes.

Early attempts to reduce niobium pentoxide by carbon were
described by von Bolton (3) and by Moissan (4). In 1907, von Bolton reported that he prepared ductile niobium. Niobium pentoxide was mixed with paraffin wax and extruded into a wire of 0.5 mm. diameter. The wire was bent into a U-shaped filament and heated to a white heat while immersed in carbon powder. From this, von Bolton claimed the preparation of brown niobium tetroxide. The tetroxide was placed into a vacuum and a direct current was passed through the brown filament until the filament reached a white heat. Von Bolton expected that niobium would be produced by electrolysis, but after an hour of heating, no metal resulted from this treatment except for a small amount at the positive pole. However, when alternating current instead of direct current was used, a quarter of an hour of heating at a white heat transformed the whole filament into niobium metal. Von Bolton claimed that elemental oxygen was evolved during this heating. With this method of producing niobium metal, only small quantities could be obtained.

Moissan (4) described his work of the reduction of niobium pentoxide by carbon. Oxide and sugar charcoal were pressed together in the presence of "essence of terebine" and heated on a bed of carbon in an electric furnace. The metallic appearing product contained about 2.3 to 3.4 per cent carbon. Undoubtedly, some oxide remained unreduced.

Kroll and Schlechten (5) reported a rather intensive
examination of the reduction of niobium pentoxide by carbon in a vacuum. A mixture of oxide (52.9 gm.) and carbon (9.6 gm.) was briquetted and heated for 36 hours at 1300°C in a partial vacuum containing some hydrogen. The pressure at the end of the heating was 20 microns. The product, containing about 9.9 per cent carbon, was crushed and mixed with sufficient oxide to remove the carbon as carbon monoxide when heated in a carbon resistor furnace. This heating was carried out in a vacuum at 1920°C. The product of this latter heating was crushed, briquetted and then heated in a vacuum at 2400°C in a high frequency furnace. The fused metal had a Rockwell B hardness of 80. Kroll and Schlechten concluded that niobium could be prepared by this method; however, this product, because of its hardness, evidently was highly impure.
II. EXPERIMENTAL

It was evident from earlier reports that to promote the reaction between niobium pentoxide and carbon, high temperatures and vacuum conditions would be required. The experiments were designed to be carried out at temperatures of 1600°C and above and at pressures of a micron or less as finishing conditions. To attain the relatively high temperatures which were necessary for this reaction, high-frequency induction heating was used. The vacuum pumping equipment consisted of an oil-diffusion pump which was backed by a mechanical pump. The metallic sponge which was obtained in each experiment was subsequently arc melted in an inert atmosphere to give a massive metal button. This arc-melted metal product was examined for hardness and workability. To test the workability characteristics, part of the arc-melted product was cold rolled at room temperature.

A. Materials

High-purity niobium pentoxide and carbon black were used in the course of this investigation. The oxide was obtained from Fansteel Metallurgical Corporation and was described as high-purity grade. According to the manufacturer, certain metal oxide impurities in this material came within the maximum limits shown in Table 1. A qualitative spectrographic analysis by the Ames Laboratory indicated that trace amounts
of aluminum, calcium, magnesium and silicon were also present. The carbon employed was designated as 100 per cent compressed Shawinigan Black. The specifications from the producer show that this carbon had an apparent density of 12.5 pounds per cubic foot; its analysis is shown in Table 2.

Table 1. Maximum limits of oxide impurities in Fansteel niobium pentoxide expressed as percentages

<table>
<thead>
<tr>
<th>Oxide of</th>
<th>Fe</th>
<th>Ti</th>
<th>Ta</th>
<th>Zr</th>
<th>Ni</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-purity Nb$_2$O$_5$</td>
<td>0.02</td>
<td>0.05</td>
<td>0.08</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2. Analysis of carbon expressed as percentages

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Moisture</th>
<th>Volatile</th>
<th>Ash</th>
<th>Ether extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.5+</td>
<td>0.04</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Results of some experiments at this laboratory indicated that the total volatiles of this carbon were slightly higher than reported in Table 2; however, the low value for the ash content was substantiated.
B. Preparation of the Charge

The experiments were conducted on a relatively small scale employing one-tenth of a gram mole of niobium pentoxide per charge. Weighed amounts of the oxide and carbon were mixed dry in a beaker. At this point the charge lacked homogeneity since there was a tendency for the loose particles to separate. To develop a better degree of homogeneity, the mixture was wetted with acetone and blended into a pasty consistency. The acetone was removed in a 100°C drying oven. The dried charge was mixed and pulverized for about one hour in a ball mill which consisted of a glass jar containing a few ceramic stones. After removing the ceramic stones, the charge was wetted again with acetone to give a paste which was then formed into shape by compacting into a glass cylinder whose dimensions were about 2.5 cm. inside diameter and 8.5 cm. high. Drying of the formed charge was accomplished in a 100°C oven; during the drying period, the charge shrank in size. The cylinder and its dry contents were weighed and then placed into a tantalum crucible whose dimensions were 3.8 cm. inside diameter and 10 cm. in height with a wall thickness of 10-15 mils. The crucible was left open at the top. The glass cylinder was carefully removed without destroying the shape of the dried charge. The empty glass cylinder was weighed to determine the weight of the charge. The tantalum crucible with the charge was then
placed into a graphite heater which was thermally insulated by carbon powder contained in a Pyrex jar. This charge-heater assembly is illustrated in the sketch of Figure 1 which represents the complete vacuum induction heating set-up.

It is to be observed in the figure that the heater assembly was centrally positioned in a 4-inch diameter upright quartz cylinder. In making the complete set-up, the lower end of the cylinder was connected to a vacuum system and the upper end of the cylinder was closed by a metal plate provided with a sight glass through which the contents of the reaction vessel could be observed. By means of a mechanical pump and an oil-diffusion pump, the system could be evacuated to a pressure of less than one micron. Power for the induction heating was supplied by a six-kilowatt Ajax-Northrup high-frequency mercury-arc converter. A photograph of the apparatus as employed is shown as Figure 2.

C. Reduction

The system was evacuated prior to heating. During this evacuation, pressures in the one millimeter to one micron range were measured by a NRC Type 501 thermocouple gauge and pressures of one micron or less were measured with a NRC Type 507 ionization gauge. Temperature and pressure values were observed at one-minute intervals during the heating of the charge. A Leeds and Northrup optical pyrometer was used to
Figure 1. Charge-heater assembly.
Figure 2. Photograph of small vacuum induction heating system.
determine the temperature of the reacting charge. For most of
the reduction period, the gas pressures developed were within
the range of the thermocouple vacuum gauge. Near completion
of a reaction, pressures dropped to the range of the ioniza­
tion gauge. When a nearly constant temperature was to be
maintained during the course of a reduction, control was
effected by manually operating the on-off switch of the high-
frequency converter. During a reduction, the evolution of gas
from the charge caused the gas pressure in the system to rise,
often to values of 700-900 microns. When a reduction was
carried out at a particular temperature, that temperature was
maintained until the pressure of the system returned to a low
value which was in the range of one micron or less.

After a run was completed, the product was allowed to
cool to room temperature in the vacuum. The system was then
opened and the product, a sintered metal sponge, was removed
from the heater and weighed. For evaluating the product of
each experiment, the metal sponge was subsequently arc melted
in a helium atmosphere on a water-cooled copper plate. The
resulting metal button was remelted three times with inversion
between meltings to complete the preparation of the arc-melted
sample.

D. Examination of the Metal Product

The metal button, which was about 20 mm. in diameter and
6 to 7 mm. in thickness, was weighed and then cut along
parallel planes perpendicular to a diameter to give sections approximately 3 mm. in thickness. Employing a "C" Brale indenter and a 60 kilogram load, Rockwell A hardness values were determined on one of these sections. Five indentations were made on each specimen and the average value was recorded for the hardness number.

Another section of the arc-melted button was used for testing the workability of the metal. Cold rolling of the section was accomplished with a laboratory hand-operated 2-high Stanat rolling mill having 2-3/4 inch diameter rolls. Before each pass, the mill was adjusted to reduce the thickness of the section by about five mils. In all tests the metal section was reduced in thickness until the metal either fractured or its thickness reached the practical limit of the mill.

Standard metallographic techniques were used to examine the microstructure of each arc-melted button. A section of the metal button was mounted in bakelite. Preliminary grinding on a belt-type specimen grinder was performed to expose the metal and to provide a flat surface for subsequent grinding and polishing. Fine grinding was carried out on a series of four mechanically driven rotating disks on which were mounted emery papers of grit sizes 240, 320, 500 and 600. Final polishing was generally accomplished on a lapping wheel which was covered with billiard cloth impregnated with
an aqueous soap solution of Linde A. Some samples required a finish polishing on a lapping wheel which was covered with a silk velvet cloth charged with an aqueous soap solution of Linde B.

The polished metal surface was first examined microscopically and then etched with a fresh solution of the following composition:

\[
\begin{align*}
9 \text{ ml. conc. } &\text{HNO}_3 \\
3 \text{ ml. conc. } &\text{HCl} \\
1 \text{ ml. } &48\% \text{ HF}
\end{align*}
\]

A photomicrograph of each etched sample was prepared by employing a Bausch and Lomb Research metallograph and conventional photographic procedures.

E. Analytical Methods

Analyses for oxygen, carbon and nitrogen were obtained on each sample. An emission spectrometric technique was used to determine the oxygen content (6). A D-C carbon-arc discharge in an argon atmosphere was employed to extract the oxygen from the metal as carbon monoxide, to dissociate the carbon monoxide into atomic oxygen and to excite the oxygen triplet at 7772 Å with sufficient sensitivity to make the oxygen determination possible. Conventional spectrographic techniques utilizing the argon emission line 7891 Å as an internal standard were used throughout the calibrations and determinations.
A Leco Conductometric Carbon Determinator was used in the analysis for carbon. In brief, a weighed amount of niobium metal was heated in a stream of oxygen to convert the carbon to carbon dioxide which was collected and absorbed in a very dilute standard solution of barium hydroxide. The conductivity of this solution was measured and comparison made with the original solution to give the weight of carbon dioxide absorbed.

Nitrogen in niobium was determined by a modified Kjeldahl method. Approximately one-gram samples of niobium were dissolved in an acid mixture (5 ml. 1:1 \(\text{H}_2\text{SO}_4\), 2 ml. 48% HF and 1 ml. 30% \(\text{H}_2\text{O}_2\)) and the solutions were partially evaporated to lower the acid content. Sodium hydroxide solution was added to the solutions of the metal samples and ammonia was then steam-distilled into a boric acid solution containing methyl purple indicator. The boric acid-indicator solution was then titrated with standard hydrochloric acid to determine the nitrogen content.
III. RESULTS AND DISCUSSIONS

The reaction between niobium pentoxide and carbon at high temperatures in a vacuum follows, very closely, the stoichiometry of the equation

$$\text{Nb}_2\text{O}_5 + 5\text{C} \rightarrow 2\text{Nb} + 5\text{CO} \quad (2)$$

A preliminary investigation showed that small deviations from the stoichiometry of Equation 2 yielded niobium containing sufficient carbon or oxygen to affect noticeably the hardness and ductility of the arc-melted metal.

The composition for a series of charges was calculated to give a series of niobium metal samples with varying carbon contents in the metal product, assuming the validity of Equation 2. These metal samples were then arc melted before testing. It was assumed that the fast cooling that follows arc melting would tend to amplify the hardness effect due to the presence of oxygen or carbon. Consequently, all of the samples were tested in the as-arc-melted condition. The results obtained for the products after reaction and arc melting in this preliminary investigation are found in Table 3.

The first column of the table is the calculated weight percentage of carbon in the product as based on the charge composition and the reaction according to Equation 2. In describing the workability of the metal samples, "rolled" and "no roll" are used here as qualitative terms. "Rolled"
Table 3. Results of the preliminary investigation

<table>
<thead>
<tr>
<th>Nominal w/o of carbon in metal product</th>
<th>Maximum temperature of reduction ºC.</th>
<th>Hardness $R_A$</th>
<th>Workability (cold)</th>
<th>Analysis (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Oxygen</td>
<td>Carbon</td>
</tr>
<tr>
<td>3.00</td>
<td>1970</td>
<td>57</td>
<td>No Roll</td>
<td>470</td>
<td>28,600</td>
</tr>
<tr>
<td>2.00</td>
<td>1916</td>
<td>49</td>
<td>No Roll</td>
<td>305</td>
<td>12,324</td>
</tr>
<tr>
<td>1.50</td>
<td>1915</td>
<td>51</td>
<td>No Roll</td>
<td>260</td>
<td>14,000</td>
</tr>
<tr>
<td>1.00</td>
<td>2030</td>
<td>47</td>
<td>No Roll</td>
<td>415</td>
<td>8,328</td>
</tr>
<tr>
<td>0.50</td>
<td>1860</td>
<td>44</td>
<td>Rolled; Edge Cracked</td>
<td>335</td>
<td>3,020</td>
</tr>
<tr>
<td>0.25</td>
<td>2000</td>
<td>48</td>
<td>No Roll</td>
<td>72</td>
<td>5,620</td>
</tr>
<tr>
<td>0.00</td>
<td>1890</td>
<td>40</td>
<td>Rolled; Minor Edge-Cracks</td>
<td>350</td>
<td>1,873</td>
</tr>
<tr>
<td>-0.25</td>
<td>2000</td>
<td>39</td>
<td>Rolled Nicely</td>
<td>160</td>
<td>452</td>
</tr>
<tr>
<td>-0.50</td>
<td>1910</td>
<td>69</td>
<td>No Roll</td>
<td>4,200</td>
<td>183</td>
</tr>
<tr>
<td>-1.00</td>
<td>1950</td>
<td>74</td>
<td>No Roll</td>
<td>3,000</td>
<td>123</td>
</tr>
<tr>
<td>-2.00</td>
<td>1975</td>
<td>70</td>
<td>No Roll</td>
<td>$\gg5,000$</td>
<td>103</td>
</tr>
<tr>
<td>-3.00</td>
<td>1960</td>
<td>68</td>
<td>No Roll</td>
<td>10,000</td>
<td>119</td>
</tr>
</tbody>
</table>
describes the quality of the metal sample which could be cold reduced to a thickness determined by the practical limit of the mill. "No roll" means that the tested metal sample fractured after a few passes through the mill. Other self-evident terms are used to further specify the quality of the workability. The negative percentages shown in the table indicate a carbon deficiency in the product with respect to the stoichiometry. The metal products actually, in these cases, contained a nominal amount of oxygen corresponding to the carbon deficiency. It should be noted from Table 3 that the nominal percentages of carbon were in fair agreement with the carbon analysis on the carbon rich side of stoichiometry. However, a similar agreement did not exist with respect to residual oxygen in the metal on the carbon deficient side of stoichiometry.

Figure 3, prepared from the data of Table 3, shows graphically the relationship between Rockwell A hardness and the nominal weight percentage of carbon for the arc-melted samples. The results of this series of experiments indicated that slight deviations from the stoichiometry would result in metal of considerable hardness and poor workability. Good quality niobium metal will have relatively low hardness and good ductility and workability in the as-arc-melted condition. It was evident from the results of this preliminary study that good quality niobium metal could be prepared by the direct
carbon reduction of the oxide; however, the amounts of
carbon and oxide, which are to be mixed together for the
charge, appear to be very critical.

Photographs of microstructures of some representative
arc-melted samples from this series are shown in Figures 4
through 11 in order of decreasing nominal carbon percentage.
The structures in Figures 4 through 7 were interpreted as
showing excess carbon as carbide, Nb₂C. These microstructures
are in accord with the results of recent work on the niobium-
carbon system reported by Elliott (7) who prepared samples by
comelting of niobium and a 6 weight per cent carbon master
alloy. The phase diagram proposed by Elliott shows that
most of the niobium samples containing carbon within the
range of analysis referred to here would solidify by a
eutectic reaction between Nb₂C and niobium metal solid
solution.

The solubility of carbon in solid niobium is 0.80 weight
per cent at the eutectic temperature of 2230°C and decreases
rapidly to about 0.10 weight per cent at 1800°C. The eutectic
composition is given by Elliott as 1.5 weight per cent carbon
which corresponds closely in carbon content and in micro-
structure to the sample for Figure 4.

A charge which was prepared according to the stoichiome-
try of Equation 2 gave metal whose microstructure is
represented by Figure 7. In this metal, Nb₂C is shown
Figure 3. Relationship between Rockwell A hardness and the nominal weight percentage of carbon for the arc-melted samples of the preliminary investigation.
precipitated within the grains of the niobium metal. The sample of Figure 8 contained about 0.05 weight per cent carbon which gave rise to some carbide precipitation within the grains of niobium. It should be noted that the composition of the metal product was not exactly what was expected from the stoichiometry of Equation 2; it was believed that the deviation was due to factors connected with experimental techniques, conditions and/or materials.

The niobium-oxygen system established by Elliott (8) reveals that the first oxide formed is NbO which melts congruently at 1945°C. There is a eutectic region between niobium and NbO; this eutectic has a composition of 10.5 weight per cent oxygen and occurs at 1915°C. According to the phase diagram, the solubility of oxygen in solid niobium decreases from 0.72 weight per cent at the eutectic temperature to 0.25 weight per cent at 500°C. The microstructures shown in Figures 9 through 11 are, then, what might be expected of arc-melted samples of niobium containing small amounts of oxygen. The microstructure of Figure 9 shows essentially one phase of solid solution. Figure 10 shows the solid solution with precipitated NbO. Figure 11 shows a dendritic pattern for the solid solution with eutectic.

It is to be noted in Table 3 that, during this preliminary investigation, the reductions were not completed at the same maximum temperature. The finishing pressures, not
recorded in the table, were of the order of a few microns but not all of the same value. In view of possible variations in the product due to these differences in finishing temperatures and pressures, it was decided to treat a similar series of charges uniformly. To meet the desired condition of uniform maximum temperature and uniform pressure, these charges were heated simultaneously in a vacuum induction system similar to but much larger than that employed for the individual charges described above.

This larger system accommodated a 16-inch diameter induction coil which heated a 9-inch diameter graphite crucible in which several small charges could be treated simultaneously. The results of a series of charges reduced at a maximum temperature of 2000°C in this unit are presented in Table 4. The workability of the arc-melted products of this series of samples turned out to be very poor. A plot of Rockwell A hardness values versus nominal percentage of carbon in the metal for this new series gave a curve similar to that illustrated in Figure 3 but displaced to higher hardness values.

This new curve shown as a solid line in Figure 12 represents the data for the samples reduced simultaneously; this curve should be compared with the dotted curve based on the data for Figure 3. The carbon and oxygen analyses of the products of the series of simultaneous reductions are
Table 4. Results of simultaneous reductions in large vacuum induction system

<table>
<thead>
<tr>
<th>Nominal w/o of carbon in metal product</th>
<th>Hardness $R_A$</th>
<th>Workability (cold)</th>
<th>Analysis (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxygen</td>
</tr>
<tr>
<td>-3</td>
<td>78</td>
<td>No Roll</td>
<td>&gt;5,000</td>
</tr>
<tr>
<td>-2</td>
<td>79</td>
<td>No Roll</td>
<td>&gt;5,000</td>
</tr>
<tr>
<td>-1</td>
<td>77</td>
<td>No Roll</td>
<td>&gt;5,000</td>
</tr>
<tr>
<td>0</td>
<td>58</td>
<td>No Roll</td>
<td>360</td>
</tr>
<tr>
<td>1</td>
<td>57</td>
<td>No Roll</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>57</td>
<td>No Roll</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>64</td>
<td>Rolled, Edge Cracked</td>
<td>38</td>
</tr>
</tbody>
</table>
in fair agreement with those of the preliminary investigations for corresponding charges. The differences in hardness might then be caused by some other factor such as nitrogen contamination. Later experiments showed that nitrogen in the final metal was much greater for metal prepared in the large vacuum induction system used for these simultaneous reductions than for metal prepared by the smaller unit of Figure 2.

Another series of reductions was run simultaneously in the large system which had the 16-inch diameter induction coil. The charges for these reductions were prepared according to the following charge composition:

\[ \text{Nb}_2\text{O}_5 + (5 + Z)\text{C} \]

where \( Z \) represents the fraction of a mole deviation from the stoichiometry represented by Equation 2. The results of this series of reductions presented in Table 5 correspond closely to those of the previous simultaneous reductions (see Table 4). The reductions giving the data recorded in Table 5 were carried out at 2000°C and for a time which was necessary for the pressure of the vacuum system to return to a low value. The nitrogen content of each of these metal samples, as suspected from earlier results, was found to be high.

It should be noted that for the samples prepared by the simultaneous reductions at uniform temperatures (see Tables 4 and 5), the charges rich in carbon yielded metal products which contained carbon commensurate with the nominal weight
Figure 12. Relationship between Rockwell A hardness and nominal weight percentage of carbon in arc-melted samples of simultaneous reductions. Dotted line based on data of individual reductions in preliminary investigation (see Figure 3).
<table>
<thead>
<tr>
<th>Z value</th>
<th>Hardness R_A</th>
<th>Workability (cold)</th>
<th>Analysis (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxygen</td>
</tr>
<tr>
<td>-0.4</td>
<td>84</td>
<td>No Roll</td>
<td>4,590</td>
</tr>
<tr>
<td>-0.3</td>
<td>80</td>
<td>No Roll</td>
<td>3,450</td>
</tr>
<tr>
<td>-0.2</td>
<td>76</td>
<td>No Roll</td>
<td>3,500</td>
</tr>
<tr>
<td>-0.1</td>
<td>68</td>
<td>No Roll</td>
<td>2,825</td>
</tr>
<tr>
<td>0</td>
<td>59</td>
<td>Rolled; Edge Cracked</td>
<td>570</td>
</tr>
<tr>
<td>+0.1</td>
<td>58</td>
<td>No Roll</td>
<td>215</td>
</tr>
<tr>
<td>+0.2</td>
<td>58</td>
<td>Rolled; Considerable Edge Cracking</td>
<td>185</td>
</tr>
<tr>
<td>+0.3</td>
<td>57</td>
<td>No Roll</td>
<td>250</td>
</tr>
<tr>
<td>+0.4</td>
<td>60</td>
<td>No Roll</td>
<td>210</td>
</tr>
</tbody>
</table>
percentages, a relationship noted also from the data for the individual reductions recorded in Table 3. However, in these same series, the charges which were deficient in carbon according to the stoichiometry of Equation 2 yielded metal products containing approximately the same oxygen content. It appears then that the volatility of the oxide is such that under the conditions of these experiments the residual oxygen content of the metal approaches some equilibrium value.

A stoichiometric reduction generally resulted in metal which was relatively low in both carbon and oxygen but of these two residual impurities, the one in slight excess could not be predetermined. This uncertainty might be associated with a number of factors such as variation in composition of starting materials, lack of uniformity in the mixed charge, variations in the reaction behavior of the charge associated with the development of different fracture patterns in the compact during heating and lack of complete reproducibility in the pressure and temperature patterns during heating to and at the maximum temperature.

In an effort to determine the lowest finishing temperature at which the reduction of niobium pentoxide by carbon in a stoichiometric charge would give good quality metal, an experiment was conducted whereby separate charges were heated to various maximum temperatures and finished at pressures of less than one micron. To promote a uniform composition in
this series of charges, a bulk mixture of this desired composition was prepared and an appropriate amount was taken for each individual reduction. The charges for this investigation were heated by the vacuum induction system which was used for the preliminary investigation and is shown in the photograph of Figure 2. The reductions in this series of experiments were all run with about the same rate of power input up to the pre-selected maximum temperatures which were held for a period of time until the pressure of the vacuum system returned to a value of less than one micron. After this condition was maintained for some time, the reaction was assumed to be essentially completed under the conditions imposed and heating was discontinued.

Results of this experiment are found in Table 6. It should be noted from the table that the reaction was nearly completed at 1600°C. For reactions performed at maximum temperatures of 1700°C and 1800°C, the carbon in the metal product was found to be very low; however, the oxygen content was much higher than expected. Although the reduction which was carried out at 1900°C gave a metal product which had good workability, the oxygen content was also high but considerably lower than the oxygen content of the products prepared at 1700°C and 1800°C. Metal prepared at 2000°C showed low oxygen which might have been expected but the carbon content appeared to be much higher than anticipated
Table 6. Results of experiment to determine lowest finishing temperature of stoichiometric reduction

<table>
<thead>
<tr>
<th>Maximum temperature of reduction (°C)</th>
<th>Final pressure (mm. Hg) at maximum temperature</th>
<th>Hardness $R_A$</th>
<th>Workability (cold)</th>
<th>Analysis (ppm)</th>
<th>Oxygen</th>
<th>Carbon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>$0.15 \times 10^{-3}$</td>
<td>48</td>
<td>Rolled; Edge Cracked</td>
<td>30</td>
<td>5,761</td>
<td>241</td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>$0.16 \times 10^{-3}$</td>
<td>57</td>
<td>Rolled</td>
<td>1,000</td>
<td>178</td>
<td>264</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>$0.26 \times 10^{-3}$</td>
<td>73</td>
<td>No Roll</td>
<td>~6,000</td>
<td>111</td>
<td>229</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>$0.31 \times 10^{-3}$</td>
<td>68</td>
<td>No Roll</td>
<td>3,300</td>
<td>137</td>
<td>441</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>$0.50 \times 10^{-3}$</td>
<td>55</td>
<td>Rolled; Edge Cracked</td>
<td>730</td>
<td>6,575</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>$0.70 \times 10^{-3}$</td>
<td>65</td>
<td>No Roll</td>
<td>1,325</td>
<td>2,696</td>
<td>183</td>
<td></td>
</tr>
</tbody>
</table>
on the basis of data at lower temperatures. This high carbon in this higher temperature treatment product might have been the result of carbon vaporization from the graphite heater which contained the reaction charge. However, the volatility of oxide from the charge at this temperature might be such that sufficient oxygen escaped without reacting to leave a high residual carbon content.

A duplicate series of charges was run in an attempt to determine the reproducibility of the data in Table 6. The results of this re-run are found in Table 7. Aside from the fact that corresponding samples in Tables 6 and 7 show considerable disagreement in the analytical data, similar trends can be noted in both series. High carbon with high oxygen characterizes the samples run at 1600°C; the lowest carbon content in both series is obtained with the 1800°C treatment while the lower residual oxygen is found in samples given the higher temperature treatments.

The relationships between the carbon content and the oxygen content and the temperature of treatment for the samples of Table 7 are shown graphically in Figure 13. The increase in carbon content above 1800°C is clearly shown here accompanied by a general lowering of residual oxygen, while below 1800°C, both carbon and oxygen are high. The graph in Figure 13 shows also the relationship between the maximum temperature of the treatment and the combined carbon
Table 7. Results of re-run to determine lowest finishing temperature of stoichiometric reduction

<table>
<thead>
<tr>
<th>Maximum temperature of reduction °C</th>
<th>Maximum Final pressure at maximum temperature (mm. Hg)</th>
<th>Hardness RA</th>
<th>Workability (cold)</th>
<th>Analysis (ppm)</th>
<th>Oxygen</th>
<th>Carbon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.14 x 10⁻³</td>
<td>53</td>
<td>Rolled; Edge Cracked</td>
<td>195</td>
<td>775</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>0.20 x 10⁻³</td>
<td>52</td>
<td>Rolled; Edge Cracked</td>
<td>185</td>
<td>614</td>
<td>432</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.20 x 10⁻³</td>
<td>55</td>
<td>Rolled Nicely</td>
<td>680</td>
<td>289</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>0.40 x 10⁻³</td>
<td>68</td>
<td>No Roll</td>
<td>2,520</td>
<td>1,157</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>0.70 x 10⁻³</td>
<td>73</td>
<td>No Roll</td>
<td>2,095</td>
<td>2,013</td>
<td>136</td>
<td></td>
</tr>
</tbody>
</table>
Figure 13. Relationship between carbon and oxygen content and finishing temperature of reduction.
and oxygen contents.

Since the data of Table 7 did not duplicate those of Table 6 but did show a similar over-all trend, it was evident that the final compositions of the metal samples did not appear to represent true equilibrium conditions for the chemical reaction in all of the reductions. It was suggested then that the preparation of good quality niobium by a direct carbon reduction of the pentoxide might be influenced by a number of factors which were not critically evaluated in these investigations. Further consideration of such influencing factors could possibly lead to future work in connection with this problem. A critical examination of the reactants and products associated with this reaction at high temperatures might lead to a better understanding of the conditions prevailing at or near the finishing temperature. The oxide and carbide activities in the system at the temperatures referred to here are important factors in determining the course of the reaction. These activities could be influenced by solid solution formation, by vaporization and by the degree of reaction under temperature and pressure variables. The effects of the volatility of carbon from the graphite heater to the charge and of oxide from the charge on the carbon and oxygen contents of the metal products were discussed earlier.

In a reduction of the type reported in this work,
carbide and oxide are the principal constituents remaining in
the metal when the reaction is essentially complete. It is
to be noted from the phase diagrams of the niobium-carbon
(7) and the niobium-oxygen (8) systems that both carbon, as
Nb$_2$C, and oxygen, as NbO, show some solid solubility in
niobium metal at temperatures around 2000°C. The completion
of the reaction, then, at this temperature will require
reaction between components that are continuously decreasing
in their activities. The lower solid solubility of the
carbide at a temperature of 1800°C would allow the carbon
to retain a constant activity to a greater degree of
completion of the reaction.

These investigations of the reduction of niobium
pentoxide by carbon showed that niobium metal could be
prepared by a direct reduction. High temperatures in the
region of 2000°C but below the melting point of niobium and
dynamic vacuum of one micron or less were the principal
experimental conditions employed throughout the course of
this study. The reaction, which followed very closely
the stoichiometry of Equation 2, began at a temperature near
1200°C and was nearly completed at 1600°C. The data indi-
cated that it might be possible to allow reduction to take
place at approximately 1800°C. After the reaction is com-
pleted at this temperature, raising of the temperature of the
reaction material to nearly 2000°C might eliminate residual
oxygen as a result of volatilization of a lower oxide of niobium.

If, then, a larger scale preparation could be derived from this work, such a process would eliminate various intermediate steps in the usual industrial production of niobium metal. A simple direct reduction below the melting point of niobium and subsequent arc melting of the metal to give a massive, good quality product might prove to be an economical process for the production of niobium.
IV. BIBLIOGRAPHY


