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# The Preparation of Tantalum Metal by the Carbon Reduction of Tantalum Pentoxide<sup>1</sup>

C. B. HAMILTON<sup>2</sup> AND H. A. WILHELM<sup>3</sup>

*Abstract.* A mixture of tantalum pentoxide and carbon when heated under vacuum conditions reacts to give carbon monoxide as essentially the only gaseous product. A temperature of about 1200° C is required to give measurable gas evolution. The degree of completion of the reaction for a certain charge and for a certain finishing pressure depends upon the temperature. In a uniform stoichiometric mixture of fine powders, the reaction goes to near completion at a temperature of about 2100° C with a finishing pressure of less than one micron. The carbon in the charge appears to be in the form of carbides at intermediate stages of the reaction. The metal is recovered from the reduction step in the form of a sponge. Solid ingots are formed by arc melting the sponge. Excess carbon (over stoichiometric) in the charge remains in the final metal as carbide. Excess oxygen can be removed by heating the metallic sponge product to about 2400° C in a vacuum. It appears that under these conditions the oxygen is volatilized as TaO<sub>2</sub>. The conditions for reaction and removal of excess oxygen suggest a method for metal preparation.

Tantalum metal, because of its strength at high temperatures and its good ductility and ease of fabrication, is one of the refractory metals receiving much attention in the search for special property materials needed in modern engineering, especially for constructing more efficient heat-power generators. To obtain this metal from its ores, the processing has for many years been directed to the crystallization of potassium tantalum fluoride as the intermediate (1, 2). The metal in powder form is produced directly from this double fluoride by sodium reduction (2) and by fused salt electrolysis (3). Within the past decade, however, a solvent extraction method for purifying tantalum in an acid fluoride system was originated at the Ames Laboratory of the USAEC (4, 5, 6). The tantalum is recovered from one of the product phases of this extraction as a high purity compound which is readily converted to tantalum pentoxide. A process for the direct use of this oxide in metal preparation is then of interest. The preparation of tantalum metal by the carbon reduction of tantalum pentoxide is the subject of this report.

Following the discovery of the element in 1802 by Ekeberg, a Swedish chemist, more than a century elapsed before a ductile tantalum was prepared by von Bolton (7) in 1905. Although he did not consider it as such, von Bolton's process appears to

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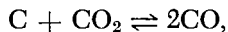
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have depended on a carbon reduction of the oxide in a vacuum. Investigation of the carbon reduction of the oxide by heat and under vacuum conditions has, since his work, been reported by Kroll and Schlechten (8) and Siemans and Halski (9).

In view of these reports on the carbon reduction of tantalum metal, it appears that high temperatures, above 2000°C, combined with low finishing pressures (< 1 micron) are possibly required to yield, consistently, good quality tantalum metal in a direct one-step reduction process. However, literature references relating to such a process have been found decidedly lacking in details. In this investigation a study of the reaction between carbon and tantalum pentoxide in vacuo has been made in an effort to derive an adequate understanding of the process so as to be able to specify more clearly conditions for the preparation of good quality tantalum metal.

#### SOME FUNDAMENTAL CONSIDERATIONS

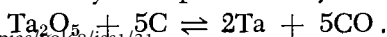
At the outset in a study of the carbon reduction of a metal oxide, consideration must be given to the carbon dioxide to carbon monoxide ratio in the gas phase in equilibrium with free carbon. The side reaction



could bear on the make-up of the charge. If at least part of the reduction of a metal oxide by carbon in a self-reacting charge takes place under conditions at which a significant amount of both of these gases are simultaneously present, then uniformity of product quality could be difficult to maintain. If a significant excess of either carbon or oxygen remains in the metal product, its properties may be decidedly altered.

Data are available on the CO-CO<sub>2</sub>-C equilibrium and values calculated for the mole fractions of the constituents in the gas phase are represented by the solid lines in Figure 1 over a temperature range for a total gas pressure of one atmosphere. Under this condition it is seen that the gas phase is essentially 100 per cent CO at temperatures above about 1100°C. If the total pressure is reduced to one tenth of an atmosphere, the gas phase is essentially 100 per cent CO at temperatures above 900°C. So at pressures of a few hundred microns, no significant amount of CO<sub>2</sub> would be expected to be present in the gas phase in equilibrium with free carbon at temperatures somewhat below 900°C.

Early exploratory work with mixtures of carbon and tantalum pentoxide demonstrated that essentially no reaction takes place at temperatures below about 1200°C under vacuum conditions. The reaction then may be represented by the expression



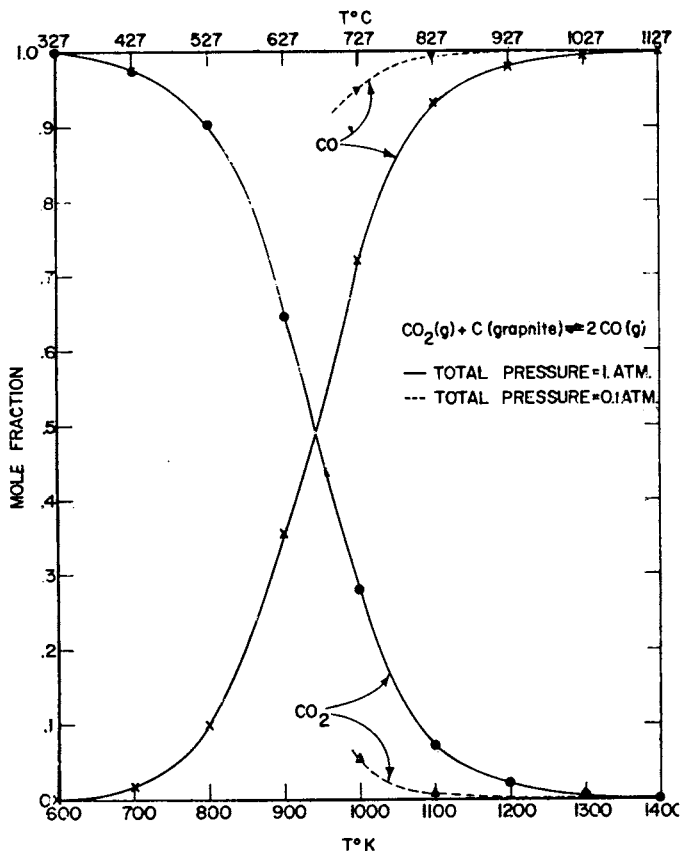


Figure 1. Mole fractions of CO and CO<sub>2</sub> in equilibrium with carbon at various temperatures.

According to free energy data, if the reduction were as simple as indicated by this reaction, a temperature of less than 1500°C would be adequate to prepare the metal. In the course of normal procedures, however, stepwise or side reactions make it necessary to heat the charge to higher temperatures under vacuum conditions in order to satisfactorily complete the reduction.

#### MATERIALS AND TECHNIQUES

The work reported here was carried out on a small scale with each charge containing generally one tenth of a gram-mole of the pentoxide. Graphite (National Carbon Grade 38) was employed in most of this study as the form of carbon to be mixed with high purity grade pentoxide (Fansteel grade T-40) in making up the charges. Before using this graphite it was given a purification treatment by leaching with hot concentrated hydrochloric acid. It was then washed and dried. This treatment

lowered the residue on ignition from 0.150 per cent to 0.043 per cent. Other forms of carbon tested were Shawinigan Black and Standard Micronex Beads, both gas carbons. However, exploratory studies revealed that there was little difference in the quality of the final product for the three different sources of carbon. The average particle size of the graphite powder was 2.6 microns while the  $Ta_2O_5$  particles averaged about 0.6 micron in diameter. The particle size of the forms of carbon seemed to be a factor in determining the amount of reaction at lower temperatures, but completion of the reaction required essentially the same finishing temperature for the different forms. Due to the greater packing density and low volatile content of the graphite it appeared to have advantages as a source of carbon for use in possible metal production studies.

To prepare a charge, weighed amounts of tantalum pentoxide powder and the carbon powder were ball milled together for one hour to insure thorough mixing. Acetone was then added to the mixture to make a paste that facilitated in compacting and shaping the charge. The acetone was then evaporated and the shaped charge was placed in a tantalum lined graphite container that served as a susceptor, or heater, for induction heating. The liner for the sides and bottom of the graphite heater was made from tantalum sheet about 10 mils thick. Powdered carbon insulation was packed around the heater in a Pyrex or silica beaker and this unit was placed on a ceramic stand and then surrounded by a quartz tube which served as the vacuum chamber. This entire assembly for heating by induction is represented in Figure 2. Power to the induction coil was supplied by a 6 kw. Ajax mercury-arc converter. The vacuum was developed by an oil diffusion pump (H6B National Research Corporation) backed by a mechanical pump (1397C Duo Seal, Welch Scientific Co.). The pressure in the system was generally reduced to  $10^{-5}$  mm of mercury before starting the heating by induction. A glass window in the top of the furnace chamber permitted the temperatures to be determined by means of an optical pyrometer. The gas that was evolved and pumped out of the system as the reduction proceeded was measured by a Wet Test gas meter.

The residual product from the reduction step was subsequently compacted generally by arc melting. The quality of the finished metal was indicated by its hardness and its fabricability. Good quality tantalum metal, which will contain less than 200 ppm of each of the common interstitial impurities (carbon, nitrogen and oxygen), can be fabricated into rod, wire and sheet (10) and can be cold rolled extensively without severe edge cracking effects. Ordinary x-ray diffraction powder patterns

were made in the study of some samples for phase make-up. Samples for metallographic examinations were mechanically polished; etching was done with a solution containing nitric, hydrochloric, and hydrofluoric acids.

### EXPERIMENTAL RESULTS AND DISCUSSION

A series of experiments was run on a charge with less than stoichiometric graphite to determine the amount of gas generated with this form of carbon over intervals of 100 degrees with increasing temperatures under vacuum conditions. The volume of gas from the system, an indication of the amount of reaction, was determined by reading the meter at the end of the period for each temperature interval. As the charge was heated a slight increase in pressure, indicating possible initiation of the reaction, was observed at about 1200°C; the temperature was then controlled at 1200°C until the pressure had dropped back

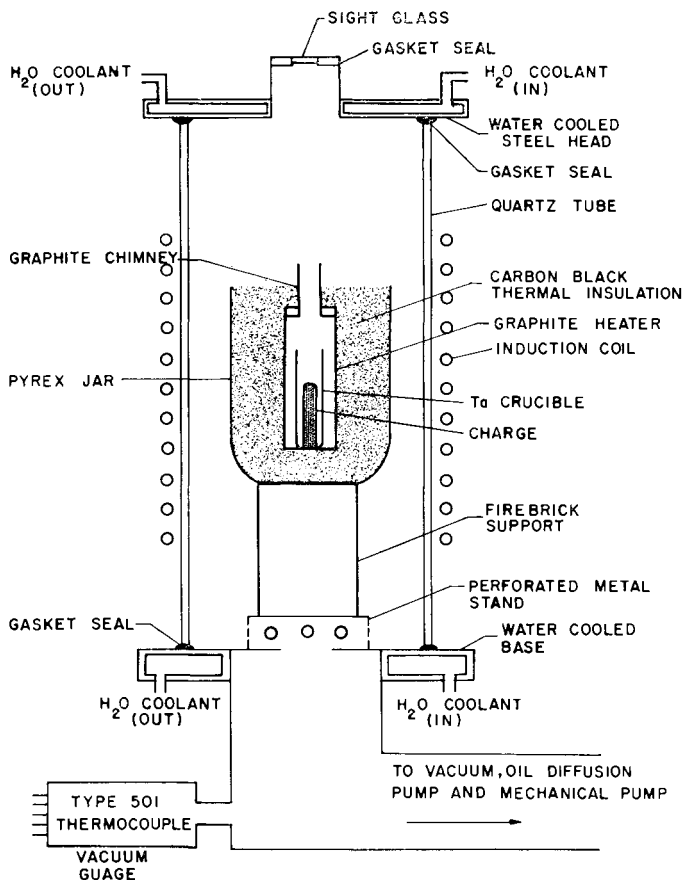


Figure 2. Sketch of vacuum-induction furnace. Schematic only—not drawn to scale.

to a few microns. The volume of gas evolved was noted. The temperature was raised 100 degrees and the operations controlled at 1300°C, until the pressure again dropped back to a few microns. The total volume of gas was noted at the end of the 1300°C heating. The temperature was further increased in steps of 100 degrees and the cumulative volume of gas noted after the pressure had dropped for each of the intervals.

Figure 3 represents, semiquantitatively, the data on gas evolution at the designated temperatures in this experimental procedure. The dashed line drawn through these points merely facilitates visual inspection of the data. There is a first maximum at about 1300°C followed by a minimum in the neighborhood

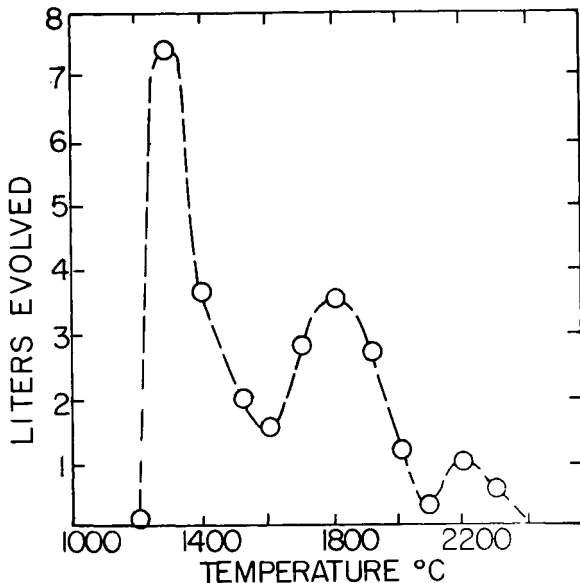


Figure 3. Gas evolved at progressively higher temperatures (100° intervals). Uncorrected. Less than stoichiometric graphite in charge.

of 1600°C. A second maximum occurred at around 1800°C and a third at about 2200°C. On the basis of similar experiments, a duplicate run would be expected to reproduce the reaction initiation, maximum and minimum temperatures within about 50 degrees of an average. In Figure 3, temperatures as read on the optical pyrometer and gas volumes as indicated by the meter are employed without correction.

A similar experiment, in which a stoichiometric amount of graphite was used in making the charge, gave maxima corresponding to only the first and second maxima of Figure 3. Corrected temperature and volume data from the stoichiometric carbon reducton experiment are plotted in Figure 4. The dashed

line again merely connects the points of interest in this scheme of representation. The third maximum of Figure 3, absent in Figure 4, was observed only in experiments where oxygen was in excess of the carbon in the charge. The solid line connecting points in Figure 4 represents the cumulative volumes of gas evolved in the experiment up through corresponding temperatures. The cumulative gas is expressed on the ordinate as per cent of the total gas evolved for complete reduction. For example, roughly 50 per cent of the carbon has been evolved as CO through the heating at about 1520°C in a vacuum. The arrows designated as 2C, 3C and 4C indicate points at which

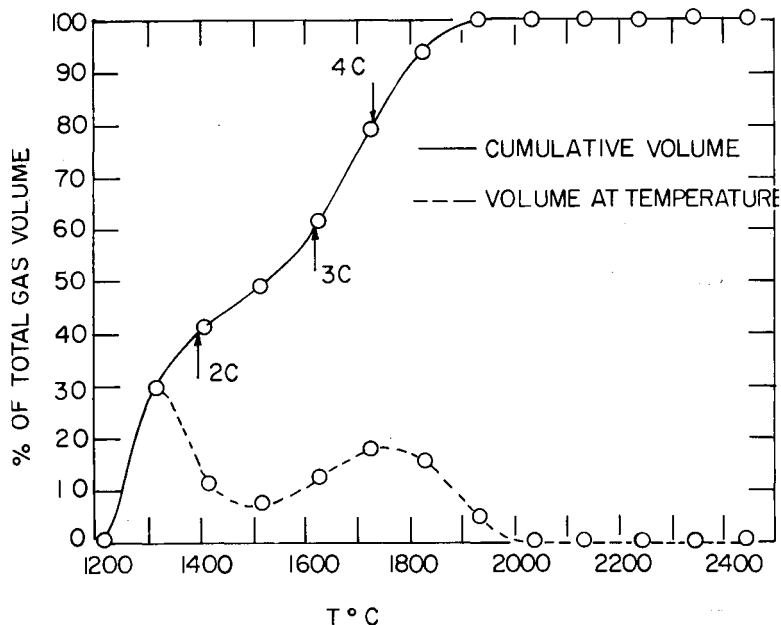


Figure 4. Gas evolved at progressively higher temperatures (100° intervals). Corrected. Stoichiometric graphite in charge.

2, 3 and 4 moles, respectively, of the graphite in the charge has reacted with one mole of  $Ta_2O_5$  to form CO.

In another stoichiometric-carbon experiment set up to obtain some indication as to the chemical species present in the charge at various temperatures, the furnace was cooled after the heating was completed at each of the temperature intervals from 1300 to 1800°C (corrected 1315°C to 1830°C) inclusive. Representative samples were taken for x-ray diffraction studies before going to the next higher temperature. It should be pointed out that the disturbances of the charge in taking these samples tended to bring about some further reaction at the lower temperatures on reheating. Although the crystal structures at room tempera-



ture cannot necessarily be assumed to exist in the charge at the reaction temperatures, they do give data on which to base speculations.

In the Debye-Scherrer diffraction patterns of the samples, a group of lines assigned to the structure of  $Ta_2O_5$  decreased in intensity as the temperature increased, but was strongly evident in the pattern of the sample that had been heated to  $1625^\circ C$ . However, a number of the more prominent lines of the pattern assigned to  $Ta_2O_5$  were still detectable in the sample that had been heated as high as  $1830^\circ C$ . The diffraction patterns of samples treated at temperatures below  $1725^\circ C$  gave no evidence of detectable tantalum metal; even the presence of metal in the  $1725^\circ C$  sample was quite questionable. The  $1830^\circ C$  treatment, however, gave a sample that yielded strong evidence of tantalum metal.

A pattern of lines assumed to be due to TaC (possibly also to TaO, if this exists) was found in samples that had been heated in the range  $1315^\circ C$  to  $1625^\circ C$  with the maximum predominance being at about  $1400^\circ C$ . A pattern of lines assignable to  $Ta_2C$  was detected in samples from the temperature range  $1520^\circ C$  to  $1830^\circ C$ . The diffraction data obtained on most of the samples showed no lines that were not assignable to patterns of the above species; the few very weak lines that were unassigned could possibly have been due to the presence of a minor amount of some intermediate oxide.

Although the room temperature x-ray data do indicate the presence of species such as  $Ta_2O_5$  in samples that have been heated as high as  $1830^\circ C$ , an answer to the question of the actual existence of the pentoxide, as such, in the charge at this temperature was not pursued. Possibly some lower oxide that disproportionated into  $Ta_2O_5$  and tantalum metal on cooling was the species at the high temperature.

The gas evolution experiments and the x-ray diffraction studies point quite definitely to the net stoichiometric reaction presented earlier as taking place in a number of steps that in the particular mixture employed may overlap to a considerable degree. Complete solid state equilibrium quite likely did not exist at the reaction temperatures. The relatively large grain size of the graphite used, the limited time at temperature and the relatively low rate of diffusion in the solid state at the lower and intermediate temperatures would contribute to this assumed condition of non-equilibrium.

The problem of expressing a precise course for the reaction, if such actually existed in this experiment, appears increasingly complex in view of the number of oxides of tantalum ( $Ta_2O_5$ ,

Ta<sub>2</sub>O<sub>4</sub>, Ta<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>2</sub>, Ta<sub>2</sub>O and Ta<sub>4</sub>O) that have been reported to exist. In the x-ray investigations, however, Ta<sub>2</sub>O<sub>5</sub> was the only oxide definitely identified in the samples after cooling to room temperature. The structure reported for TaO would, by the x-ray techniques employed in this investigation, be indistinguishable from TaC, and vice versa, in the powder patterns.

The CO gas evolution for the first maximum of Figure 4 is the result of a reaction between Ta<sub>2</sub>O<sub>5</sub> and carbon at the solid-solid interface of the particles to give TaC (and possibly TaO). The reaction does not go to a state of completion but slows down because of the distance separating the residual reactants. This build-up of TaC increases through the 1415°C treatment.

Since tantalum subcarbide, Ta<sub>2</sub>C, structure was detected and the TaC pattern showed a slight decrease in intensity in the x-ray patterns for the sample that was heated to 1520°C, it may be assumed that some TaC had reacted with an oxide at this temperature. However any reaction to form tantalum metal with subsequent reaction between the metal and TaC could also give the observed result.

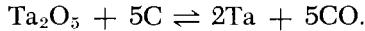
The increase in gas evolution at 1625°C could be associated with further reaction brought about by the fusion of the pentoxide, thus allowing better contact between the reactants. The x-ray evidence also points to the presence of more Ta<sub>2</sub>C and much less TaC in the 1625°C product, possibly indicating further reaction of the monocarbide with oxide. At the end of the heating for the 1625°C interval, the species arranged in order starting from the residual core of an original graphite particle and moving outward, might be assumed as C, TaC, Ta<sub>2</sub>C, Ta, Ta<sub>4</sub>O, TaO and Ta<sub>2</sub>O<sub>5</sub>. However, some of these species, if they did exist, were in such small quantities that they were not detected.

At 1725°C there appears to be no liquid phase so the CO evolution would depend largely on diffusion, essentially in the solid state, for reaction to take place. Quite likely by completion of this temperature interval all of the free carbon has been consumed since TaC no longer is detected in the 1725°C product.

By completion of the reaction period at 1830°C, the over-all reaction is about 94 percent complete with Ta<sub>2</sub>C and especially tantalum metal appearing to be present in high proportions. A species of a tantalum oxide, other than the Ta<sub>2</sub>O<sub>5</sub>, has not been identified for this high temperature. At this temperature, however, there has been observed some evidence of a small amount of liquid phase in the charge. Fusion here would be assumed to be connected with an oxide phase and not with the metal and subcarbide phases.

As the temperature is further increased it is assumed that the

Ta<sub>2</sub>C and an oxide continue to react through the means of diffusion to give a residue of essentially tantalum metal at about 2100°C. The net over-all reaction then being



In the assumed reactions at the various stages discussed above, further effects such as solid solutions and combinations between reactants and products at the temperatures involved could complicate the picture further. However, the analysis in the discussion above lends interpretation for practical aspects of the problem of preparing tantalum metal by the carbon reduction of Ta<sub>2</sub>O<sub>5</sub>.

The third maximum in Figure 3 was found to be associated with excess oxygen in the charge. The question as to how such oxygen is evolved from tantalum metal has been the basis for a number of speculations and experiments. It was assumed by Von Bolton that free oxygen was given off when tantalum oxide was heated to a high temperature. On the basis of experiments on columbium, it has been assumed by some, through analogy, that the oxygen from tantalum is evolved as TaO. Others have assumed that Ta<sub>2</sub>O<sub>5</sub> was the species of oxide that volatilized from the metal at high temperatures. A combination of TaO and Ta<sub>2</sub>O<sub>5</sub> has been considered as possible, while even a combination of TaO and metal volatilization satisfied data for some very high temperature experiments.

If only metal oxide volatilization from the charge were the total effect at the highest temperature range for the experiments performed here, no gas evolution from the system would be observed for the third maximum. Since the whole charge is within a graphite heater, however, any metal oxide evolved has ample opportunity to react further to form carbon monoxide, and it is this product that shows up as a measurable gas from the system to give the third maximum of Figure 3.

A series of experiments was run in an effort to obtain information as to the nature of the oxide species that is evolved from essentially carbon-free metal in the temperature range around 2250°C in vacuum. Charges were prepared containing stoichiometric and various degrees of less than stoichiometric carbon. These charges were heated through their reaction temperature zones and then heated through the temperature range required to evolve the oxide in question. The residual products were cooled and weighed as tantalum metal.

The data from this series of experiments are plotted in Figure 5. The residual metal yield in per cent, based on the total

weight of tantalum introduced into the charge, is plotted against the number of moles of carbon per mole of  $Ta_2O_5$  making up the original charge. No data were obtained with less than 3 moles of carbon per mole of  $Ta_2O_5$  since such low carbon samples were so high in oxide that fusion occurred and this complicated the recovery of residual metal. The solid straight line drawn from point P and extended by dashes to the intercept at 1 mole of carbon per mole of  $Ta_2O_5$  is a calculated line based on yields of metal assuming that the residual oxygen vaporizes at the high temperature as  $TaO_2$ . The general chemical reaction that expresses this over-all result to give the calculated

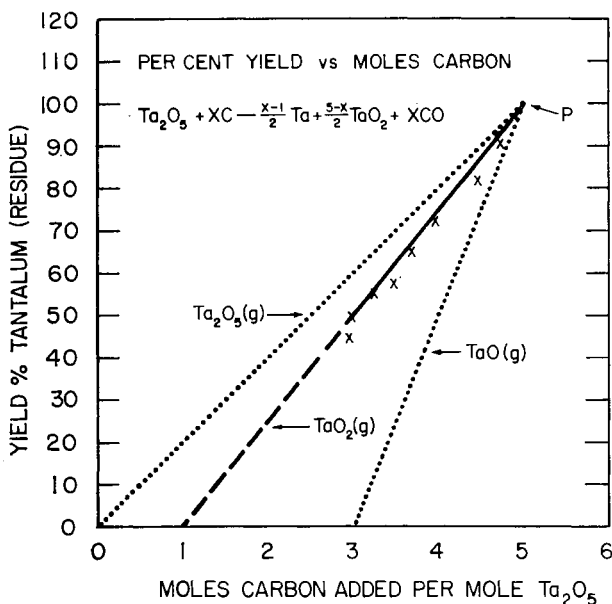


Figure 5. Yield of residue (based on 2 Ta) vs moles of carbon per mole of  $Ta_2O_5$  in charge. Experimental data indicated by crossmarks.

line, where X equals the moles of carbon per mole of  $Ta_2O_5$ , is inscribed in the figure.

The dotted line from point P to the intercept at zero moles corresponds to an assumed vaporization of the oxygen as  $Ta_2O_5$ , whereas the dotted line from point P to the intercept at 3 moles corresponds to the oxygen leaving the metal as TaO. It is to be noted that the plotted data of the experiments correspond more closely to the line for  $TaO_2$  as the volatile oxide species from tantalum metal at the temperature employed. The  $TaO_2$  species also fits a series of similar experiments in which mixtures of tantalum metal powder and  $Ta_2O_5$  were employed in a series of charges.

The problem of removing oxygen from the metal has been studied in connection with certain commercial processes for tantalum metal. Tantalum from the sodium reduction or electrolysis of potassium tantalum fluoride is recovered as a powder. The powders are compacted into bar form by pressing in dies. The bars are subsequently heated in vacuum for hours at temperatures approaching the melting point of the metal in order to remove oxygen. Considerable densification of the metal takes place during this treatment. The oxygen, especially near the end of the treatment, reaches the surfaces of the bars by essentially diffusion in the solid state. At the surface the oxide then vaporizes from the metal.

In the carbon process described here, the product at the end of the reduction has a rather open or spongy structure with fissures and crevices to allow gaseous diffusion as well as solid state diffusion to aid in the escape of the oxide species from the metal. Figure 6A shows the macrostructure (3X) of a finished sponge. The avenues for escape of gas from the internal portions of the metal sample are quite evident. A view of the microstructure (60X) of this metal (Figure 6B) shows that the structure on the micro basis is also quite open.

It has been demonstrated (11) that carbon in excess of the oxygen in a sample of tantalum metal cannot be removed by volatilization from the solid metal in a vacuum at temperatures approaching the melting point of the metal. It appears, then, that the most practical means for preparation of good tantalum metal by the carbon reduction of the pentoxide is to start with

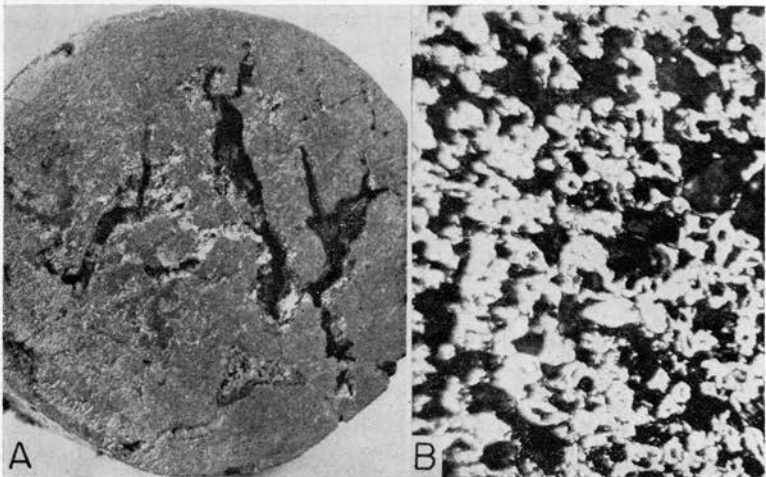


Figure 6. A. Macrostructure (3X) of sponge metal. Not etched.  
B. Microstructure (60X) of sponge metal. Not etched.

mixtures containing slightly less than stoichiometric carbon, complete the carbon reaction at about 2000°C to 2100°C and then heat the sample to about 2400°C in a good vacuum to volatilize out the excess oxygen, leaving a sponge for subsequent melting.

Sponge metal prepared by carbon reduction of the pentoxide is subsequently arc melted to give a compact ingot. The metal will have a hardness of less than 45 Rockwell A, and it can be rolled to thin foil without intermediate annealing. A typical analysis of a sample of metal prepared as suggested above by carbon reduction of the oxide will show carbon and oxygen contents of less than 200 ppm and 100 ppm, respectively. Subsequent electron-beam melting reduces the hardness of this metal to below the range of the Rockwell A scale.

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