

THE REDUCTION
of
TUNGSTIC OXIDE
to
TUNGSTEN

T H E S I S

by

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The purpose of this investigation is to study some methods of reducing Tungstic oxide (WO_3) to metallic tungsten from the standpoint of commercial applicability.

Previous Work:

The manufacture of tungstic oxide has been investigated by Wolochow Undergraduate Thesis (C.I.T.) 1924, and a method developed for its production from scheelite. The concentrated mineral is fused with soda ash and the mixture lixiviated with water. The soluble sodium tungstate which is thus formed is treated with HCl and the insoluble tungstic oxide precipitated. Wolochow worked out a method for the purification of this crude oxide and the purified product was used as the raw material for this series of experiments.

There seems to be but two practical methods available at the present time for the reduction of the oxide.

(1) Reduction by solid reagents such as carbon in the form of charcoal. For instance: $2WO_3 + 3C = 3CO_2 + 2W$

(2) Reduction by means of gaseous reagents such as Hydrogen or volatile hydrocarbons such as would be found in illuminating gas. For instance: $WO_3 + 3H_2 = W + 3H_2O$

Tungsten melts at 3350 degrees C. and is the highest melting element known today. Because of this extremely high melting point it is impossible to have a reduction reaction

take place in a molten mix. The reduction must take place between the particles of the oxide and the molecules or the particles of the reducing agent, whether the reducing agent is gaseous or solid. In either case it can be seen that to effect a complete reduction the oxide must be ground to extreme fineness. In cases where the solid reducing agent is used, not only must it be ground very finely but the charge must be mixed intimately also. In this way only can complete reduction be hoped for.

There are commercial processes in use today which represent the two methods above named: A powdered charcoal method is in wide use in Europe and hydrogen has found general application in this country.

In the former method the WO_3 is finely ground and mixed intimately with finely powdered charcoal. The mixture is placed in a closed clay crucible and heated to a temperature from 900 - 1000 deg. C. According to reports Chem. & Met. 23,696, (1920), the carbon and oxide mixture varies from an excess of 10% carbon to 100%. After roasting, the charge is cooled out of contact with air (usually under charcoal) to prevent the reoxidation of the heated metal. When it is cool it is finely ground and washed with water to remove the excess carbon. This process depends on the great difference in specific gravities of the metallic

tungsten and the reducing agent. It has been stated, Chem. & Met. 23,696, (1920), that by this method a product containing 98.5% tungsten metal can be obtained. The carbon content is reduced to .3 to .8%. This metallic product is suitable for work where only moderate purity is required - such as the manufacture of high speed steels.

The hydrogen reduction method undoubtedly yields a much purer metal -- there being none of the reducing agent left in the final product. This renders a metal of well over 99% purity which is well adapted for the manufacture of electric light filaments. This hydrogen method is used by the largest manufacturers of tungsten metal in the country - The Fansteel Products Co., and the General Electric Company.

In the present investigation both methods were studied on a laboratory scale.

THE CARBON REDUCTION METHOD

The main objects in trying out this method of reduction were to determine the purity of the product with respect to the carbon content and to determine the efficiency of reduction on a small scale.

The methods of analysis used were comparatively simple. It was required to determine:

- (1) The amount of unreduced WO_3
- (2) The amount of carbon in the product after washing.

(3) The amount of the loss of tungsten due to the washing, for the removal of the carbon.

In the 1st and 2nd experiments, determinations were checked in duplicate as far as possible. The method for removing the unreduced WO_3 consisted in boiling the reduced charge in dilute (about 6N) NH_4OH . The solution was filtered after being washed thoroughly with water, and the residue was used for No. 3 determination. The filtrate was evaporated somewhat to enable more convenient handling and to remove the excess NH_4OH before acidifying. While the solution of ammonium tungstate was still boiling, an excess of HCl was added and the heating continued until the yellow WO_3 precipitate came down completely. This was filtered off on a fine paper, ignited and weighed. The second series of runs used a Gooch filter which obviated the possibility of re-reducing the W metal by the paper. The WO_3 thus obtained represented the unreduced oxide that was dissolved by the ammonium hydroxide. It was found later, that this did not accurately represent the total unreduced WO_3 present in the charge. It has been found that WO_3 that has been strongly ignited, does not readily dissolve in NH_4OH . The addition of a small concentration of Na_2CO_3 renders this solution complete. All previous runs were checked over, using this method of dissolving the unreduced oxide.

In nearly all experiments there was difficulty in completely removing the unreduced oxide from the charge. In every case the metal was treated until no further oxide could be dissolved. In some instances this took five treatments with ammonia and Na_2CO_3 .

The only way in which a satisfactory precipitate of WO_3 could be produced, that is one which would stick well to a filter, ^{was} _^ to concentrate the solution to a volume of about 100 cc. and acidify strongly with HCl while the solution was kept boiling vigorously.

The determination of the second quantity listed above (i.e., the amount of carbon) was somewhat simpler as far as technique was concerned. An ordinary combustion train for the determination of carbon in a metal was set up, using KOH in a Geissler bulb for the absorption of the liberated CO_2 . Pure oxygen was used to save time and insure complete combustion. A temperature around 800 deg. C. seemed to be all that was necessary to produce a good oxidation of the metal. Weighed samples were placed in the combustion tube, the oxygen turned on and the tube heated. The run was continued until a constant weight was recorded on the absorbing bulb. Precautions were taken to insure the absence of any CO_2 in the gas entering the apparatus. Carbon content found in this manner

was expressed in terms of the percentage of the fused charge.

The determination of the tungsten loss on washing (the third determination) was more difficult as it was hard to get a standardized procedure which would reduce all determinations to a comparable basis. On account of this inaccuracy that must be encountered, a number of runs were made in order to get an idea of the loss. The sample after being treated for the removal of the unreduced oxide was washed with water and the washings were filtered through the same filter that was used to remove the solid matter in the unreduced oxide determination. In all experiments the washings were continued until the mixture came clear after settling for three minutes. In most cases this took three to five treatments. It can be easily seen wherein lies the difficulty in making such a procedure as the above a standard one. There may be differences in the fineness of the roasted charge although care was taken to grind it as fine as possible. If ground too fine too fine a greater number of washings become necessary owing to the slower rate of settling of the particles.

The filter on which the lost tungsten and the excess carbon were deposited was dried, ignited, and weighed. The tungsten loss was reported as % of original metal. In the first and third determinations there was a possibility

of re-reducing the oxide to the metal. In every experiment however, the ignition was long enough and in the presence of an excess of air so that re-oxidation after the reduction would take place and the residue would be the WO_3 . It can be seen that some error would also be introduced in the tungsten loss determinations due to the fact that the excess carbon from the run is present. This has been compensated for by calculating the amount of ash that would be present from the excess carbon. The ash content of the charcoal was previously determined. Any inaccuracy that may arise from this source will be on the safe side for a commercial process.

EXPERIMENTAL WORK

Table No. 1.

Run No.	Charge	Time (Mins.)	%WO ₃ in Product	% Reduction	Remarks
10	12.0 WO ₃ 1.8 -C	20	14.76	82.9	A slight amount of surface oxidation little slagging -1000C.
11	12.0 WO ₃ 1.8 -C	25	15.29	81.7	Surface oxidation now marked; interior more crystalline than #10 900° 1000°
12	12.0 WO ₃ 1.8 -C	30	4.68	96.36	Metallic particles Charge came out in layer masses - slight fusion to crucible 1000 deg.
13	12.0 WO ₃ 1.8 C	35	1.29	98.71	Caked fairly hard. Fused to bottom of crucible - product grayer than #10,11, 12 - 1000 deg.
14	12.0 WO ₃ 1.8 -	45	0.82	99.20	Charge fused and had to be drilled out. Good metallic particle very evident. 1000 deg.
15	12.0-WO ₃ 1.8-C	35	2.14	98.8'	Brown color-caked Had to be drilled out. Fused to cruc.

The above results derived from the first determination show that the reaction can be carried out practically to completion at the end of a 45 minute heating. It will be noticed however, that at the longer periods of heating the fusion becomes more bothersome. In all charges that were run over thirty minutes there was a fusion that rendered the recovery of a good part of the charge irrecoverable. It is evident then that in order to have an efficient commercial process we cannot use clay crucibles, as they lower the yield and are apt to go to pieces under a high temperature.

As the runs grew longer there was observed an increasing preponderance of metallic particles and a smaller amount of the black powder that resulted from the shorter runs. This might furnish a good idea of the progress of the reaction though no accurate estimate could be made. In the last runs where the reaction was nearly complete there was little of the black mixture to be seen, and the particles seemed larger sizes.

There is some discrepancy in the first two values of the % of WO_3 in the product. It might be caused by a difference in surface oxidation or by a lump of WO_3 accidentally passing through the mortar uncrushed.

TABLE 2

Run #	Charge	Time	Temp.	# of washings	% in Prod.	Remarks
1	30-WO3 4.5 s-C	45	900 D.	4	1.01	Low temp. black powder - few metallic particles
2	25-WO3 2.5-C	40	1000- 1100	5	0.81	Fusion - large crystall masses - metallic
4	25-WO3 2.5-C	30	900 1000	1	0.76	Fused badly; blue color due to poor reduction
5	25-WO3 2.5-C	35	800	1	0.62	No metallic particles; black, fine powder.
6	25-WO3 2.5-C	30	900	3	0.93	Metallic glaze on crucible.
7	25-WO3 2.5-C	25	1000	4	0.85	Few metallic particles.

The values of the carbon content, which were determined according to the second method of analysis already listed, show conclusively that the carbon content is not merely a function of the number of washings, but that it depends on other factors as well. If it were the case that the number of washings alone determined the purity of the product with respect to carbon, we would expect a decrease in the percentage carbon with an increase in the number of washings. It is probable that a great deal depends on the extent of the reduction of the charge and consequently the state of aggregation of the metal.

The effect of increasing the carbon in the entering charge may be seen plainly by comparing the first run with one of the others. Too great an extent of carbon in the original mixture makes it hard to remove from the product. There is therefore a ratio of carbon to WO_3 in the original mixture which will give the most economical results from the point of view of carbon content and efficiency of the reduction.

TABLE 3.

Run #	Charge	Time	# Wash	%W ₃ lost	Remarks
3	2.5-WO3 2.0-C	35	5	1.10	Little slagging. Settled slowly.
4	2.5-WO3 2.5-C	30	1	1.21	Particles settled slowly. Solution not clear when washing removed.
6	2.5-WO3 2.5-C	30	3	0.44	Settled fairly slowly
7	25-WO3 2.5-C	25	4	0.36	
8	25-WO3 2.5-C	30	3	0.51	Black on filter paper
9	12-WO3 1.8-C	15	3	0.98	Settled quickly
10	12-WO3 1.8-C	20	6	1.39	Metallic particles on filter paper.
11	12-WO3 1.8-C	25	7	.90	Settled very slowly
12	12-WO3 1.8-C	30	3	.2	Not much excess carbon
13	12-WO3 1.8-C	35	4	.3%	Settled very quickly. Little black on filter paper.
14	12-WO3 1.8-C	45	2	Trace	Settled quickly. Very slight ppt. of WO3 from washings.

The results above show that it is perfectly possible to run this process and keep the metallic losses well under 1%. Little can be gathered from this data besides this fact, as the figures themselves show no regular variation either with the number of washings, the time of heating, or with the constituents of the charge.

CONCLUSIONS: The results obtained show that it would be possible to put such a process as the carbon reduction method in commercial use and obtain tungsten metal economically, but not necessarily profitably. The reaction would be made to take place almost completely if the charge was heated for 55 minutes at a temperature above 1000 deg. C. The experiments also show that it would be impossible to use the ordinary clay crucible under these conditions, as their reactions to sustained heat cause a loss of the product. Future experimental work only will show the best material for the reduction vessel. There are numerous possibilities to choose from although all of them are far more expensive than the clay crucibles. If this reaction were to be put into commercial use it would be necessary of course to use larger apparatus. A larger combustion chamber and larger crucible would be necessary and also provision would have to be made for the removal of the fused charge without allowing it to come into contact with the air.

On a large scale this would be necessary to prevent the partial reoxidation of the hot metal. An arrangement could be effected whereby the crucible is removed directly to a bed of charcoal and buried therein till cool.

As to the carbon content of the product, the results are so consistently low that undoubtedly a commercial apparatus could be designed to keep the carbon content as low as it was in the experimental runs. Ordinary settling tanks might be satisfactory for this purpose. Experiments would have to be run however on the commercial apparatus to determine the fineness of the grinding and the time of settling. Such determinations could not be made satisfactorily a laboratory scale as they would depend a great deal on the shape and the size of the apparatus used.

The determinations of the metal loss in the removal of the carbon show that it is a very economical method of removal. It should be kept down to 1% or less if the proper conditions of grinding and settling are maintained. If in a commercial plant it was found that the washing loss was becoming too high the washings could be filtered and dried and the coke returned to the charge. In this way the loss could be reduced materially although the cost of such a filtering and drying might be excessive in comparison with the value recorded.

In any case it ought to be perfectly possible to produce

a product of sufficient purity for alloy steels.

The following is an estimate of the cost:

100 #WO ₃ @ \$.604(Wolochow cost of production)	\$60.40
15# powdered charcoal @ \$.06(current price)	.90
Total cost of materials	<u>\$61.30</u>

Assuming a 97% yield (including reduction losses and washing losses) we would get 76.8# of tungsten metal.

This would have a value (current prices) of .95 per #.

Value of product	\$73.00
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The difference between cost and value of product given above is \$11.70. Out of this must come the production costs and overhead expenses.

With the comparatively small difference in cost and value of product given above it is possible that after subtracting the cost of production there would be little or no profit remaining. The increase in value of the materials represents only 19% of their cost. This is the profit that would be derived if there were no production costs.

To put this process on a profitable basis, would require a very efficient plant and an axtermely low overhead. It would be almost necessary to produce the tungstic oxide at the same plant in order to cut down the handling charges. I would not recommend the carbon method as being profitable on a large scale under the existing prices. A rise in the price of tungsten metal would perhaps render the process workable.

THE HYDROGEN METHOD

This method is the one used to a large extent in this country by the Fansteel Company, and the General Electric Company. The reaction is carried out in an electric furnace at a temperature of 1100 - 1200 degree C. The oxide is placed in shallow layers on nickel dishes and placed in the quartz tube of the furnace. Hydrogen is preheated by passing it through a jacket surrounding this tube and then passed over the charge. The excess H_2 which does not react with the oxide is dried by passing through $CaCl_2$ and recirculated through the apparatus. The run is continued by the Fansteel Company for seven hours, at the end of which time the furnace is cooled and the charge removed. The product resulting from this method is a fine grey powder of remarkable purity.

EXPERIMENTAL WORK

A number of shorter runs were made to determine the extent of the reduction of the oxide. The apparatus used was an electric muffle of the ordinary type equipped with a silica tube. Several runs were made using a nickel container for the oxide but in every case the nickel crumbled and fell in pieces on removal of the charge. It was so mixed with the tungsten that recovery of the latter was impossible. Following this^a number of runs were made using a porcelain combustion

boat. Two of these were filled with WO_3 and placed in the furnace. Hydrogen was passed through to sweep out any air that was in the apparatus and the current turned on. A temperature of 1100 deg. was used for the runs as the heating elements would not stand a higher temperature.

The results for a few of the more representative runs are given in Table 4. In all cases the procedure was the same.

TABLE NO. 4

Run No.	Time	%Reduction	Remarks
1	1½ hrs.	50.8%	Front boat showed 59.5% reduction
2	1 hr.	42.4%	Grey powder - little caking.
3	2 hrs.	62.7%	Good metallic lustre
4	3 hrs.	97.9%	Fine homogenous grey powder. Metallic lustre.

The product resulting from the above method was free from carbon and contained nearly 100% tungsten. These results show that a complete reduction could be effected at this temperature and under these conditions in less than seven hours. Of course in this reaction a great deal depends on the method of placing the charge in the furnace. The oxide should be in as thin a layer as possible so as to expose the greatest surface. The charge shrinks markedly

during the reduction and the final volume is less than half of the original. I would not recommend the placing of the oxide more than $\frac{1}{8}$ inch deep, as the time for reduction will be increased far out of proportion to the amount of product.

It would be desirable to find some material that would stand this high temperature well and yet have a minimum amount of breakage. Some high temperature alloys such as a ferromolybdenum would make perhaps the most satisfactory containers for the charge. Porcelain is not practical for this purpose as the breakage is too high.

Where hydrogen is available in a large quantity it might be profitable to operate this process. The advantages over the carbon method are obvious. There is no treatment necessary to remove the excess reducing agent and there is therefore less handling. The heating costs would run about the same as those of the carbon, but would vary widely according to the location.

Several runs were also made using illuminating gas as the reducing agent but no satisfactory results were obtained. The reduction to metal did not proceed to any marked extent at the end of four hours and the product was contaminated with carbon resulting from the cracking of the hydrocarbons in the illuminating gas. There was, however, a large proportion of one of the lower oxides of tungsten formed which gave the product a deep blue color when water was added. The blue

particles were so fine as to be unfilterable.

Whether or not a gas having a higher proportion of hydrogen to carbon would effect this reduction without the formation of carbon remains to be seen, but as long as there are plants putting out an excess of hydrogen (i.e. an electrolytic oxygen plants) there is little need of using illuminating gas for a reducing agent.

Suggestions for Future Work.

In connection with this problem there has arisen in my mind several possibilities, as far as future work is concerned. Some of them may be carried out on a laboratory scale while others deal with the large scale production.

The possibility of using some other gas such as natural or illuminating gas for a reducing agent seems possible should the cost of hydrogen become prohibitive. To be sure, the results obtained in this work ~~were~~^h using one of these agents (illuminating gas) did not meet with very marked success. However there still remains the possibility of trying a method of pre-cracking the gas (which is really made up of a wide variety of hydrocarbons) into simpler compounds having a smaller proportion of carbon to hydrogen. Undoubtedly some sort of a preheating apparatus could be designed which could effect this cracking and remove the free carbon formed. This also suggests the possibility of lampblack as a by-

product in the manufacture of tungsten.

A natural gas containing a large percentage of methane, CH_4 , might be suitable, although the known properties of methane seem to show that reduction would be next to impossible since methane is a very stable compound. Heating with strong oxidizing agents has little or no effect on its decomposition even at high temperatures.

The use of carbon monoxide is another possibility --- possibly there is another use for blast furnace or producer gas here. At any rate I think it would be worth while to test out the possibilities of a pure CO or a CH_4 mixture. Little or no idea of the behavior of CO with WO_3 can be gained from the reduction with carbon, as the latter reaction is evidently one where all the oxygen for the CO_2 comes originally from the oxide. In the reduction of many substances it has been found that the reduction is really due to the CO in the reaction and not directly to the carbon. This case is found to be true in the blast furnace production of pig iron.

The use of catalysts has never been touched on in connection with this reaction. Little is known of the adsorbing properties of either metallic tungsten or of tungstic oxide, and therefore little is known of the reducing reaction in the presence of catalysts.

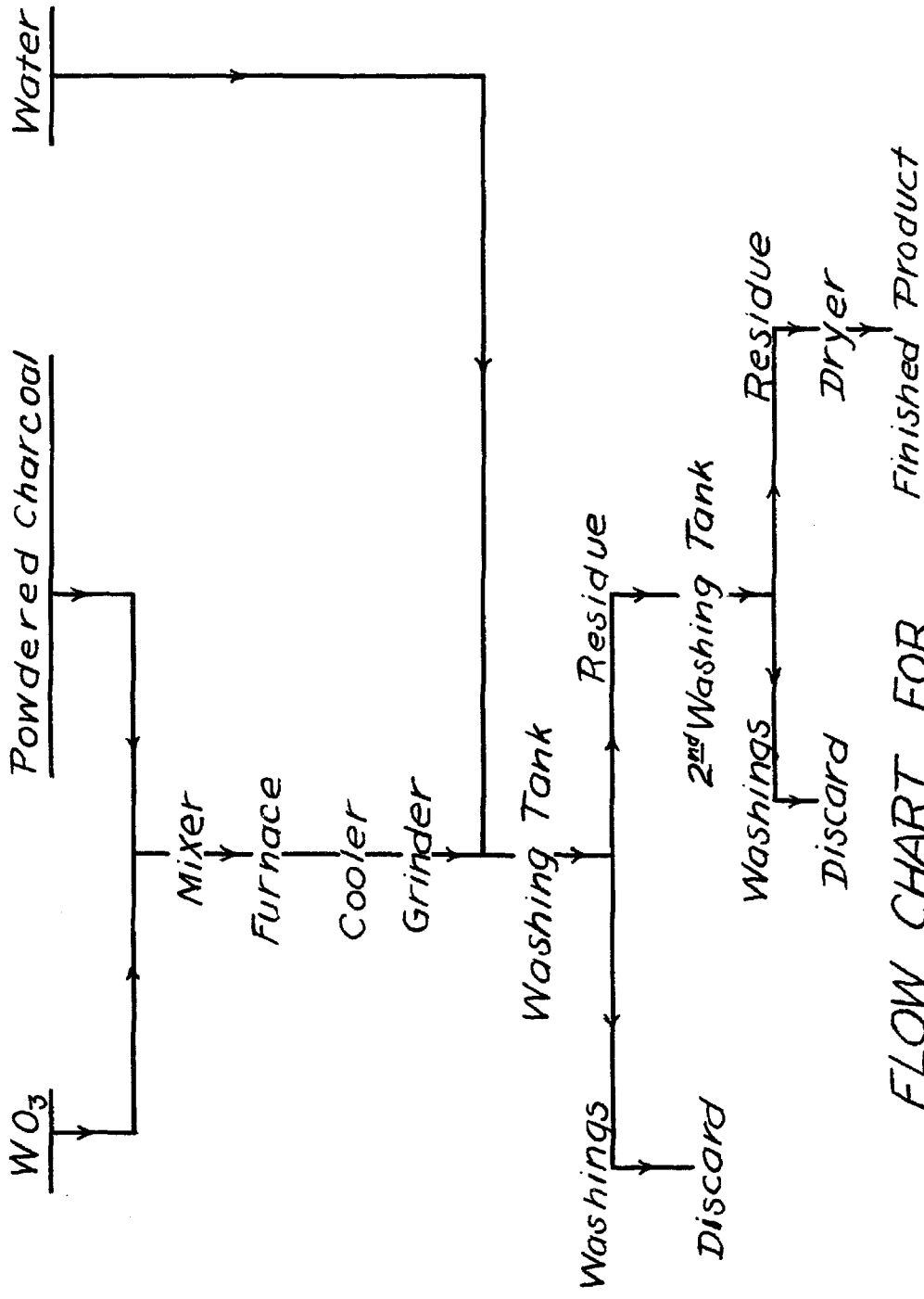
The formation of the blue oxide by the reduction with illuminating gas suggests the possibility of a new product. The blue was of a deep clear shade and was formed in a colloidal form. If a suitable adsorbing agent could be found for this compound there might be a future in using it as a dye or a pigment for special purposes. Its deposition on the sides of a test tube giving a clear, even, color may indicate a possible use in making blue stained glass. A gradual shading into the yellow WO_3 could be produced by careful heating in the presence of a limited amount of air.

It would be interesting to know the action of some of the powdered metals such as aluminum on tungstic oxide. There is a possibility there of a new method of reduction which would give a satisfactory product for most purposes.

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FLOW CHART FOR PRODUCTION OF TUNGSTEN FROM TUNGSTIC OXIDE