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The Separation of Tungstic Oxide from Scheelite and its Subsequent Reduction with Hydrogen

Dave Jones

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THE SEPARATION OF TUNGSTIC OXIDE FROM SCHEHELITE
AND ITS SUBSEQUENT REDUCTION WITH HYDROGEN

by
Dave Jones

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

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BUTTE, MONTANA

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INTRODUCTION

In 1871 K. W. Scheele isolated a new acid from the mineral now called scheelite, a naturally occurring calcium tungstate. This mineral, prior to Scheele's discovery, was termed tungsten; consequently, the acid was called tungstic acid. In the following year Bergman detected the acid in wolframite and the element, tungsten, and some of its compounds were prepared in his laboratory. Tungsten was destined to be called one of the rarer metals until Oxland\(^1\) in 1847 developed and patented a process for the manufacture of tungsten, tungstic acid, and sodium tungstate from Cornwall cassiterite which carried small percentages of tungstic oxide. Oxland\(^2\) was granted another patent in 1857 which dealt with the manufacture of iron-tungsten alloys. This patent forms the basis for the preparation of the alloy used in the modern high-speed steels of today. Tungsten attained its true place in the industrial field when it was found that the metal was superior in all respects to carbon for use as a filament in electric incandescent lamps and this position was further enhanced by its use in the alloy steels.

The ores of tungsten are few in number, the most important ores being of the isomorphus series of the tungstates of iron and manganese. When the mineral contains less than twenty per cent manganese tungstate, it is termed ferberite, and when it contains more than 80 per cent manganese.

1. British Patent 11848, 1847
2. British Patent 3714, 1857
tungstate it is termed hubernite, the balance in each case being iron tungstate. When the percentage composition of the mineral varies between the above limits, the mineral is termed wolframite. All of the mineral of this series are sold under the trade name of wolfram. Wolframite is usually black, with a hardness of 5½ and a specific gravity of 7.5. Scheelite is the only other important ore mineral of tungsten, but it is found in considerably lesser quantities than wolfram. Scheelite ranges in color from white to brown with a specific gravity of 6 and a hardness of 4½.

The largest known deposits of tungsten ores occur in the continuation of the Indo-Malayan Mountains, which extends through Burma, Malaya, China, Japan, and Chosen. Production of tungsten concentrates was started in 1910 in Burma, and in 1911 this country was the world's largest producer. China produced but little until 1916, but has since supplied over fifty per cent of the world's requirements.

The South American deposits are found in Bolivia and Argentina. These deposits are very extensive but owing to their low tungsten content, they have never been developed.

Tungsten is widely distributed in the United States, being often associated with gold ores. The largest deposits occur in Colorado and California. It is also found in Canada, the producing districts being in New Brunswick, Nova Scotia, and the Yukon.

Australia today produces most of the scheelite on the market, but this amounts only to a small proportion of the total tungsten concentrates that are produced. The scheelite
is associated with molybdenite and bismuthenite in Queensland. Large deposits of scheelite have also been found in Tasmania.

The production of tungsten in Europe represents only a small portion of the total world output. Wolframite is found in association with cassiterite at Cornwall, but it has never been more than a by-product of the tin industry. The largest deposits in Europe are in Portugal, however, its occurrence is noted and sometimes exploited in Spain, Russia, Germany, and Sweden.

Tungsten ores never occur in a massive form. The ores are found in narrow veins, frequently associated with cassiterite, molybdenite, and bismuthenite, and in granitic intrusions of granites and of metamorphic rocks. The tungsten content of the ore mineral generally runs from 0.5 to two per cent, although in rare cases it has amounted to six per cent. The concentrates obtained by crushing and tabling the ore contain 60 to 70 per cent $WO_3$. Where tin minerals are present, a separation can be effected by making use of the magnetic properties of wolframite. Scheelite, however, is nonmagnetic but in the case of its occurrence in Tasmania, the gangue garnet is magnetic which allows a simple method of recovery. The concentration of wolframite ores is troublesome because the wolframite has a micaceous structure, and fine crushing causes high tabling losses; therefore, the ore should be concentrated in as coarse a form as possible. Scheelite causes no trouble in this respect since it does not have a laminated structure. The only major im-
purities contained in tungsten ore concentrates are calcium, silica, manganese, and iron.

There are three types of deposits which lend themselves to different types of mining: loose surface deposits that are the results of the weathering of the tungsten-bearing granite, partly disintegrated veins near the surface, and deeper veins from which the mineral can only be extracted with high costs. At present the main type of deposit being worked is the former.

Tungsten is in many respects a metal of extremes. It has the highest melting point of any of the metallic elements, the highest modulus of elasticity, the lowest vapor pressure at any temperature, and the lowest coefficient of thermal expansivity. Tungsten was considered at one time to have a very low tensile strength; however, since the metal has been produced in a coherent form, it has been found to have the highest of all of the elements, its tensile strength being in excess of 600,000 pounds per square inch in the wire form. This coherent tungsten is formed by a combination of heat treatment and mechanical work on the powdered metal. Before this coherent form was developed, tungsten was regarded as one of the most brittle of the metals; today it can be drawn into very fine wire. Tungsten also has a very high specific gravity, the average being 19.32.

Tungsten has four isotopes with the respective atomic weights of 182, 183, 184, and 186. The value accepted at the average atomic weight is 184. Tungsten has valences of
2, 3, 4, 5, and 6. The atomic number of tungsten is 74.

Tungsten has three major general uses in the industrial field:

(a) Tungsten compounds employed in the arts as mordants, pigments, etc.

(b) Crude tungsten metal, generally in the form of powder for making ferrotungsten and tungsten alloys.

(c) Pure tungsten, in the form of sheet, rod, or wire, for use in lamps, thermionic valves, X-ray tubes, etc.

Although the greater part of the ore that comes to the market today is consumed by the first two groups, the great importance that tungsten has assumed, both industrially and scientifically, is due to the work directed to the production of pure tungsten for use as a filament in electric lamps.

As the high melting point of tungsten (3370°C.) precludes the casting of the metal, and the fact that even after casting, the metal is very brittle, it is an exceedingly difficult problem to shape the metal for a durable lamp filament. Just and Hannaman¹ in 1904 developed and patented a process for making tungsten filaments. The process consisted of mixing pure tungsten powder with an organic binder, extruding the paste through a die and then heating to remove the binder, thus leaving behind a pure tungsten filament. This method produced tungsten in the shape of a fragile wire. Another interesting attempt was made by Kuzel² who formed a gelatinous pasty mass of metallic tungsten by striking an arc

¹ British Patent 23899, 1904
² British Patent 7655, 1904
between tungsten electrodes under water. The material contained no binding medium, but was sufficiently plastic to be extruded through a die into fine threads. A single wire of crystalline tungsten was formed when this fine thread was heated to a high temperature in hydrogen, the heating being accomplished by electric current. Many other methods for making suitable tungsten filaments were attempted, one being the use of amalgams. An amalgam of cadmium-mercury was mixed with tungsten powder and the paste then formed into a wire, the amalgam being removed by thermal means. Another method was the making of nickel-tungsten alloys which were drawn into wire, and the nickel being subsequently removed by volatilization. These wires all have the same disadvantage as the previous one in that they are very fragile.

It was not until 1909 that Coolidge\(^1\) was successful in making ductile tungsten from the metal powder. By suitable heat treatment and mechanical work he accomplished the feat of making a ductile lamp filament.

In all of the previous processes another material to act as a binder was employed to give to the powder a state of plasticity. This was subsequently removed by some chemical or thermal means, leaving a filament of pure tungsten which was suitable except for its brittleness. Obviously, the trouble was that the metal was not in a coherent form. The problem of making ductile tungsten was therefore not a problem of purifying the metal but having it in the proper physical

\(^1\) British Patent 23499, 1909
form. By using a sufficiently high temperature to start with, it was found that if the metal was subjected to mechanical work, its ductility was increased until finally it became so ductile that it could be rolled, or drawn into wire, at room temperatures.

PREPARATION OF TUNGSTIC OXIDE

The first step in the production of pure tungsten is the preparation of the oxide. It is therefore necessary to separate the oxide from the other constituents of the concentrate. As tungstic acid is insoluble in acid solutions, the separation is effected by filtering the precipitate formed by acidifying soluble tungstate solutions. When this precipitate is dried below 170° C., it contains about seven per cent water which approximates the theoretical proportion for tungstic acid, $H_2WO_4$. The anhydrous oxide is obtained by calcining the acid at a dull red heat. The industrial methods of the extraction of the oxide from the concentrates are roughly divided into two classes: those dealing with wolframite, and those treating scheelite, although in some cases, the process is applicable to both. The method of separation and the degree of purity of the final oxide product have important influences on the nature of the metallic tungsten resulting from treatment of the oxide.

The preliminary treatment of scheelite almost always consists of direct decomposition with mineral acid when the calcium goes into solution, and the tungstic acid, together with insoluble impurities like silica, remains as a sludge. The reaction is represented by the equation:

$$CaWO_4 + 2HCl = WO_3 + CaCl_2 + H_2O.$$
The digestion is carried out in enamelled iron pans, eighteen inches square and eight inches deep. Ten liters of muriatic acid are placed in these pans and heated to 80°C., and six kilograms of ore mixture are stirred in. The temperature is maintained for four hours with frequent stirring. After this period of digestion, fifteen to twenty liters of water are added and the mixture boiled. On cooling the heavy tungstic acid settles readily, and the liquid is then decanted. The tungstic acid is washed once with boiling water, and when dried contains about 98 per cent WO₃, the chief impurities being iron, calcium, and silica.

Tungsten forms a series of volatile chlorides and oxychlorides when subjected to heat in the presence of chlorine or some volatile chloride. This property forms the basis of another method of separating tungsten from its ores. The most important of these compounds are the hexachloride, WCl₆, boiling point 347°C., and the oxychlorides, WO₂Cl₂ and WOCl₄, both of which are volatile below 300°C. All of these compounds when added to water hydrolyze and yield insoluble tungstic acid.

An electrolytic method for the production of sodium tungstate from wolframite has been developed but has not been found economical for industrial application. The cell is an inverted bell jar. The anode is a plate of nickel or a twelve per cent Mo-Ni alloy, placed horizontally at the bottom of the jar. The electrolyte is a twenty-five per cent solution of caustic soda. A paste, made by mixing ground wolframite and the electrolyte, is spread on the anode. The
cathode is any resistant metal such as platinum. On the passage of current through the cell, oxidation takes place at the anode, iron and manganese being converted into the insoluble oxides, Fe$_2$O$_3$ and Mn$_3$O$_4$. At the same time the tungstic acid goes into solution in the electrolyte as Na$_2$WO$_4$.

**PURIFICATION OF TUNGSTIC ACID**

The crude tungstic acid or sodium tungstate contains up to two per cent impurities which should be removed. If the crude product is to be used in the manufacture of ductile tungsten, the highest possible degree of purity is necessary. These impurities will vary some, due to the constituents of the ore and the methods of separation, but as a general rule they are silica, manganese, iron, calcium, titanium, tin, molybdenum, and sodium. The quality of the finished product is dependent upon the purity of the oxide reduced. It is a relatively easy matter to reduce the total impurity to 0.1-0.05 per cent, but rather lengthy and difficult methods are required to lower this percentage or to remove the last traces of the impurities.

One method of further purifying the crude oxide is by further solution and reprecipitation of the $\text{H}_2\text{WO}_4$. The difficulty encountered is with the physical state of the precipitated acid. Precipitated $\text{H}_2\text{WO}_4$ from soluble tungstate solutions by HCl is exceedingly difficult to separate from the accompanying chloride solution due to the state of subdivision of the acid. Both the color and the state of subdivision are determined by the conditions of the precipitation, and vary over a wide range. The use of hot concentrated
solutions is suggested; however, this purification method is not recommended due to the difficulties of filtration. The precipitate carries some impurity down with it; also some NaCl is contained in the precipitate. It is almost impossible to completely wash this sodium chloride from the precipitate, yet it is imperative that this be removed because it has a detrimental effect on the reduction of the oxide as will be explained later.

Another method of purification is the precipitation as calcium tungstate. The soluble sodium tungstate is agitated and an excess of calcium chloride solution is added. The white precipitate of CaWO$_4$ is washed by repeated decantation with water. This calcium tungstate is run into a constant boiling hydrochloric acid solution; the resulting coarse yellow tungstic acid being recovered by filtration.

The method suggested for the removal of alkalis, which are difficult if not impossible to remove from the acid by ordinary chemical means, is an electrolytic process. An electrolytic cell consists of a porous pot filled with crude tungstic oxide, made into a paste with the electrolyte, and a platinum rod inserted as an anode. The cathode may be of lead, and sulphuric acid (sp. gr. 1.2) forms the electrolyte. A current of three amperes is passed through the cell, which requires about five volts. Oxidation occurs at the anode, and iron, manganese, and the alkali metals are converted into the soluble sulphates which the tungsten is slightly oxidized but remains insoluble. The wash oxide is then transferred to a porous pot and forms the cathode of another cell having
a lead anode. Arsenic, sulphur, and silica go into solution while the oxides of tungsten are reduced to a lower form. The electrolyte is chosen with regard to the impurities to be removed, as, for example, oxalic acid for the alkalis, or hydrochloric acid for iron.

REDUCTION OF THE OXIDE

The high melting point of tungsten prohibits its manufacture in a cast state. At the present time refractories have not been developed to the point where they will withstand these high temperatures, and even if they were, cast tungsten is too brittle to have any industrial application. All the tungsten produced today is in the powder form, although it may be sintered together. The methods of reduction are varied and differ in the purity of the final product. Tungsten powder is used for two distinct purposes: the manufacture of tungsten sheet, wire, etc., and for alloying with other metals. In the first case, purity is absolutely imperative. For alloying, a less pure product may be employed. In the case of a pure final product, hydrogen has lent itself so well to the conditions that it is universally used for the reduction of tungstic oxide to pure tungsten powder.

In the technical reduction of the oxide, the material passes through all stages of oxidation before being reduced to the metal. The distinctive color of the three oxides:

\[ \text{WO}_3 \text{---------yellow} \]
\[ \text{WO}_5 \text{---------deep blue} \]
\[ \text{WO}_2 \text{----------chocolate brown} \]

make their recognition easy, and if the reduction were to be
stopped at intervals and the material examined, these changes in color would be found to occur progressively as the reduction proceeds. The final equation for the whole reduction may be stated as

\[ \text{WO}_3 + 3\text{H}_2 = \text{W} + 3\text{H}_2\text{O}. \]

From this equation, it can be seen that if hydrogen is being constantly supplied, the gases removed, and the proper temperature maintained, the reaction will go to completion to the right.

The following table\(^1\) shows the stages in the reduction of tungstic oxide:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Appearance</th>
<th>Approximate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>Green blue</td>
<td>(\text{WO}_3 - \text{W}_2\text{O}_5)</td>
</tr>
<tr>
<td>500°C</td>
<td>Intense blue</td>
<td>(\text{W}_2\text{O}_5)</td>
</tr>
<tr>
<td>550°C</td>
<td>Dark blue</td>
<td>(\text{W}_2\text{O}_5)</td>
</tr>
<tr>
<td>575°C</td>
<td>Purple brown</td>
<td>(\text{W}_2\text{O}_5 - \text{WO}_2)</td>
</tr>
<tr>
<td>600°C</td>
<td>Chocolate brown</td>
<td>(\text{WO}_2)</td>
</tr>
<tr>
<td>650°C</td>
<td>Brown black</td>
<td>(\text{WO}_2 - \text{W})</td>
</tr>
<tr>
<td>700°C</td>
<td>Grey black</td>
<td>(\text{W})</td>
</tr>
<tr>
<td>800°C</td>
<td>Grey</td>
<td>(\text{W})</td>
</tr>
<tr>
<td>900°C</td>
<td>Metallic grey</td>
<td>(\text{W})</td>
</tr>
<tr>
<td>1000°C</td>
<td>Coarse metallic</td>
<td>(\text{W})</td>
</tr>
</tbody>
</table>

In the technical reduction a number of factors complicate a relatively simple process. These factors have important

influences on the properties of the finished metal powder. By suitably arranging the conditions of reduction, the product can be made to vary greatly in size. Material as small as one-half a micron in diameter to as large as 500 microns in diameter can be made, but the most modern methods of working tungsten demand a material which averages two microns in diameter. The particle size increases with the temperature of reduction, 900°C, giving a particle size averaging three microns in diameter. To obtain a fine powder, the temperature should not exceed 800°C.

Two methods are in use for carrying out the reduction in hydrogen, one continuous and the other intermittent. In the intermittent method a number of silica tubes, about three inches in diameter and five feet long, are placed side by side in a gas-fired furnace from which they project about six inches at each end. Before being inserted in the furnace, each tube is charged with 800-900 grams of tungstic oxide which is placed in the center of the tube where the temperature is constant. A current of 400 liters of dry hydrogen per hour is passed through each tube. As a safety measure, the unused hydrogen is burned as it escapes at the open ends.

The time of reduction also effects the particle size. It is common practice to reduce the oxide in two separate stages. It is reduced only to the WO₂ stage in the first operation at a temperature not above 700°C. The second stage reduces the WO₂ to metallic tungsten, and the temperature should not exceed 850°C. if a very fine powder is desired. These two periods take a total time of six hours.
The fine metal is more economically produced by the continuous process. The furnace uses two inch iron pipes, twelve feet long. Heat is supplied by fifteen gas burners which are connected to the gas and compressed air lines. The temperature of reduction varies in the tube continuously from one end to the other. Five thermocouples are in contact with the tubes, enabling the operator to maintain any temperature desired. A temperature gradient is maintained so that there are two stages of reduction; the first stage being the reduction of $WO_3$ to $WO_2$, with the temperature being from 500-700°C, the second stage being the further reduction of the oxide to the pure metal. The tungstic oxide is spread in thin layers on nickel or iron boats and inserted in the cold end of the furnace and slowly pushed through the iron tubes against the hydrogen stream. In this process the large amount of hydrogen needed demands that the hydrogen be purified and re-used. The projecting ends of the tubes are water-cooled to allow the boats to be removed without waiting for them to cool.

Tungsten powder was first produced by reducing the oxide with carbon. Before the hydrogen reducing process was developed, this method was used for preparing tungsten for electric lamp filaments. Its use today is for the production of crude tungsten for use in the manufacture of alloys.

Tungsten combines directly with carbon above 950°C, forming two carbides, $W_2C$ and WC. Both carbides are stable up to 2400°C; therefore, the tungsten powder formed will be contaminated with some carbon in the form of tungsten carbide.
For complete reduction of the oxide, a temperature above 1050°C. is necessary. The state of subdivision and the time of heating influence the progress of the reduction as in the case of hydrogen.

The most convenient form of carbon to use is lampblack with as low an ash content as is possible. The tungstic oxide and lampblack are intimately mixed in a pug mill. This material is then placed in graphite or fire-clay crucibles and the covers firmly luted on. These crucibles are then heated to the desired temperature, and the proper time taken to attain these temperatures. The material should be cooled in a reducing atmosphere to prevent reoxidation.

A great deal of experimental work has been directed to the aqueous solutions of the soluble tungstates but the results have not been satisfactory. This electrolysis results only in producing a lower state of oxidation, and the metal has never been prepared by this method.

The salts of pure alkaline tungstates fuse readily without decomposition, and therefore, lend themselves to electrolysis. The eutectic mixture of lithium, potassium, and sodium tungstates melts at 400°C. while the melting points of pure alkaline tungstates lie between 750-950°C. By the electrolysis of fused normal sodium tungstate at 950°C., using a current density of fifteen amperes per square centimeter, tungsten is obtained in the form of a powder. A current efficiency of 60-80 per cent is obtainable. If the temperature is not high enough, the tungsten bronzes have a tendency to form.
In all of the aforementioned processes the tungsten has been produced in a powdered state. This form of tungsten is suitable for the making of alloys, however, for the manufacture of ductile tungsten, a subsequent treatment of the powder is necessary. The powder is first pressed into a rod by a hydraulic press, using pressures up to twenty-five tons per square inch. This rod is then heated in hydrogen to 1000°C. to sinter the powdered metal. This sintered rod or briquette is heated almost to its melting point also in hydrogen. The material is next treated to mechanical work in a "swaging" or hammering machine. This product of the swaging machine is again heated and drawn into wires of the desired form. In all cases the hydrogen is present to prevent oxidation.
EXPERIMENTAL

The laboratory method of separation of tungstic oxide from the concentrate was simple decomposition of the concentrate by hydrochloric acid. A flow-sheet of the laboratory procedure would be expedient at this time.

Concentrate 68% WO₃

\[ \text{HCl} \]

Digestion for several hours at 100°C.

\[ \text{Filtration} \]

\[ \text{Residue SiO}_2, \text{H}_2\text{WO}_4 \]

\[ \text{NaOH to great excess} \]

Digestion for several hours at 100°C.

\[ \text{Filtration} \]

\[ \text{Residue SiO}_2 \]

Discarded

\[ \text{Filtrate} \]

\[ \text{Na}_2\text{WO}_4, \text{NaCl} \]

Boiling HCl to excess

\[ \text{Filtration} \]

\[ \text{Precipitate--estimated at 97% H}_2\text{WO}_4 \]

Dried under 170°C.

\[ \text{NH}_4\text{OH to excess} \]

Evaporation

\[ \text{Dilution with H}_2\text{O} \]

\[ \text{Filtration} \]

\[ \text{Residue ammonium paratungstate crystals} \]

Dried under 170°C.

\[ \text{Reduction with hydrogen} \]

\[ \text{Filtrate} \]

\[ \text{H}_2\text{O} \]

Tungsten Powder
The process is not difficult to follow, although it is tedious. It is recommended that MnO₂ amounting to 0.5 per cent by weight of the charge be added to insure complete oxidation of the iron. The filtration is difficult due to the nature of the precipitated tungstic oxide.

The digestion in all cases was carried on in a seven inch porcelain casserole. The charge of concentrate was approximately 200 grams. To this was added about 400 cubic centimeters of 50 per cent HCl. The casserole was placed on the hot plate and allowed to simmer for several hours at approximately 100°C. The mixture was filtered while hot in a vacuum filter. Some difficulty was encountered in that this hot mixture decomposed the filter papers, but this difficulty was overcome by decantation and subsequent diluting of the pulp and again heating before filtration. The filtrate and the decanted liquid is composed of FeCl₃, CaCl₂, and H₂O and is discarded. The residue contains SiO₂ and also some of the filtrate because the mixture is, as mentioned before, exceedingly difficult to filter and wash.

The residue is then removed from the filter and is again returned to the casserole with a great excess of NaOH added. This NaOH changes the H₂WO₄ to soluble Na₂WO₄, and a separation of the silica from the tungsten salt is effected. The filtration procedure of the soda solution is very rapid if the mixture is filtered while hot. The silica is discarded and the filtrate is treated to precipitate the impure tungstic acid. The filtrate is heated to about 100°C. and boiling HCl is added to the solution. This addition of the HCl
should be as rapid as possible, since the nature of the precipitated tungstic acid is directly dependent upon the way that the acid is added. If the procedure is as above, the precipitate will be a coarse yellow hydrated oxide; but if the acid is added to the filtrate as a cold dilute solution, the precipitate formed will be of a white colloidal nature which flocculates upon heating. The coarse oxide is fairly easily filtered while the separation of the flocculated $H_2WO_4$ from the $NaCl$ solution is almost impossible. This precipitate, whether colloidal or coarse, is difficult to wash, and it is impossible to obtain a pure product by washing and filtration. It becomes necessary to further purify the hydrated oxide if a pure product is desired.

The method employed in the laboratory for the purification of the impure oxide was the crystallization of the tungsten as ammonium paratungstate. The tungstic acid is soluble in $NH_4OH$ with the formation of a hydrated paratungstate, having the general formula, $5(NH_4)_2.12WO_3.xH_2O$. This salt is insoluble in water and can best be prepared by the rapid evaporation of the solution of tungstic acid and ammonium hydroxide. The fine white crystals of the paratungstate are recovered by filtration. This crystallization does not remove all of the iron, and it was necessary to take the paratungstate into solution and recrystallize it. The crystals were decomposed by boiling with 40 per cent hydrochloric acid and again crystallizing. These crystals can also be made to take the form of long slender needles if the conditions of precipitation are so regulated. One precaution to be noted is that the tung-
stic acid becomes insoluble in NH$_4$OH if heated much above 170°C.; that is, the dehydrated tungstic oxide is insoluble in NH$_4$OH but it is still soluble in the sodium and potassium alkalis. The tungstic oxide may be recovered by heating the dried crystals to a sufficiently high temperature to remove the water and ammonia by volatilization.

The laboratory reduction of the oxide was carried on with hydrogen which was generated by the action of dilute sulphuric acid on zinc shavings. The type of furnace used was a small electric furnace which was developed for use in the carbon determination of steel. The tube used was of fused quartz. A charge of ten grams of the purified oxide was placed in a porcelain boat and inserted in the tube. The heating circuit was closed, and the dried hydrogen allowed to flow through the tube. It is necessary to have an entire absence of air in the tube. The hydrogen at the temperatures of reduction would unite with the oxygen of the air to form water and this reaction at these temperatures is explosive. No trouble was encountered in this respect since the hydrogen was constantly passing through the tube during the heating period, and therefore, there was no possibility of air entering. The temperature was maintained for one hour at 850°C.; that is, as soon as this temperature was attained, it was kept constant for one hour. The heating current was turned off after this reducing period but the passage of hydrogen was continued because at this temperature, the reduced metal would re-oxidize in the presence of oxygen. The passage of the hydrogen eliminates the possibility of air coming in contact with the hot reduced metal.
The reduced powder obtained by this reduction was finely divided and black in color. Coarse metallic tungsten was not obtained. Reduction was stopped several times and the different colors of the oxides noted.

In the first laboratory preparation of the oxide the unpurified oxide was inserted in the furnace, and reduction was carried out. The product of this test was a golden-yellow bronze agglomerate. This product is a member of a series of reduction products of the alkali and alkaline earth tungstates. They have been termed "tungsten bronzes" because they can be used as substitutes for bronze-powders. Their intense and vivid colors and their remarkable chemical inactivity make their adaptation to the paint industry possible. This term is applied to finely-divided or powdered metals and alloys such as brass, bronze, aluminum, and copper, which when mixed with a suitable binder such as varnish or amyl acetate, can be used as paints for ornamental and decorative purposes, and for protecting iron, etc., against corrosion.

The color of the tungsten bronzes ranges from golden-yellow, reddish-yellow, purple-red, violet, blue, to bluish-black. As the proportion of tungsten increases, the color of the bronzes changes in the order given. In thin layers, the bronzes are more or less translucent, and the color by transmitted light may be complimentary to that by reflected light.

light. These bronzes are usually crystalline, generally as cubes or needles. Their specific gravity is high, ranging from 6.5 to 7.5. They are insoluble in water; and with the exception of H₂F₂, they are not attacked by the usual acids.

It is a known fact that the low cost producing deposits of tungsten are being depleted. Soon it will become necessary to exploit the other known deposits, and this will cause an increase in the cost of tungsten. This increased cost could be reduced if a cheaper method of reduction was discovered or if the present methods were improved.

Tungsten has a value to civilization very large in proportion to the amount used. Tungsten is available in the crude state at approximately $1 a pound, yet, one could afford to pay $330,000 per pound for it for lamp filaments and still obtain light at the same cost as with carbon filament lamps. Its value in high speed steel is so great in comparison with the quantity used, that during the war, tungsten was classed as the second most important metal, although it was used in lesser quantities than any other metallic element except those belonging to the precious metal group.

It is suggested that this problem of the reduction of tungsten be further investigated. An attempt should be made to reduce the time and the cost of reduction. A suggestion would be that the electrolysis of fused salts be especially studied, with the view in mind to reduce the cost and make the process industrially applicable.
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