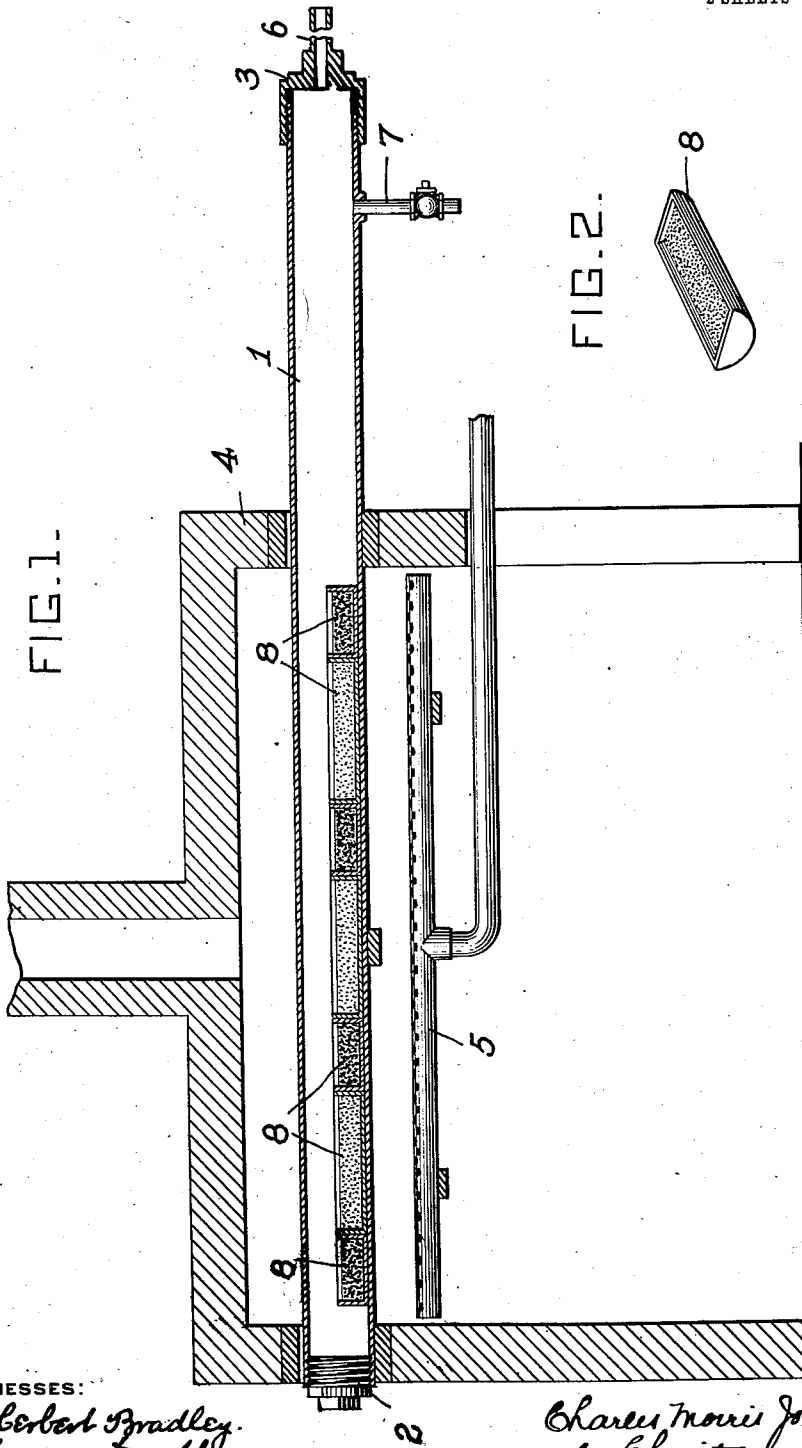


C. M. JOHNSON.
METHOD OF REDUCING METALLIC OXIDS.
APPLICATION FILED JUNE 19, 1909.

964,868.

Patented July 19, 1910.

2 SHEETS—SHEET 1.



WITNESSES:

J. Herbert Bradley.
Theodore Buff.

INVENTOR

Charles Morris Johnson
by Chasity and Chasity
Atty's

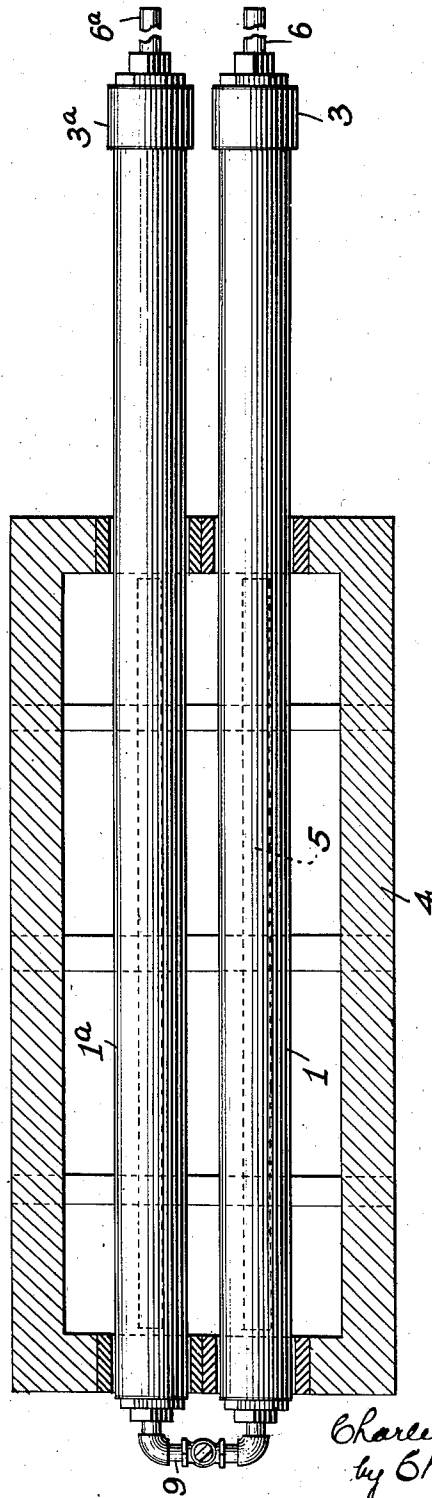
C. M. JOHNSON.
METHOD OF REDUCING METALLIC OXIDS.
APPLICATION FILED JUNE 19, 1909.

964,868.

Patented July 19, 1910.

2 SHEETS—SHEET 2.

FIG. 3.



WITNESSES:

J. Herbert Bradley
Theodore Duff

INVENTOR

Charles Morris Johnson
by Christy and Christy
Atty

UNITED STATES PATENT OFFICE.

CHARLES MORRIS JOHNSON, OF AVALON, PENNSYLVANIA, ASSIGNOR TO CRUCIBLE STEEL COMPANY OF AMERICA, A CORPORATION OF NEW JERSEY.

METHOD OF REDUCING METALLIC OXIDS.

964,868.

Specification of Letters Patent. Patented July 19, 1910.

Application filed June 19, 1909. Serial No. 503,112.

To all whom it may concern:

Be it known that I, CHARLES MORRIS JOHNSON, residing at Avalon, in the county of Allegheny and State of Pennsylvania, a citizen of the United States, have invented or discovered certain new and useful Improvements in Methods of Reducing Metallic Oxids, of which improvement the following is a specification.

My invention relates to improvements in reducing metallic ores and oxids, and more particularly to the reduction of tungsten oxids, and the object of my invention is to produce metallic tungsten in a commercial manner and peculiarly free from impurities.

Tungsten oxid has heretofore been reduced in a crucible by mixing it with charcoal and bringing the mixture to a high temperature. A difficulty in this operation has been the presence of an excess of carbon, which together with the ash from the carbonaceous material employed, it is practically impossible to eliminate, and which remains as a dross or impurity in the metallic tungsten produced by this operation.

My invention consists in bringing the tungsten ore or oxid to a reducing temperature in a closed chamber in which is contained in addition to the body of ore or oxid to be reduced a body of carbon or other carbonaceous material, separated from bodily contact with the tungsten ore or oxid, and which at such temperature will effect the reduction of the tungsten ore or oxid.

In the accompanying drawings which form part of this specification, I have shown an apparatus in which my improved method may be performed. I do not limit myself to any particular form of apparatus, but a description of this apparatus will serve to explain my invention.

Figure 1 shows in vertical longitudinal section a reducing furnace in which my improved method may be performed. Fig. 2 is a view in perspective and on larger scale of one of the receptacles used in charging the furnace. Fig. 3 shows in plan a modification of the structure.

Like parts are designated by the same numerals in the several figures.

The furnace chamber is shown in the drawings at 1, and as there shown, this chamber may conveniently be formed of a section of iron pipe closed at its opposite

ends by caps 2 and 3. The chamber is mounted in a furnace 4; preferably, removably mounted therein; and I have found it advantageous, though by no means necessary, to have a substantial part of the chamber protrude beyond the furnace wall. Any adequate means of heating may be employed. In the drawings I have shown gas burners, 5.

One head, 3, of the cylindrical furnace chamber is removable, to afford access to the interior, and, as shown, there is a gas vent from the chamber, which in this case is conveniently arranged to pass through this removable head 3, and to protrude in the small pipe 6. In the floor of the chamber I conveniently form a small valve-controlled escape port 7, for drawing off moisture which may collect by condensation within the chamber.

I provide a series of receptacles, which for a chamber of the shape shown are conveniently semi-cylindrical in form and relatively short as compared with the entire length of the chamber, and in these receptacles the materials for the reducing operation are charged. If, for example, the furnace chamber is 9 feet long and 6 inches in diameter, these small receptacles will be of sufficient diameter to permit their ready introduction into the chamber, and in length they may be from 6 inches to 1 foot. Some of these receptacles I fill with the ore or oxid to be reduced; some of them I fill with carbon, or carbon-containing substance, preferably finely divided charcoal. The ore-containing receptacles I conveniently make about one foot long, the carbon-containing receptacles about 6 inches long.

I charge the furnace by introducing in succession a number of receptacles containing the substances requisite to accomplish the desired reduction. Preferably, I first introduce a smaller receptacle filled with charcoal, which will be pushed along to the rear end of the furnace chamber as other receptacles are introduced. Following the carbon-containing receptacle, I introduce a larger receptacle filled with the ore or oxid to be reduced, and after it another smaller carbon-containing receptacle, and so I introduce the receptacles with their different contents in alternation, until I have charged into the furnace chamber all of the material

which I desire to treat, or all that it will hold—preferably so arranging the successive receptacles that each ore- or oxid-containing receptacle shall have a receptacle containing
5 carbon on either side of it.

The gas vent above described will in the charging of the furnace be guarded by a body of carbon-containing material, maintained at oxidizing temperature during the
10 operation at a point adjacent to the vent, so that any entering air which might otherwise reach and reoxidize the furnace charge will as it enters give up its oxygen to this body of carbon-containing material. This result
15 is effected by introducing last of all while charging the furnace a receptacle filled with carbon-containing material.

It will be understood that it is not essential that there be separate removable receptacles for each of the two substances which
20 constitute the furnace charge. One substance may be charged loose into the furnace chamber and the other introduced in receptacles.

When the furnace chamber has thus been charged, I apply heat, until the temperature of the chamber is brought approximately to 1000° C., and I maintain approximately that temperature throughout the operation.
30 At this temperature, the reaction occurs, the carbon in the carbon-containing vessels combines with the oxygen of the air within the chamber to form carbon monoxid which fills the chamber. Carbon monoxid in turn reacts
35 with the tungsten oxid, taking oxygen from the tungsten oxid to form carbon dioxide; and the carbon dioxide, as it is formed, in the presence of carbon, takes up more carbon to form again carbon monoxid. Thus the
40 operation goes on, the carbon combining with the oxygen of the tungsten oxid, until the supply of oxygen thus available is substantially consumed; and, if the initial charge of tungsten oxid was pure, the resultant body will be chemically pure metallic tungsten.
45

It will be observed from the foregoing description that my method is performed within a single uninterrupted chamber, and does
50 not require the forcing of currents of gas to and fro through the apparatus, but that on the contrary the reaction occurs automatically when the method which I have described is followed.

In the foregoing specification I have described what theoretically are the reactions which take place within the furnace chamber. I do not limit my invention by, nor
55 make it dependent upon, the absolute accuracy of that theory. All that is capable of absolute detection by the senses is that when these two bodies of tungsten oxid and carbon are brought to such a temperature in a closed chamber and maintained at that temperature for a sufficient time, the tungsten
65

oxid is reduced at the expense of the volume of carbon introduced, that volume diminishing as the operation proceeds.

During the progress of the operation, gas will be escaping through the small pipe 6,
70 leading through the head 3 of the furnace chamber, and this escaping gas may be ignited as it escapes. The escaping gas is carbon monoxid, which is generated in amounts exceeding what is necessary to maintain the
75 operation, and this escaping carbon monoxid burns to carbon dioxide. The flame so burning at the escape end of the pipe 6 is a means to detect when the operation is completed, for the flame will continue so long
80 as carbon monoxid is generated, but when the tungsten has been wholly reduced and the supply of oxygen is gone, the flame will fail.

When the reduction is brought to completion, as will be detected by the fall of the flame at the vent from the furnace chamber, the heat is cut off, and the furnace and its contents allowed to cool before the charge
90 is drawn. During this time of cooling the vent 6 will be plugged, to prevent the ingress of air, which otherwise freely entering would tend to reoxidize the product before it has become sufficiently cool to resist such oxidation.
95

Instead of allowing the excess of reducing gas to escape freely as described, I may utilize it to reduce a further body of oxid, as illustrated in Fig. 3. The vent 6 of chamber 1 is there plugged, but the chamber opens
100 through a valve-controlled passage 9 to another like chamber 1^a, also heated, and the carbon monoxid escaping into this second chamber there reacts with a further charge of oxid; and from chamber 1^a, any excess of
105 gas escapes at the vent 6^a. The charge in chamber 1^a may be entirely of oxid, or bodies of carbon-containing material may be present there also if desired.

I preferably prolong the chamber 1, beyond the furnace wall 4 at the end where the gas escapes, as shown in the drawings, because in that arrangement cooling will be hastened and there will be less danger of reoxidization by air which may leak in in
110 small quantities; furthermore there is practical difficulty in making the cap 3 secure if in operation it is subjected to a high degree of heat. When the furnace has cooled below the point where tungsten will take up
120 oxygen, the charge may be drawn, and it will be found that the receptacles in which the tungsten oxid was charged contain metallic tungsten.

It will be understood that instead of cooling the furnace after each operation, the chamber 1 may be made removable (as indicated in Fig. 1) and drawn out on the completion of the operation, to be replaced
125 by another newly charged chamber.
130

The method which I have described as accomplished in the use of the apparatus shown and described may be modified in the following particulars, that, instead of introducing the tungsten ore or oxid entirely separate from bodily contact with the carbon, a certain amount of carbon or carbon-containing material in finely divided form may be mixed with the body of the charge of tungsten oxid; but in such case, the amount of carbon so mixed with the tungsten oxid must not be more than sufficient to accomplish the desired reduction, and there should be present in the furnace chamber an additional body of carbon, bodily separated from the tungsten oxid, which additional body of carbon shall continue the reduction, beyond the point where the carbon which is mingled with the tungsten oxid fails, and shall carry on the operation from that point to the desired conclusion. Thus an excess of carbon in the finished product is avoided.

Instead of the yellow tungsten oxid of commerce (WO_3) I may in like manner use other tungsten oxids and compounds, as for instance, the scale which is formed upon, and has been removed from the surface of tungsten steel, or other steel of which tungsten is a component. In such case, the operation is performed without substantial change from that described, reducing again to suitable metallic form the valuable tungsten containing scale or oxid.

The body of carbon, though preferably in form of finely divided charcoal, may be of any preferred form; finely divided coke may be employed, or even the drillings and filings of irons which are rich in carbon, though I believe these substances less satisfactory.

It will be understood that the operation may be employed not only for obtaining metallic tungsten from the commercial oxid of tungsten, but from the same material I may obtain lower oxids of tungsten in which the oxygen content is relatively small. This will be accomplished by stopping the operation short of the point at which metallic tungsten is obtained. At what point the operation shall be terminated to obtain the desired low oxid may be determined experimentally. Tungsten, like iron, combines with oxygen to form a series of oxids, each of which has its recognized character and commercial uses, the yellow oxid (WO_3) being richest in oxygen. The blue oxid of tungsten, for example (W_2O_5), may be obtained by this process in relatively short time; it has recognized commercial value as a pigment, and may be valuable for other uses.

I have in this specification described apparatus for performing my improved method, but it will be understood that I do not limit myself to the particular apparatus shown, it being only requisite that the re-

ducing operation be performed in a chamber closed to ingress of air, in which is contained, in addition to the body of ore or oxid to be reduced, a separate body of carbon or carbon-containing substance.

It will be understood too, as has been intimated in the body of the specification, that the invention is not limited to the reduction of tungsten, but may be employed in the reduction of the oxids of tungsten alloys, particularly in the reduction of the scale which forms upon tungsten steel; it may also be employed in the reduction of the oxids of other metals, and alloys of other metals, notably vanadium, molybdenum, chromium, and various steels containing these valuable materials, now largely used in tool steels.

It will of course be understood that the temperature of the operation must be suited to the particular substance treated. Molybdenum oxid, for example, is volatile at a relatively low temperature.

The material of which the receptacles are formed in which the furnace charge is placed may vary, and of course the chamber wall may be of any preferred material. I have shown chamber walls formed of iron pipe; it is good material, since the temperature at which the operation is conducted is below the melting point of iron, and the gas within the chamber is during the operation a reducing gas. In like manner, I preferably form the receptacles of wrought-iron, which in the operation is protected from oxidation by the reducing gas, but I may employ some other metal, as nickel for example, or I may employ non-metallic material, as for example fire-clay, fused silica, or porcelain.

When chemically pure tungsten is my end, I preferably do not mix any carbon content with the tungsten oxid, for though the carbon might be wholly removed, some ash would surely remain, but where a less pure though commercially satisfactory tungsten is desired, I preferably mingle carbon with the charge of tungsten oxid and employ a separate body of carbon in the manner already described, because in so doing I greatly shorten the time consumed in the operation.

It will thus be seen that while my method is capable of giving me chemically pure metal, it is so far within my control that I can produce also lower from higher oxids; and further, if it is desirable to have a product containing carbon, I can secure the presence of that element in the desired amount.

In some cases I have found it desirable to introduce into the interior of the reducing chamber, while the operation is in progress supplemental quantities of a gas of a reducing nature, as for example natural gas. These quantities of gas may be introduced from time to time as the operation progresses.

I have found that an excess of natural gas is undesirable in that it tends to produce a

deposit of soot, but in moderate quantities I have found it advantageous in assisting the reduction. Gas may be introduced at the beginning of the operation if desired, to expel the air entirely, and at the end of the operation to exclude the air entirely.

My invention may be more fully understood by explaining certain structural features of the furnace herein described.

It will be found that if tungsten ore or oxid to be reduced be placed in a compact mass within a crucible as in the ordinary procedure, and if the reducing operation be carried on in a furnace chamber of ordinary proportions, great difficulty will be experienced in excluding air, and under ordinary working conditions the product will be inferior because of the deleterious effect of entering air; relatively long intervals of time will be consumed in the heating and cooling of the furnace which is economically a disadvantage in itself, and incidentally affords the opportunity for the ingress of air in larger and more deleterious quantities.

The furnace chamber which I employ is elongated in one dimension and made small in cross section, and the charge is in like manner extended to form a long body of relatively small thickness and with relatively great extent of exposed surface, thus, as the drawings show, and as already stated, the furnace chamber may consist of a length of pipe of cast or wrought iron or steel, this pipe being of relatively great length compared with its diameter and lying preferably in horizontal position, and the receptacles for the charge may be boats of incomplete cylindrical form open at one side. The dimensions of the boat as explained above are such as to permit of their ready insertion and removal into and from the furnace chamber.

I am aware that it is not new to reduce metals in furnace chambers having the form of a pipe; but in the prior use of furnace chambers of such form, so far as I am aware, it has been necessary to employ in combination with such furnace chambers, supplemental apparatus to generate reducing gases and drive such gases in streams through the furnace chamber. Now it is characteristic of my furnace, and herein lies my invention, to employ a prolonged furnace chamber and provide it with a vent to the atmosphere of relatively small size; in such an arrangement the reducing operation will proceed when the proper temperature is attained without the necessary assistance of any accessory part or instrumentality.

I have found that my improvements in furnace construction are such that in the preparation of tungsten for the making of tungsten steel it is not necessary to follow the process herein above described, but the old process herein above referred to, and

heretofore found defective and inadequate to give a tungsten of sufficient purity for steel-making, may be employed.

By following the process herein above described a tungsten of great purity may be obtained in my furnace, the purity far exceeding that heretofore readily obtained for commercial purposes, and a purity greater than the conditions of steel manufacture require; but even the old process heretofore found faulty for steel-making may be practiced in my improved furnace; that is to say, the ore or oxid and the carbon-containing material may be mingled and charged in a single mass into the furnace and, proper proportions of ingredients being maintained, a tungsten of sufficient purity for steel-making may be had.

I claim herein as my invention:

1. The herein described method of reducing metallic oxids which consists in inclosing within a single chamber a body of the oxid to be reduced, and a separate body of carbon-containing material, heating the chamber to a temperature at which the carbon will unite with the oxygen of the oxid, and maintaining that temperature until the desired reduction has been automatically effected.

2. The herein described method of reducing oxids of metals of the tungsten-vanadium-molybdenum-chromium group, which consists in inclosing within a single chamber a body of the oxid to be reduced, and a separate body of carbon-containing material, heating the chamber to a temperature at which the carbon will unite with the oxygen of the oxid, and maintaining that temperature until the desired reduction has been automatically effected.

3. The herein described method of reducing tungsten oxid which consists in inclosing within a single chamber a body of the oxid to be reduced, and a separate body of carbon-containing material, heating the chamber to a temperature at which the carbon will unite with the oxygen, and maintaining that temperature until the desired reduction has been automatically effected.

4. The herein described method of producing metallic tungsten which consists in maintaining at a reducing temperature a body of tungsten oxid, together with the body of carbon-containing material bodily separated from the body of tungsten oxid, within a single closed chamber, until the desired reduction is automatically accomplished.

5. The herein described method of reducing metallic oxids which consists in mingling a body of the oxids to be reduced with the quantity of carbon insufficient in amount to effect reduction to the desired degree, and introducing such mixture together with a separate body of carbon-containing material into a closed chamber, and maintaining a re-

ducing to a temperature until the desired reduction has been accomplished.

6. The herein described method of reducing the scale of tungsten steel which consists in introducing a body of such scale together with a separate body of carbon-containing material into a single closed chamber, heating such chamber with such charge within it to a reducing temperature, and maintaining such temperature until the desired reaction is automatically accomplished.

7. The herein described method of reducing metallic oxides which consists in inclosing with a chamber a body of the oxide to be reduced, and a separate body of carbon-containing material, heating the chamber to a temperature at which the carbon will unite with the oxygen of the oxide, introducing into the chamber a body of reducing gas,

and maintaining the chamber at a reducing temperature until the desired reduction has been effected.

8. The herein described method of reducing ore, which consists in heating together in a closed chamber, a body of ore to be reduced and a body of carbonaceous material, and causing the gaseous by-products of reduction to pass to the atmosphere through a prolongation of the closed chamber which is subjected to a temperature lower than the reduction temperature of the main portion thereof.

In testimony whereof, I have hereunto set my hand.

CHARLES MORRIS JOHNSON.

Witnesses:

CHARLES BARNETT,
FRIEDA E. WOLFF.