

UNITED STATES PATENT OFFICE.

ALFRED J. LIEBMANN, OF NEW YORK, N. Y., ASSIGNOR TO NATHAN HOFHEIMER, OF NEW YORK, N. Y.

PROCESS FOR THE MANUFACTURE OF DUCTILE BODIES OF HIGH-FUSING METALS AND ALLOYS OF THE SAME.

1,111,698.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, ALFRED J. LIEBMANN, a citizen of Switzerland, residing at No. 55 West Ninety-fifth street, in the city, county, and State of New York, have invented certain new and useful Improvements in the Process for the Manufacture of Ductile Bodies of High-Fusing Metals and Alloys of the Same, of which the following is a specification.

This invention relates to the production of ductile bodies, masses, rods or ingots of tungsten, molybdenum, titanium, uranium and similar high-fusing metals or alloys thereof. The products resulting from the operation of my invention are designed to be ultimately used in the manufacture of metallic bodies consisting of the above mentioned metals or their alloys for the purposes which the physical and chemical properties of these metals obviously predestine them, as for instance, filaments for incandescent lamps, supporting hooks for such filaments, heating appliances, all sorts of wires and cables which have to stand a very high tension, targets for X-ray tubes or similar apparatus, contacts for magnetos and similar devices where there is a frequent making and breaking of an electric circuit, wire cable, netting and other similar appliances where a high resistivity against chemicals of all kinds, especially acids is required.

My invention consists in the process, more particularly herein described and claimed.

In the following description I shall refer particularly to the metal tungsten, but I wish it to be distinctly understood that it is not to be inferred that tungsten is the only metal to which this invention relates, for it also relates to the metals mentioned above and in general to all high-fusing metals and their alloys.

By means of the present invention, I obtain a compact mass of pure tungsten metal which is ductile without any further treatment and which may thereafter, within certain limits, be treated mechanically the same as steel may be treated mechanically and can be worked in the same manner as steel can be worked, into any required shape or form. Under certain precautions it can even be worked down into exceedingly fine wires which can be used for incandescent lamp

filaments. It has been known quite generally that the final success depends to the largest extent upon the preparation of an ingot or billet of tungsten in which the original crystalline character has been destroyed, or in which the crystalline structure of the tungsten body has been prevented from becoming coarse and the body at the same time becoming brittle.

In carrying out my invention, I take a quantity of metallic tungsten powder and intimately mix it with tungsten tri-oxid WO_3 or some lower oxid of tungsten. It will thus be made possible to obtain a coherent body of tungsten from a tungsten powder of almost any structure whatsoever, thus gaining a distinct advantage over the previous methods known to the art, for as a rule previous investigators have had to confine themselves to material within narrow limits, with regard to its physical or molecular condition.

I have discovered that I can use a tungsten metal powder of almost any size of grain by simply choosing a similar sized grain of tungsten oxid powder which is to be mixed with the metal powder. A further wide possibility of variation is given by changing the amount of the tungsten oxid which is to be mixed with the metallic powder of different coarseness, inasmuch as the larger the size of grain of tungsten metal, the more tungsten oxid of similar grain is to be mixed therewith and vice-versa. So also a still further possibility is given in the free choice of a higher or lower oxid of tungsten which is to be mixed with the metal powder inasmuch as the larger the size of the grain of the tungsten metal, the higher the oxid which is to be used therewith and vice-versa. By the expression "higher or lower oxid" means that the chemical composition of the oxids used may be between WO_3 and W_2O .

In carrying out my invention, it is possible to transform tungsten powders of different structures into such bodies as ingots or rods by simply using a sufficient amount and a sufficient kind of tungsten oxid particles which will be scattered among the particles of powdered tungsten. It is obvious that the dense structure which is desirable in the final ingot suggests in itself the use of a material of not too coarse a grain.

I wish it to be clearly understood, how-

ever, that I have succeeded in producing ingots which may be quite easily worked even from the coarser powder by simply using the proper amount of tungsten oxid of similar grain. As a general rule, I prefer to use a material of fine grain of high specific gravity. In order to destroy the original crystalline character, it is necessary to favor the formation of aggregates of crystals. I have observed that the closer the contact of the single particles, the easier this formation of crystal aggregates will take place. Another means to this end, most naturally is, that the material should be pressed together as closely as possible, therefore I submit the powdered mixture to a very high pressure before subjecting it to further treatment.

In the carrying out of my invention, as one of the initial materials essential thereto, I select a tungsten metal powder which has been obtained by one of the various methods that are well known, but which preferably should not be of too coarse a grain. The volume should be such that if 10 grams of it are tapped in a measuring cylinder, its minimum volume will not be less than one cubic centimeter and its maximum volume not more than two cubic centimeters. I wish it to be clearly understood, however, that it is within the purview of my present invention to use either metallic powders of greater or smaller molecular volume which can be brought into a workable ingot by simply selecting a suitable powdered oxid to be mixed with it.

When a very fine powdered metal tungsten is used, as above described, I mix therewith a tungsten oxid of as fine a grain as can possibly be obtained. The reason for this, is to distribute the particles of powdered oxid as much as possible among the particles of powdered tungsten metal, so that the oxid can be of the greatest help in the formation of crystal aggregates in as many places as possible. Such tungsten oxid is obtained by dissolving commercial pure tungsten oxid first in ammonia water, diluting the solution and then precipitating the tungsten oxid out again by administering hydrochloric acid while at the same time steam is blown through the solution, which should not be very concentrated in order to allow the oxid to precipitate out in as fine a grain as possible. In no case should the size of the grain be coarser than to permit 10 grams of it, when tapped in a measuring cylinder, to amount to more than 3.5 cubic centimeters in volume. If the grain should be too large, these oxid particles would shrink so much in size, that their desired action would be impossible or they might even be detrimental to the structure of the ingot, for the reason that there would be the possibility of the formation of infinitely small holes therein.

I have found by experiment that if the grain is too large, the formation of crystal aggregates is impaired and destruction of the originally coarse crystalline structure is not obtained. For the best result I have found that about 1% of this fine powdered tungsten oxid should be mixed into the pure powdered tungsten metal, and to insure that it is properly distributed the two materials should be passed together through a very fine mesh sieve and thoroughly and intimately mixed together. When coarser particles are used not more than 5% of powdered tungsten oxid should be mixed with the metallic tungsten powder, as I have found that more than this amount of oxid not only is of no advantage but even has a tendency to make the resulting body or ingot brittle. The mixture thus formed is then brought into a steel mold which is capable of withstanding a very high pressure without any of its parts moving one upon the other. This high pressure is necessary to bring the particles of powdered metal and the particles of powdered oxid in as close a contact with each other as possible, in order to facilitate their combined action during the subsequent treatment of the same. The coarser the grain of material used, the higher the pressure should be, but as a rule, I have found that a pressure of about 40 to 50 tons per square inch is sufficient. The mold to be used should be composed of several parts which can be separated from each other very gently and in such a way that the compressed mass or body when exposed by the removal of the parts of the mold does not show any cracks or splits whatsoever. This coherent mass or body is now gently pushed from the supporting plate on to another plate of some heat resisting material, as for instance, tungsten molybdenum, nickel or some composition of high-fusing oxids and is then simultaneously exposed to what I term a combined reducing and sintering operation. In the carrying out of my invention, I have found that this combined operation takes place in such a way that single particles of the powdered metallic tungsten begin to sinter, while at the same time, the particles of powdered tungsten oxid (which are intimately distributed in between and are surrounded by the particles of powdered metallic tungsten) are being reduced. After the oxid particles are completely reduced to metallic tungsten, these particles will also sinter together with the surrounding tungsten particles into an absolutely uniform body of pure tungsten metal which has the desired quality of being ductile. The particles of tungsten oxid act during the combined reducing and sintering operation as some sort of a flux for the other particles of metallic tungsten and gently assist in

the formation of the uniform body of pure tungsten metal having the essential quality of ductility.

The combined process of reducing and sintering must be carried out most carefully but it gives an unlimited number of ways to obtain the final tungsten body in which the original crystalline character has been destroyed.

The combined action naturally will have to be carried on in a reducing agent. The reducing action starts at a comparatively low temperature, that is at dark red, while the sintering process actually starts later and does not progress very far until a very high temperature, even a temperature very near the melting point of tungsten is obtained. According to the invention, it is therefore quite easy to regulate the forming of the ductile body by simply carrying on the combined reducing and sintering operation either at a lower temperature or at a higher temperature depending upon the structure of the original material. If held for a long time, at a relatively low temperature, the reduction of the tungsten oxid will be carried very far, and may even be carried to the complete reduction of the oxid into the tungsten metal before the actual sintering process sets in. On the other hand, by quickly bringing up the tungsten body to a very high temperature, the sintering will set in before the reduction of the tungsten oxid has progressed very far. It can easily be seen therefore, that between these two extremes there is covered every possibility and it is only a question of skill and experience that will determine for each and every material the necessary amount and condition of the powdered tungsten oxid which is to be mixed in with the powdered tungsten metal and the regulation of temperature and other variable facts as hereinafter described, during the combined reducing and sintering process, in order to obtain a compact body of ductile tungsten.

As I have previously stated, the combined reducing and sintering operation can be carried out in any reducing agent, but as a rule I prefer hydrogen. Where pure metal, without oxid is used it is not necessary to employ a reducing agent, as any inert atmosphere or even a vacuum will be sufficient to allow the sintering operation to take place; while in the present invention, the presence of a reducing agent is absolutely necessary.

There is still, however, a possibility of delaying the reducing action as against the sintering action, or to precipitate the reducing as against the sintering operation. If the first should be desirable, the reducing agent, for instance hydrogen, can be diluted by some inert gas, for instance nitrogen, or there might even be added a gas or vapor of oxidizing power, for instance water vapor.

On the other hand, if the reducing action should be precipitated and the sintering action delayed, this can be very easily accomplished by not carrying out the combined operation in a quiet atmosphere of hydrogen, but in a moving current of the same. By this means, the water vapor pressure in the parts directly surrounding the coherent mass will be kept very low and therefore the reduction, which naturally is a reversible operation, takes place much more quickly than if the treatment took place merely in a quiet atmosphere of hydrogen. At the same time the stream of hydrogen which is a gas of very high thermal conductivity will delay the obtaining of a high temperature and thereby work in the desired direction. It has been found desirable in most cases to have a slow speed of the sintering process and at the same time a high rate of reduction, as it is found that thereby the formation of the crystal aggregates is favored and the finally resulting ingot is more ductile than if an opposite procedure is followed.

I therefore carry on the combined operation as a rule in an atmosphere of pure hydrogen which is flowing in a constant stream over the coherent tungsten body. This results in the quick removal of all reaction products, which if left in the immediate vicinity of the material would tend to reverse the action and considerably decrease the rapidity of the reduction. I have found that it is quite necessary to carry on the reduction process to the very end in every case, for whatever purpose the final product is to be used, while the sintering process is not quite so material. It is quite sufficient for some purposes to completely reduce the tungsten oxid in the body and sinter it at a temperature of about 1600° to 2000° C. It is necessary, however, to carry the sintering process much farther, if the final product in view is to undergo great physical tests; as for instance, when it is ultimately desired to produce a filament for incandescent lamps, or a contact for magnetos or other like devices. In these cases, the temperature of the body is brought up as close as possible to the fusing point of the metal itself.

The step of the combined reducing and sintering operation will now be more particularly described.

The plates or boats containing the compressed bodies are pushed into a tube of a suitable material which may be heated by an electric current. I prefer to use tubes for this purpose which are of a non-conducting material such as magnesia, alumina or quartz which are wound with some suitable resistance material as for instance, tungsten or molybdenum wire, nickel wire, platinum foil or other wires of similar nature and a constant stream of hydrogen is

maintained during the entire operation which can be carried out at any temperature between red and a bright white heat, according to the proportion which is desirable
5 between the reducing and sintering operations. As a rule this furnace is kept at a temperature of about 800° to 1000° C. for a period of 15 to 30 minutes for each charge. The furnace structure as above described is
10 similar to that illustrated and described by R. Winne and C. Dantsizen in their article published in the *Transactions American Electro-Chemical Society*, vol. XX, 1911, pages 289-90. Such a furnace is shown by
15 the authors in Fig. 2. in vertical length section. The boat with the compressed body is then gently pushed into a cooling chamber at the end of the heating tube and when cooled the body is clamped at both ends into
20 contacts of an electric circuit over which a bell is placed and through this bell a hydrogen stream is passed. In this apparatus an electric current is passed through the body and the combined operation of reducing and
25 sintering is continued and completed by bringing the body up to the required temperature which is predetermined by the ultimate use to which the article is to be put as previously mentioned. In some instances,
30 I bring the temperature up to as high as about 2700° to 2800° C. This temperature should be reached in progressive steps which are slower when the reducing action is to be completed before the sintering is completed,
35 or quicker when the reduction is to be delayed. As a rule the maximum temperature is reached within about 15 minutes, and upheld for about the same length of time. The cooling off is conducted sufficiently
40 slowly to prevent the air from being sucked in by contraction of the heated atmosphere inside the bell.

The size of the body which I most commonly use is about 8" in length and $\frac{1}{4}$ " square in its cross sectional dimensions. To
45 fully sinter a body or rod of this size, as a rule a current of about 1600 amperes at about 11 volts is required, while a hydrogen stream of 300 to 500 liters per hour is
50 passed through the covering bell. The hydrogen gas before entering the vessel in which the reducing and sintering operation takes place, should be absolutely pure and free of oxygen and at least toward the end
55 of the operation perfectly dry. To this end, I pass it through a series of cleansing and drying devices. The resulting ingot of metallic tungsten is ductile and of an exceedingly fine crystalline structure. No
60 coarse crystals will be found in it, which if present would tend to impair the ductility. Therefore these ingots can be rolled, or drawn by any of the well known methods commonly employed by those skilled in the
65 art in the manufacture of steel, nickel, cop-

per or other metals and thereby they can be transformed into any shape or form desired.

When the ductile body or ingot produced as above described is used for the production
70 of drawn wire for filaments in incandescent lamps, I have observed that the filaments after burning in the lamp for some time show a tendency to develop a coarse crystalline structure and become brittle, especially if such lamps are being burned on an
75 alternating current circuit. In order to prevent this brittleness, I add to the tungsten powder at the same time as it is being mixed with the tungsten oxid, some oxid or mixture of oxids which will tend to lower the
80 vapor pressure of the tungsten and thereby prevent, or at least retard the formation of coarse crystals which are the cause of the extreme brittleness of the wire. It is not
85 necessary to use large amounts of these admixtures of oxids, and as a rule I use no more than $\frac{1}{2}$ % of the combined weight of the mixture of tungsten metal and tungsten
90 oxid.

I have found that titanium or chromium oxid or mixtures of the same give good results, but I do not want to limit myself to these as almost any oxid which has the same
95 tendencies will produce the same beneficial result.

Instead of adding oxids as such, I have found it convenient to add them in the form of another compound of the same metal or
100 metals which will ultimately, especially after being heated, result in the desired oxids. To this end, I preferably use the nitrates which are as a rule easily soluble in water and can be mixed into the tungsten metal and tungsten
105 oxid mixture very conveniently in their watery solution and which when heated dissociate into the oxid and nitrogen oxids which latter are given off as gases.

Having now described my invention, what I claim as new and desire to obtain by
110 United States Letters Patent is:

1. The process for the manufacture of ductile bodies of high-fusing metals, which consists in mixing metallic powder with a
115 powdered oxid of the same metal subjecting the mixture to a high pressure to form a compact mass and then submitting the formed mass to a combined reducing and sintering operation.

2. The process for the manufacture of
120 ductile bodies of high-fusing metals, such as tungsten which consists in mixing into the metallic tungsten powder, about 1% of powdered tungsten oxid, subjecting the mixture to high compression thereby forming a
125 mass of suitable dimensions and then submitting the formed mass to a combined reducing and sintering operation as and for the purpose described.

3. The process for the manufacture of 130

bodies of ductile tungsten which consists in intimately mixing metallic tungsten powder with powdered tungsten tri-oxid forming the mixture into a body of suitable dimensions by compression and then simultaneously subjecting the same to a combined reducing and sintering operation.

4. The process for the manufacture of bodies of ductile tungsten which consists in intimately mixing into metallic tungsten powder approximately 1% of powdered tungsten oxid so that the particles of tungsten oxid are strewn in between the particles of powdered metallic tungsten, forming the mixture into a compressed mass of suitable dimensions and then submitting it to a combined reducing and sintering operation which results in the sintering of the particles of metallic tungsten and the complete reduction of the particles of powdered tungsten oxid to metallic tungsten and subsequently sintering the particles of metallic tungsten so reduced to the surrounding tungsten particles, thereby forming a uniform body of ductile tungsten.

5. The process for the manufacture of ductile bodies of tungsten which consists in intimately mixing tungsten metal powder of substantially uniform grain, with tungsten oxid powder of substantially the same size of grain so that the particles of tungsten oxid are strewn in between the particles of powdered metallic tungsten then forming the mixture into a compressed mass of suitable dimensions and then submitting the said mass to a combined reducing and sintering operation, thereby forming a uniform body of ductile tungsten.

6. The process for the manufacture of ductile bodies of tungsten which consists in mixing with metallic tungsten powder, the grains of which are substantially uniform in size, powdered oxid of tungsten, the chemical composition of which is between WO_3 and W_2O , then forming the mixture into a pressed mass of suitable dimensions

and then submitting the pressed mass to a combined reducing and sintering operation.

7. The process for the manufacture of bodies of ductile tungsten which consists in intimately mixing the metallic tungsten powder of comparatively small size grain with powdered tungsten oxid of similar sized grain, then forming the mixture into a body of suitable dimensions by compression and then subjecting the same to a combined reducing and sintering operation.

8. The process for the manufacture of ductile bodies of tungsten which consists in intimately mixing together powdered metallic tungsten of comparatively large size of grain with powdered tungsten oxid of similar sized grain of an amount not exceeding 5% thereof, then forming the mixture by compression into a compact mass and then submitting the mass to a combined reducing and sintering operation.

9. The process for the manufacture of bodies of high-fusing metals or their alloys, which process consists in mixing into powdered metal, powdered oxid of the same metal compressing the mixture thus obtained into a suitable mold and then submitting the formed piece to a combined reducing and sintering operation.

10. The process for the manufacture of ductile tungsten which consists in reducing and sintering a compact mass of powdered tungsten metal and powdered tungsten oxid intimately mixed together so that the particles of tungsten oxid will be completely surrounded by the particles of tungsten metal, the oxid acting as a flux during the reducing and sintering operation.

In witness whereof I have hereunto set my hand at the borough of Manhattan, city and State of New York, this second day of June, 1914.

ALFRED J. LIEBMANN.

In presence of—

ISABEL R. RICHARDS,
AGNES C. O'CONNELL.