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METHOD OF MANUFACTURING ALLOYS OF TUNGSTEN AND OTHER HIGHLY REFRACTORY METALS RELATED TO IT.

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1,110,303. Patented Sept. 8, 1914.

Fig. 2

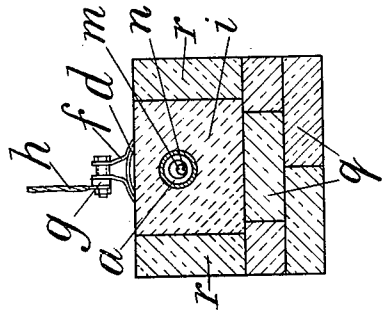
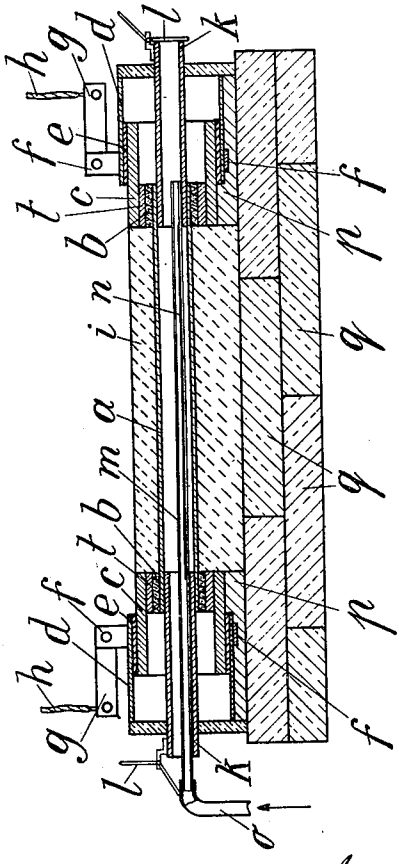


Fig. 1



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UNITED STATES PATENT OFFICE.

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METHOD OF MANUFACTURING ALLOYS OF TUNGSTEN AND OTHER HIGHLY REFRACTORY METALS RELATED TO IT.

1,110,303. Specification of Letters Patent. Patented Sept. 8, 1914.

Application filed August 25, 1908, Serial No. 449,752.

To all whom it may concern:

Be it known that I, HANS KREUSLER, a subject of the German Emperor, and residing at Wilmersdorf, near Berlin, Germany, have invented a certain new and useful Improved Method of Manufacturing Alloys of Tungsten and other Highly Refractory Metals Related to It, of which the following is a specification.

The present invention relates to alloys of tungsten and other highly refractory metals related to it, particularly molybdenum.

More particularly, the invention relates to alloys of these metals with nickel. These alloys have on the one hand a very high percentage of tungsten, molybdenum and the like, and on the other hand the property of being very ductile, so that they can be drawn out into very fine wires. Further, these alloys having a small percentage of nickel have the property that the nickel can be completely removed from them again without it being necessary to fuse them. In addition, the alloys with a high percentage of tungsten and a small percentage of nickel resist the action of acids and other chemical materials in a particularly high degree, so that in many respects they behave like a precious metal.

All these properties accrue to the mentioned alloys only when the percentage of nickel is not less than about 1% and when the percentage of the metal of the tungsten-molybdenum group is not less than about 60%. If the percentage of tungsten is less than the amount mentioned, it is found, for example, that it is no longer possible to drive off the nickel electrically *in vacuo* without the alloy fusing. If the percentage of nickel is less than 1%, the alloy is not sufficiently ductile. Even with 4½% of nickel the ductility of the alloy is still very slight, and only with about 5% and more are alloys obtained which correspond to the highest requirements which can be demanded.

Alloys consisting of 85 to 95% of tungsten and 15 to 5% of nickel, particularly alloys of 90% tungsten and 10% nickel prove to be of very special utility, but a part of the nickel may be replaced by iron or other metals. For example, an alloy consisting of 90% tungsten with 5% nickel and 5% iron is found to be very good.

The tungsten may also be wholly or partially replaced by other highly refractory metals, particularly by those of the tungsten-molybdenum group, such as chromium, tungsten and molybdenum.

The finely drawn wires of such alloys are of special technical importance in the art of making electric incandescent lamps, because they possess great mechanical resistance; they can therefore be easily manufactured into filaments which then are attached to the electrodes and placed in a highly rarefied atmosphere or in a vacuum, and are then heated in such manner by passing through them an electric current that the total quantity of nickel is driven out again, so that a pure tungsten filament is finally obtained. This method is described in more detail hereinafter.

In order to make alloys of tungsten or of another metal related to it with nickel, which have only a small percentage of nickel and which are ductile, the following method is preferably employed: The metal of the tungsten-molybdenum group and the highly refractory metals which in addition are possibly to be incorporated in it are united with nickel to form a uniform homogeneous metallic mass at as low a temperature as possible, and in any event at a temperature below the melting point of the metal of the tungsten-molybdenum group. In order to do this, tungsten and nickel may, for example, be mixed in an exceedingly finely divided state with one another and be made plastic with the aid of a suitable agglutinant, for example paraffin. As small a quantity as possible of the agglutinant is employed. The plastic mass is brought into the form of a small rod and is then gradually heated until the agglutinant is removed again and the metallic powders are baked together forming a rod of sufficient mechanical strength. This rod is then heated further until a quite homogeneous and ductile metallic mass is produced which, however, still maintains the form of the original small rod.

A specially suitable aggultinant is a colloidal solution of a trungsten compound which can be reduced completely to tungsten by hydrogen, for example colloidal tungstic acid, or still better a colloidal plastic mass of tungsten compounds made by

heating dry tungstate of ammonia to about 270° C. and then boiling the mass in water, such as is described in the American Patent No. 956,979, filed June 22, 1907. When such an agglutinant is employed tungsten and nickel in the finest pulverized form, or instead of them still better an oxid of tungsten and nickel monoxid are mixed with the reducible plastic mass of tungsten compounds which serves as agglutinant, and a small rod is made from the mass thus obtained. This small rod may have a length, for example, of from 20 cms. to 30 cms. and a diameter of 1 to 2 mm. for example. The rod dries easily and is then very firm, and is placed in an electric furnace which consists of an electrically heated pipe or tube. The latter may consist, for example, of carbon with a lining of nickel or other material of very great stability in heat, quartz being particularly suitable.

In the accompanying drawing one embodiment of such a furnace is represented by way of example, Figure 1 being a longitudinal section and Fig. 2 a cross-section through the same.

Referring to the drawing, over each end of the heating pipe *a* there is pushed a short, well-fitting carbon tube *b*. The ends of the heating pipe *a*, which are strengthened in this manner, are surrounded by carbon sleeves *c*, the latter being connected with the tubes *b* by a cement *t*, for example a solution of caramel and powdered graphite. Each carbon sleeve *c* is fitted into an iron pipe *d* with intermediate layers *e* of sheet aluminium or copper sheet. On the iron pipes *d* there are clamped flat iron shackles *f* carrying flat pieces of copper *g* to which the feeders *h* are connected. The part of the heating pipe *a* which is left free is surrounded with granulated carbon *i* and is thus protected from burning. Also, in order that the parts near the electrodes, to which the air most easily comes, be not burnt, a pipe *k* is fixed in each end of the heating pipe *a* and these pipes *k* are closed by covers *l* which are only opened when the temperature is being measured with the optical pyrometer or when the tube is being charged, and on one side also during the incandescing process. The intermediate spaces *p* are filled with chamotte and the entire furnace is placed on a layer of fire-brick *q* and is also inclosed at the sides by fire-bricks *r*. The quartz tube *m*, in which the small rod *n* which is to be reduced is situated, is placed into the furnace. A current of hydrogen is supplied through the conduit *o* and the temperature is gradually increased.

The reduction of the rod by the hydrogen then begins. In order to completely reduce it and to obtain a rod which is as uniform and strong as possible, it is preferable to increase the temperature only quite gradually so that after about an hour it has reached about 1100° C., which is well below the melting point of nickel. In order to be quite certain that all the residue of oxygen is removed from the mass and to simultaneously give the rod the sufficient strength, the temperature is then raised again for about five to six minutes to about 1400° C. It is then preferable, for supervising the process, to remove the rod from the furnace after it has cooled. A fairly uniform mass is obtained which now consists solely of tungsten and nickel. The percentage of nickel in the finished body can be calculated in advance and the quantity of nickel monoxid, tungstic oxid, and the plastic mass of tungsten compounds, can be proportioned in such manner that after the reduction a material of quite definite composition is produced.

If the rod shows that the reduction has taken place uniformly and if it shows a uniform structure in all its parts free from cracks, it is placed again in the furnace and heated again in a hydrogenous atmosphere, which serves as a protection from oxidation, to above 1400° C. The temperature which the rod now attains to must be carefully watched, and for this an exact optical pyrometer preferably is used, by means of which the interior of the furnace can be seen through a window arranged at the end of the tube and which admits of the temperature being determined directly by observing the emission of light from the rod, as is generally known to experts in the art.

The temperature is now raised by the current in the heating resistance surrounding the pipe, or, in the event of the pipe itself serving as the heating resistance, the current which flows through the pipe itself, being quite gradually increased with the aid of a variable resistance. The temperature is raised a small amount, say ten degrees, at a time, and each time the rod, after it has cooled, is taken out of the furnace again in order to test the degree of its ductility. That the rod begins to be ductile is shown by the wire being able to be premanently deformed at any one place by bending it, without it noticeably losing in strength at the bend. The degree of ductility is determined by the larger or smaller amount of bending which the wire can stand. Greater degrees of ductility admit of the wire being bent repeatedly to and fro at one and the same place. The number of times which the wire can be bent a definite angle at one and the same place without it fracturing or perceptibly losing in strength at this place may be used as a measure of the ductility.

If, when removed from the furnace, the rod does not yet show the desired ductility, or the highest obtainable ductility for the alloy concerned as determined in a preliminary test, it is placed afresh in the furnace

and heated afresh in the hydrogenous atmosphere to a temperature which is still a few degrees higher, and so on until the desired result is obtained. In the case of an alloy of 90% tungsten and 10% nickel this temperature is, for example, about 1510° Centigrade. In the case of other alloys other temperatures are found at which the desired result is obtained. If the critical temperature is exceeded, in the majority of instances the ductility of the rod is completely destroyed and the rod cannot be made ductile again. Therefore near the critical point, which is ascertained by a preliminary test for a definite alloy, special care is necessary and near this point the temperature is preferably raised only for a very short time by a rush of current which is sent through the heating resistances, whereupon the material is then always tested afresh.

When a rod of the desired ductility is obtained, it can be shaped mechanically by rolling, drawing, hammering and the like. A wire consisting, for example, of 7 to 20% nickel and 93 to 80% tungsten, which has been obtained in the above described manner, may for example be drawn out into the very finest wires, such as are able to be used for the manufacture of metallic filaments for electric incandescent lamps and for many other purposes.

If a body obtained by mechanically working up such an alloy be placed in a very highly rarefied atmosphere, for example in the receiver of an air-pump, and if it be heated by passing through it an electric current, the temperature being gradually increased without it rising to the melting point of the alloy, however, the nickel contained in the body is vaporized again, without the body changing in shape. A body of tungsten possessing the original shape and having a correspondingly smaller percentage of nickel remains behind, or also a pure tungsten body, when the vaporizing process is continued for a correspondingly long time. In this manner it is possible to make solid bodies of tungsten without having recourse to a fusing process. This method can be put into practice particularly easily with wires which are drawn from the alloy. The ends of the wires are connected to the leads connected with a suitable source of electric current, and the entire wire is placed in the receiver of an air-pump, whereupon the air is exhausted until a vacuum exists, and the wire is heated to red heat by sending through it a current, whereupon by gradually increasing the strength of the current the temperature is increased in such manner that the nickel begins to vaporize. When the method is continued for a sufficiently long time a filament is obtained which is perfectly free from nickel and which is excellently suited as a filament for electric incandescent lamps.

For the latter purpose the wire is first brought into the shape suitable for the incandescent lamp, is attached to electrodes, and hereupon is liberated from the nickel by passing through it an electric current. The wire is then placed in the lamp-bulb, whereupon the latter is exhausted and sealed in the manner usual in the manufacture of electric incandescent lamps.

What I claim as my invention and desire to secure by Letters Patent is:

1. A metallic alloy containing more than sixty per cent. of metal of the tungsten-molybdenum group and more than one per cent. of nickel, and having the property of ductility.

2. A metallic alloy containing ninety-five per cent. to seventy-five per cent. of tungsten, not more than fifteen per cent. of nickel and not more than ten per cent. of another metal, and having the property of ductility.

3. A metallic alloy containing eighty-five per cent. to ninety-five per cent. of tungsten and fifteen per cent. to five per cent. of nickel, and having the property of ductility.

4. A metallic alloy containing ninety per cent. of tungsten and not less than five per cent. of nickel, and having the property of ductility.

5. A metallic alloy consisting of ninety per cent. of tungsten, five per cent. of nickel and five per cent. of iron, and having the property of ductility.

6. The herein described method of producing the homogeneous and ductile alloys containing tungsten which consists in making a plastic mass of an oxid of tungsten together with nickel monoxid and a colloidal solution of a tungsten compound which can be reduced completely to tungsten by heating in hydrogen, shaping the mass, drying, and then slowly reducing by heat in a current of hydrogen at a temperature below the melting point of tungsten and subsequently gradually increasing the temperature until the metallic constituents of the rod unite to form a homogeneous and ductile mass.

7. The method of producing homogeneous ductile alloys of metal of the tungsten-molybdenum group and nickel which consists in heating an intimate mixture of said metals to a temperature between the limits at which alloyage takes place and the critical point at which the resulting alloy changes from a ductile to a brittle state.

8. The method of producing homogeneous, ductile alloys of metal of the tungsten-molybdenum group and nickel which consists in gradually heating in an inert environment an intimate mixture of said metals in the form of a coherent article to a temperature sufficiently high to alloy said metals

while preserving substantially the shape of said article, then increasing the temperature by steps in accordance with intermediate tests to secure ductility, and then reducing the temperature.

9. The method of producing a homogeneous, ductile alloy containing about 90 parts tungsten and ten parts nickel which consists in preparing from finely divided materials, an intimate mixture of said metals, gradually heating in a hydrogenous atmosphere to a temperature of about 1510° C., and then discontinuing the heating to prevent destruction of ductility of the alloy.

10. A metallic alloy containing about 85 to 95 parts of tungsten and about 15 to 5 parts of nickel.

In testimony whereof I have signed my name to this specification in the presence of two witnesses.

HANS KREUSLER.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.