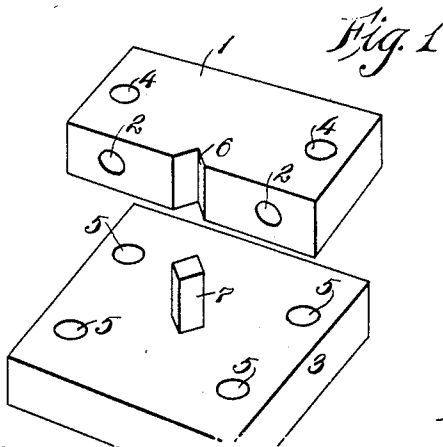
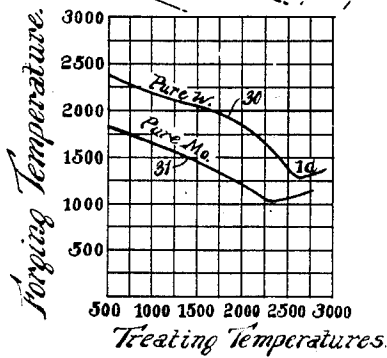
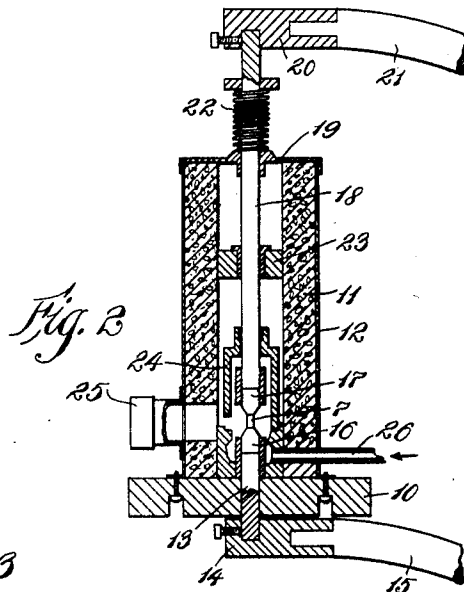
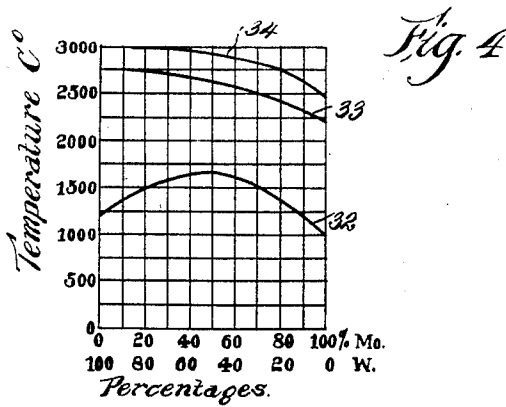


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 ALLOY OF TUNGSTEN AND MOLYBDENUM.
 APPLICATION FILED JUNE 3, 1916.

1,236,384.

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UNITED STATES PATENT OFFICE.

FRANK A. FAHRENWALD, OF CLEVELAND, OHIO, DEDICATED, BY MESNE ASSIGNMENTS, TO THE GOVERNMENT OF THE UNITED STATES OF AMERICA AND TO THE PEOPLE OF THE UNITED STATES OF AMERICA.

ALLOY OF TUNGSTEN AND MOLYBDENUM.

1,236,384.

Specification of Letters Patent.

Patented Aug. 7, 1917.

Application filed June 3, 1916. Serial No. 101,502.

(DEDICATED TO THE PUBLIC.)

To all whom it may concern:

Be it known that I, FRANK A. FAHRENWALD, a citizen of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented a certain new and useful Improvement in Alloys of Tungsten and Molybdenum, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings.

This application is made under the act of March 3, 1883, chapter 143 (22 Stat. 625) and the invention herein described and claimed may be used by the Government of the United States, or any of its officers or employees in the prosecution of work for the Government or by any person in the United States without the payment of any royalty thereon.

This invention relates to a composition of matter containing tungsten and molybdenum together with the process of making the same. Owing to the extremely elevated melting points of these materials it has so far been impossible to alloy either with the other or with any other substance by the usual fusion methods. The present invention relates to the method of incorporating these two metals together without the necessity for fusion, and subsequently, by repeated mechanical working under predetermined temperature and metallographic conditions, to reduce the composition to such a state of ductility, malleability, and tensile strength as shall fit it for use in the arts.

My researches have shown that the strength and ductility of these metals depend upon the fostering of an amorphous condition therein, as against a crystalline condition, and I have discovered that the said amorphous condition, while it can be secured by mechanical working with the somewhat indefinite time and temperature conditions set forth in the Coolidge Patent No. 1,082,933 dated December 30, 1913, can be secured far more exactly and positively by a system of heat treatment using times and temperatures much different from those suggested in that patent; and as regards the production of a composition containing both tungsten and molybdenum, such metallo-

graphic control is absolutely prerequisite to the obtaining of a practical material.

It has for some time been suspected that the elasticity and tensile strength of metals were due largely to the occurrence of such metals in an amorphous form, and these qualities were seriously impaired by their occurrence in or reversion to a crystalline form. One indication of this resides in the fact that crystalline metals when fractured always break across crystals, and never where the adjoining crystals meet. For this same reason, metals having large or coarse crystalline texture are always far inferior in strength to those having a fine grained crystalline structure. It has also been noted that the crystalline structure can be broken up by suitable mechanically cold working so as to increase the amorphous condition and with it the strength of the material. Following the studies of Rosenhain and Ewing (*Philosophical Transactions*, Vol. CXCI, page 355—1900; and *Proceedings of the Royal Society*, Vol. CXC, page 85—1899) my researches show that upon the occurrence of the necessary mechanical stress each crystal becomes sheared into a larger or smaller number of leaves or plates which slide one upon the other, the metal along these lines or planes of shear being temporarily liquefied by the strain and changed from the crystalline to the amorphous condition, this amorphous material thereafter binding the crystal plates together as a kind of cementing material which is both harder and stronger than the crystalline material which it surrounds. (See *Transactions of the American Institute of Mining Engineers*, February 1916, pp. 103—149.)

Ordinarily this distortion is not carried to the stage at which the crystals are completely converted to the amorphous form, and hence the mass consists of one component in two phases, one of which is in a metastable condition. In the case of ordinarily undercooled liquids, the presence of the stable (crystalline) form tends to produce true equilibrium immediately, but in the case of metals, the sluggishness of the molecules at temperatures so far below their normal melting point under normal pressure

as our ordinary temperatures prevents this transformation. However if the temperature be raised considerably, even to a point short of complete fusion, the kinetic energy of the molecules rises until, at a certain point, the fragments of crystals which remain are able to impress their orientation upon the molecules of the amorphous substance and thus slowly restore it to the crystalline condition. This restoration may be effected either by the subjection of the material to a high temperature for a short time, or to a comparatively lower temperature for a longer time, just as the "temper" of a steel tool may be "drawn" either by subjecting it for a few minutes to the action of the fire or by allowing it to lie in the sunlight for a few days or weeks.

It will be evident from the foregoing that for each metal there must be a critical time-temperature relation, above which the kinetic energy of the molecules is so great as to permit their returning at once to the crystalline form when displaced by mechanical distortion, and below which, mechanical workings will produce a permanent amorphous condition.

If force be applied to any crystalline metal at any temperature sufficiently elevated so that the kinetic energy of the molecules is able to restore a crystalline condition after the withdrawal of the force, no permanent amorphous condition of the material is secured. It is not even certain that even a temporary amorphous condition results, though it is probable that such is the case during the time that the force is actually exerted; however the equiaxing forces are exerted immediately upon the withdrawal of the impressed force and the permanent condition of the metal is not at all changed. This operation is called "hot working" and the temperature at which such hot working begins varies for every metal. For example hot working of tungsten does not begin until some 1800° C., but hot working of gold is accomplished only slightly above ordinary room temperatures. If the temperature of the metal is below a certain critical point, then any force impressed from without tending to change the shape or condition of the crystals will produce a permanent change therein with the creation of a permanent amorphous condition, the kinetic energy of the molecules being too small to produce any equiaxing. This operation is called "cold working", and for tungsten this temperature ranges downwardly from about 1800° C. For gold this temperature begins at some point near our ordinary room temperatures. However if such a metal, after being cold-worked for a time, be temporarily subjected to the temperature of hot working the equiaxing effect will be produced and the traces of cold work-

ing will be more or less completely removed depending upon the temperature, the time, and the degree of distortion of the crystals. Thus in the case of a very fine wire or a very thin edge of any metal whatever wherein the process of cold working has been carried out to a very complete extent, the qualities of hardness, stiffness and ductility produced will be accompanied by such an intense molecular strain that a degree of equiaxing will be produced in a shorter time or with lower temperatures than in a case where the crystal structure has not been so completely broken down.

While it is obvious from the foregoing that no amorphous condition can be obtained in any metal by working the same mechanically above its critical temperature, it has also been known empirically that for many metals a certain minimum temperature is necessary for the beginning of the deforming operation since below that temperature the metal will not respond whatever but will break or fly to pieces. This is exhibited by bismuth and antimony at ordinary temperatures; by tin and zinc in winter weather; by iron, steel, copper, gold and nearly all metals at the low temperatures produceable by liquid air. However there is for each metal a range of temperatures, below the critical point where hot working leaves off, during which the crystals retain such a degree of plasticity as to admit of mechanical working with the production of a certain amount of amorphous material and without the immediate return of such amorphous material to the crystalline condition. After the production of this amorphous material has commenced in a more or less uniform way throughout the mass the temperature of the working can be gradually decreased, since the amorphous material appears to prevent the disruption of the metal, and the production of new amorphous material is correspondingly accelerated.

My experiments show that with tungsten, molybdenum and gold the amorphous condition is produced most quickly and in the largest possible degree when the cold working of the metal is commenced at the lowest practicable temperature, although this temperature will vary depending upon the violence of the mechanical forces to which the mass is subjected. Thus if metallic crystalline tungsten is merely forged by hammering between comparatively flat surfaces, a metal will preserve its integrity at a considerable lower temperature than if it be swaged, rolled, drawn or otherwise more vigorously distorted.

I have also discovered by practical experiments (which in this case serve merely to verify the results of logical deduction) that the maximum amorphous condition is secured, and is secured in most uniform

measure, when the structure of the tungsten metal at the beginning of the mechanical cold-working consists of a uniform formation of comparatively fine crystals, and I have found that this uniform fine crystalline structure can be secured, with pure tungsten, pure molybdenum, and with alloys of the two in any desired proportion, by suitable heat-treatment of the material just prior to the beginning of the cold-working. In the case of both of these metals, the reduction temperature is far less than the fusion temperature, wherefore the metallic substances are originally obtained in the form of amorphous powders. These powders, either pure, or mixed in any desired proportion, are compacted into briquets under great pressure (about 200,000 pounds per square inch). I have found that with a tungsten briquet of this nature the most satisfactory crystalline condition was obtained when the material was subjected for about 10 minutes to a temperature of about 2600° C. which resulted in a very finely crystalline mass with many intercrystalline boundaries not clearly defined and appearing to indicate the presence of amorphous material even before mechanical working was begun. If the temperature is increased much above 2600° C. the briquet becomes more coarsely and irregularly crystalline, and at temperatures much less than 2600° the crystalline structure is scarcely sufficiently pronounced to form a good departure for mechanical working.

My researches also show that within certain limits the lower the sintering or heat-treating temperature, the higher is the initial temperature necessary for forging. While, on theory, cold-working is more important than hot-working to produce the amorphous condition desired, yet the cold-working stage must be approached by such slow degrees as shall prevent the destruction of the material in the process; for until sufficient amorphous material has been built into the metal by mechanical working at elevated though constantly decreasing temperatures, the metal will not admit of any cold-working whatever. However it is desirable on theory, and experiment fully substantiates the same, that the lower the initial forging temperature, the more rapid and uniform is the growth of the amorphous condition. I have discovered that with pure tungsten subjected to the heat-treatment above suggested, to wit 2600° C. for ten minutes, the forging temperature is only about 1275° C., which is lower than can be obtained under any other conditions. For practical shop-work I recommend an initial forging temperature somewhat higher than this in case a more violent distortion be secured as by swaging or rolling; say about 1500° C.

With pure molybdenum, the same condi-

tions are present, though the time and temperature required for heat treatment and the temperature required for the forging are both lower than for the treatment of tungsten. I have obtained the best results when a briquet made under a pressure of about 200,000 pounds per square inch was subjected for about one minute to a temperature of about 2300° C., which resulted in a very finely crystalline ingot of rather homogeneous condition. This ingot could be forged like tungsten, though at a slightly lower temperature, approximately 1000° C.

When the ingot is made of a mixture of molybdenum and tungsten metals it is found that the formation of crystallites and crystal growths proceeds in the same manner as with the separate metals, (due to the fact that the same are mutually soluble in all proportions in the solid state) although the temperature representing a certain grain size changes with the relative amounts of the components, as shown in Fig. 4. This temperature bears a somewhat uniform relation to the proportions of the ingredients as is shown by the continuous inclination of the treating-temperature curve, but it is curious to note that the forging-temperature curve bears a completely different relation, being substantially at a maximum when equal parts of the two metals were employed, and at a minimum in the case of the pure materials.

The mixed metals when treated in this way form true solid solution alloys. They possess the qualities of ductility, malleability, rigidity, elasticity and tensile strength in a most remarkable degree, and microscopical examination shows that the ingredients form a complete series of solid solutions, depending however upon mechanical working and not upon fusion due to heat. By the process herein described I have been enabled to produce articles of tungsten, molybdenum, and of their alloys more cheaply and certainly than heretofore and of a more uniform texture and of a high degree of mechanical reliability. These materials, on account of their cheapness, strength, and resistance to corrosion are peculiarly advantageous in many dental, scientific, and philosophical uses.

In many cases one of these alloys of tungsten and molybdenum will be found far superior to either of the metals alone. Thus in dental use, as in dental pins, it is frequently desirable to employ a rod or wire of great stiffness and reliability, yet with a minimum of size, owing to the importance of avoiding unnecessary weakening of the foundation structure. In many respects tungsten appears to form an extremely satisfactory material for this purpose, especially when coated with gold or other non-oxidizable metal as described in my Patent No.

1,228,194, issued May 29, 1917. However the ductile tungsten, even when made with the most extreme care, frequently exhibits treacherous spots where the crystallization system has either reasserted itself or has not been sufficiently overcome. An alloy of tungsten and molybdenum is found to possess even greater strength, hardness and elasticity than either tungsten or molybdenum alone, and responds to the cold-working process in such a way that the treacherous spots are less frequently found than in pure tungsten; also the equiaxing temperature of the alloy is higher than that of either of the component metals, so that the annealing of the same under ordinary manipulation is less to be feared.

In the drawings accompanying and forming a part of this application I have illustrated certain steps and characteristics of the discoveries and inventions hereinbefore described. In these drawings Figure 1 is a perspective view of a part of a briquet mold, illustrating also a briquet from which my improved alloy is made; Fig. 2 is a vertical sectional view through a resistance furnace of the type wherein said briquet may be heat-treated and forged; Fig. 3 is a chart illustrating the relation between the heat treating temperatures and forging temperatures of tungsten and molybdenum separately; Fig. 4 is a similar chart showing the treating and forging temperatures of tungsten-molybdenum series.

Describing the parts by reference characters, 1 represents one side of a briquet mold, with which there is employed a second identical member (not shown). These mold members are secured tightly together by suitable bolts passing into the apertures 2—2, and are secured to a suitable base member 3 by the use of other bolts passing through the apertures 4—5. The adjacent faces of the members 1—1 are notched as shown at 6, and in the mold space thus formed the finely divided metals, after being thoroughly mixed in the proportions desired, are compacted into a briquet 7 by the employment of high pressure as by a hydraulic press or like device.

In Fig. 2 I have illustrated a resistance furnace in which the said briquet is introduced for its next treatment. 10 represents the base of the furnace which may be of fire clay or the like, and 11 the body of the furnace which is also of refractory material preferably embraced by a casing 12. Projecting through the bottom of the furnace is a post 13 preferably of copper secured to a foundation plate 14 to which is attached the electric cable 15. The top of the post 13 is provided with an electrode point 16, preferably of fused tungsten, above which is a second movable similar electrode point 17 secured to the lower end of the bar 18 which

is preferably of copper. The upper end of this bar projects slidably through the cap 19 and is provided with the striking head 20 to which is attached a second cable 21. A coil spring 22 serves to support more or less of the weight of the bar as may be desired, while a suitable sleeve 23 of refractory material inside the furnace restrains the flow of gas therethrough. Other shields at 24 may also be employed if desired. The briquet 7 is introduced between the terminals 16, 17, directly beside an observation window 25 formed in the furnace wall, through which heat determinations may be made by the use of a suitable pyrometer. A reducing gas like hydrogen or an inert atmosphere like nitrogen is introduced by way of the tube 26 and finds its way out through the various apertures. In use the member 14 is suitably supported, the parts arranged as illustrated, and the desired temperature is secured by passing current through the cables 15 and 21 for the time required. The temperature is then allowed to fall to the desired forging point, after which forging is begun by hammering upon the terminal 20, the furnace being allowed to cool in proper degree during and between the forging operations.

After the formation of a suitable degree of amorphous condition under this forging operation, the material can be swaged, rolled, drawn or otherwise worked to the required elasticity, ductility and tensile strength.

In Fig. 3 the curve 30 illustrates the relation between the heat-treating and forging temperatures for pure tungsten, and 31 the similar relation for molybdenum. In each case it will be seen that the curve exhibits a marked angularity and my experiments show that the most satisfactory metal condition is secured with heat-treatments and forging temperature corresponding to this point. In the case of an alloy of tungsten and molybdenum this minimum forging temperature is increased in each case over its value for the pure metal, its maximum being reached with an alloy of equal parts of the two metals, as shown by the curve 32, Fig. 4. In this figure 33 represents the heat-treating temperature curve, which for each alloy composition is that which permits of the lowest forging temperature, and 34 represents the assumed fusion temperature under ordinary pressure conditions.

After the alloying of the two metals has begun under the pressure induced, amorphous condition herein described, its growth may be fostered in any of the well known modes, by hammering, rolling, swaging, or drawing.

Having thus described my invention, what I claim is:—

1. In the process of rendering tungsten ductile, the step of first subjecting a briquet

of the finely divided metal to a temperature of about 2600° C. for about ten minutes and thereafter forging the metal beginning at about 1300° C. and working downwardly from the last named temperature.

2. The process of making alloys which consists in compacting under great pressure a mixture of the finely divided metals in the desired proportion, heat-treating the mass until a predetermined crystal development is secured, and finally cold working the mass until the mingled amorphous substances are obtained.

3. The process of alloying two crystalline metals of a highly refractory nature which consists in compacting together under great pressure a mixture of the metals reduced to a very fine state of subdivision, heat treating the mixture until a predetermined crystal

development is secured, forging the mass at the lowest practicable temperature, and finally cold working the mass.

4. The process of alloying tungsten and molybdenum which consists in compacting together under great pressure a finely powdered mixture thereof in the desired proportions, sintering them for from ten minutes and 2600° C. for tungsten to about one minute and 2300° C. for molybdenum depending upon the proportions, forging the mass at a temperature of about 1700° C. for an alloy of equal parts downwardly in each direction to about 1300° C. for tungsten or about 1000° C. for molybdenum, and finally cold working the mass.

In testimony whereof, I hereunto affix my signature.

FRANK A. FAHRENWALD.