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R. D. HALL ET AL.

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CONSOLIDATION OF METAL POWDER

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Fig. 2.

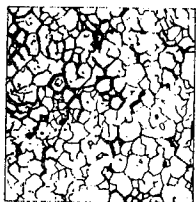


Fig. 3.

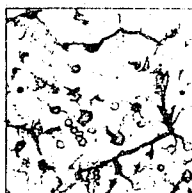
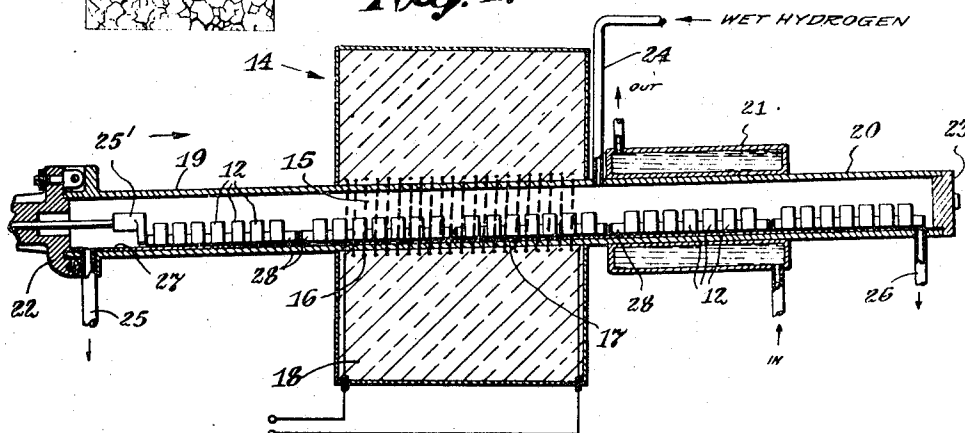


Fig. 1.



INVENTORS
R. D. HALL
J. H. RANAGE
BY *J. H. Ranage*
ATTORNEY

UNITED STATES PATENT OFFICE

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CONSOLIDATION OF METAL POWDER

Roy D. Hall, Pottersville, and John H. Ramage,
Bloomfield, N. J., assignors to Westinghouse
Electric Corporation, East Pittsburgh, Pa., a
corporation of Pennsylvania

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32 Claims. (Cl. 75-22)

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This application is a continuation-in-part of and replaces our application Ser. No. 486,812, filed May 13, 1943, similarly entitled, and our application Ser. No. 511,392, filed November 23, 1943, and entitled "Manufacture of refractory metal articles."

This invention relates to the consolidation of metal powder, and more particularly to an improvement in the method of forming metal into desired shapes in a convenient and economical manner.

The principal object of our invention, generally considered, is an improvement in powder metallurgy and more particularly such in connection with the manufacture of molybdenum and tungsten, alloys of molybdenum and tungsten, and alloys of molybdenum, tungsten and molybdenum-tungsten with small proportions of other metals, into desired shapes.

Another object of our invention is to form desired shapes of coherent metal capable of being forged and rolled by a method of powder metallurgy in which a pre-sintering or baking step, formerly employed and thought necessary in connection with the manufacture of such metals as molybdenum and tungsten, is eliminated, and the final sintering step to nearly the temperature of fusion is made unnecessary.

A further object of our invention is the consolidation of metal powder to form dense coherent metal by pressing the powder enough to handle, and heating the pressed shape in a gaseous atmosphere to a temperature at which there is a reversible reaction between said metal and said atmosphere.

A still further object of our invention is the method of manufacturing metal shapes, and particularly of such difficultly workable metal as molybdenum and tungsten, involving the mere pressing to the desired form, and then heating to a much lower temperature than previously thought necessary in a mixture of gases which react between one another and the metal in a reversible manner at said temperature.

Another object of our invention is to greatly accelerate, at any temperature, the rate of sintering of pressed coherent metallic masses, by heating in an atmosphere that reacts reversibly with the metal or metals used, and thereby induces more rapid crystallization than would occur in an inert atmosphere as the result of temperature alone.

A further object of our invention is the consolidation of metal powder to form dense coherent metal of special shapes, which may

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ordinarily only be formed by machining and other similar working operations, by pressing, mild firing in a protective atmosphere, moist hydrogen, or other mixture between which and the metal there is a reversible reaction, shaping the fired article to finished size while allowing for subsequent sintering shrinkage, and finally heating said shaped article in moist reducing gas to a temperature at which a reversible reaction occurs, until the particles of metal are sintered to the desired strength.

A still further object of our invention is to produce articles of refractory metal in which the machining and other similar working operations is performed subsequent to a mild baking operation, but prior to the final sintering treatment.

Other objects and advantages of the invention relating to the particular features, will become apparent as the description proceeds.

Referring to the drawing illustrating our invention:

Fig. 1 is a longitudinal sectional view, partly in elevation, of a furnace for giving pressed metal a heat treatment.

Fig. 2 is a 200 magnification of an etched surface of an ingot of molybdenum, produced in accordance with our invention, and having a surface grain count of about 20,800 per square millimeter.

Fig. 3 is for comparison a similar magnification of the etched surface of an ingot of molybdenum produced in accordance with the old or conventional "bottle" treating method, the surface grain count being about 750 per square millimeter.

In accordance with our invention, we propose in the manufacture of molybdenum, tungsten, and alloys thereof as subsequently more fully defined, to eliminate the baking or preliminary sintering treatment, except where we wish to machine or otherwise shape the article while in a relatively soft condition, and conduct the final sintering treatment at a very much lower temperature than formerly thought necessary, making the process operable by preferably saturating the hydrogen-bearing treating gas with water vapor at a convenient temperature, and employing a treating temperature corresponding with that at which a reversible oxidation-reduction reaction between the metal and the components of the treating gas occurs. The use of a gas bringing about a reversible reaction between the associated elements, gives a method of cementing or coalescing bodies to a dense mass approximately equivalent in density and structure to

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what would occur if the metal were actually melted and cast in a mold, the action, however, occurring, at practical speeds, at temperatures far below the melting point of the metal employed, and between about 50% and 70% of the melting temperature as measured in degrees C., instead of between 90% and 95% of said melting temperature.

It will thus be seen that the fundamental principle of our invention is the sintering or coalescing, of the particles of molybdenum and/or tungsten powder, by adding to the thermal agitation produced by heating alone, a chemical agitation by the atmosphere, allowing for a reversible reaction. This increases the range of atomic motion, whereby the atoms extend their spheres of influence or attraction, bringing them within the range of mutual attraction which results in closer bonding, higher density, and finally intercrystalline contact and growth. The result is a closely-sintered structure similar to a casting, and capable of being forged or worked under appropriate conditions. We thus directly obtain metal consolidated in such shape that no appreciable finishing is required.

In making use of our invention we employ a reactive atmosphere to bring about such chemical agitation. By the term reactive atmosphere, we mean one which at the temperature employed brings about a chemical reaction to thereby form a compound, which is decomposable at the same temperature into metal and the reacting constituent of the atmosphere. By increasing the time and greatly decreasing the temperature, the effect of the reactive atmosphere is increased.

Although we prefer water vapor in hydrogen as a reactive atmosphere, the vapor becoming steam at sintering temperatures we may instead employ one resulting from the combustion of illuminating gas and air to give a definitely reducing hydrogen-bearing atmosphere, and impregnate the same with water vapor. The gas which carries the steam must be such that reduction of the metal oxide, by the reducing component of the gas, takes place at the same temperature as oxidation of the metal by the steam. Said gas may therefore be hydrogen, or hydrogen-bearing gas containing carbon monoxide, a hydrocarbon, or mixture of one or more reducing gases. Thus we are able to use the so-called "water gas," cracked illuminating gas, dissociated ammonia, or any hydrogen-bearing mixture which carries water vapor and is definitely reducing with respect to the metal oxide being treated. On account of using steam which dissociates to liberate hydrogen when it acts as an oxidizing agent, there is necessarily free hydrogen involved in the reaction and we therefore like the term "hydrogen-bearing" atmosphere as the preferred reactive atmosphere. Such atmosphere acts to reduce any oxide of molybdenum and/or tungsten formed by the steam before it leaves the ingot, thereby building up adjacent crystals, the larger ones at the expense of the smaller, until a dense ingot results.

We will illustrate this specifically for molybdenum, but a similar process is applicable to tungsten, in a mixture of hydrogen and steam.

By reversible reaction we mean one which takes place in both directions at a selected temperature. For example $\text{Mo} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2 + 2\text{H}_2$. In other words, the associated materials are in the state of flux, the molybdenum in this case for example, being subject to oxidation by steam,

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and molybdenum dioxide being, in turn, subject to reduction by hydrogen.

The equation for tungsten is similar to that for molybdenum, above shown.

As an explanation of how the reaction occurs, it is suggested that an atomic phase, or sort of vapor phase, of the metal exists at the moment of these chemical reactions, so that the atoms are by forces of crystallization drawn toward crystal nuclei and incorporated therewith. These forces are great enough to cause shrinkage of the apparently rigid body at temperatures well below the melting point, giving mechanical properties approximating those obtained by actual fusion of the powder and casting to shape.

As a specific example of what has been accomplished by our invention, a molybdenum ingot formed by pressing the powder under standard conditions, was fired in hydrogen saturated at about 40° C. with water vapor, in a furnace at a temperature of 1630° C. for about two hours. When removed it had shrunk from 1" to $\frac{1}{4}$ " in section and was apparently fully treated. It forged readily, being in all respects the equivalent of an ingot treated in the conventional manner.

In accordance with the present method, we have, therefore, held pressed molybdenum pieces in a reactive atmosphere at a temperature to between 1500° C. and 1700° C., for a period of $1\frac{1}{2}$ to 3 hours, thereby obtaining both the unforeseen results of complete treating at low temperature and much more uniform conditions of such treating, in that using a furnace for such treatment gives a uniform heat throughout the cross section of the articles and throughout the length, thus giving greater uniformity and no end loss. This makes it possible to extend the treating to bodies of a great variety of sizes and shapes and not be limited to the use of bars or rods of approximately uniform cross section.

The dependence in treating has been transferred from temperature alone, to a reactive atmosphere and a much lower temperature, but applied for a much longer time to permit the reactive atmosphere to do a considerable part of the coalescing or crystallizing. The application of heat as an outside source, instead of internally to produce the treating temperature, has greatly increased the metal uniformity. As a result we obtain and use for fabricating, an ingot of uniform and smaller grain size than that which is usually obtained by the previous method where the grain size varies from one end of the ingot to the center, increasing in size and then decreasing.

In other words we have accomplished, by the heating to a temperature well below what was considered to be the necessary final sintering temperature, what has previously been accomplished by both a preliminary sintering and a final sintering to nearly the temperature of fusion.

Our invention, therefore, involves an improvement in the process, while at the same time making a better product, and one more uniform from end to end. For example, the density of molybdenum ingots previously obtainable by the former process is from 9.6 to 9.7 gm./cc. In accordance with our method, similar densities are obtainable. Densities ranging up to 10 have been obtained at treating temperature below 1650° C., and between 1500° C. and 1700° C., as compared with temperatures of about 2200° C. formerly thought necessary, by using higher than normal pressures.

Such molybdenum ingots, or products produced in accordance with the present method, a highly-magnified example of which is illustrated in Fig. 2, are found to have an unusually high grain count, up to about 28,000 grains per square millimeter of etched surface, with an average of about 13,000 grains per square millimeter. It has been further found that no molybdenum produced by the present method has a grain count less than 8,000 grains per square millimeter of etched surface.

This high grain count in a refractory metal, such for example as molybdenum, produces an entirely new and unforeseen result and has never occurred when produced by any other method, within the knowledge of the applicants. As far as applicants are aware, no molybdenum has ever been produced in accordance with previous practice, a highly-magnified example of which is illustrated in Fig. 3 with a count of over 2,000 grains per square millimeter of etched surface, with the average count being about 800.

The product of the present method is not only high in grain count, but has greater uniformity and greater overall density. In accordance with the present method, the furnace treating temperature, as hereinabove pointed out, can be accurately controlled; whereas in other methods, such for example where the temperature is due to the passage of electric current through the pressed body, a variation in temperature occurs from end to end of the body, giving an entirely different result from that obtained by the present method, in that heretofore the uniformity of grain size, desired density, and high grain count was unattainable.

The present invention, therefore, brings about a new product having desirable properties in the form of smaller and more uniform grains, more uniform and greater density, as well as general uniformity in physical properties throughout the entire body or ingot.

Although we have described the treatment of molybdenum in hydrogen saturated with water vapor at about 40° C., yet this saturation may be effected at lower or higher temperatures. For example, the saturation of the hydrogen may be at about as low a temperature as 30° C., or even as low as ordinary room temperatures of say about 20° C., and the furnace temperature may be lower than 1630° C., in fact as low as 1550° C. or less, for molybdenum. The lower the temperature, however, the longer the necessary treatment, and the longer the treatment the less the moisture content of the atmosphere need be. Molybdenum treated in moist hydrogen at 1550° C. for two hours was entirely satisfactory.

By virtue of our invention, we have made it possible to simplify the equipment necessary for the sintering or treating operation, giving at the same time better uniformity and control of grain size and crystalline structure. The treatment also removes carbon from the ingot and prevents carbonization taking place during the treating operation.

Although we are not limited to any special form of furnace used for performing the heat treating operation, yet a desirable furnace for both tungsten and molybdenum is disclosed in the Romanelli et al. Patent No. 2,367,617, dated January 16, 1945. In this furnace, there is shown how a continuous rod or bar of tungsten may be heat-treated and a similar treatment may be applied in the practice of our invention. Of course, in the present instance, instead of using dry hydro-

gen gas, we use water-impregnated hydrogen or hydrogen-bearing reducing gas, and on account of the initial fragility of the pressed ingot, it must be supported if fed continuously through the furnace, as shown for the tungsten rod 89 of said patent. We may rather merely support it on the bottom of the resistor tube 26 during the treating operation. It is desirable, however, that it be supported above the bottom of the heating element, and on pieces of material of the same character as that treated, so that the treating gas circulates all around the ingot, and contamination from supporting blocks is avoided. The desired treating temperature may also be obtained by induction.

Other types of furnaces which may be used for the heat-treating of molybdenum are respectively illustrated in the Kelley Patent No. 1,894,825, and the Dantsizen Patent No. 2,079,494. In other words, instead of heating inside of a hollow resistor element, the heat treating of molybdenum may be performed inside of an alundum tube heated by an external coil of tungsten or molybdenum wire, the ingot to be treated being desirably supported above the alundum or other suitable tube and resting on metal of the character of the ingot, rather than on a carbon or other dissimilar plate or blocks. Such furnaces are not suitable for treating tungsten, since the reaction is extremely slow at 1550° C., requiring several hours to show a measurable amount of sintering, and temperatures above 1600° C., say from about 1700° C. to 2000° C. or higher are desirable. Furnaces for temperatures above 1700° C. are disclosed in the Hall et al. Patent No. 2,404,060 and the Hall Patent No. 2,404,059.

In the manufacture of complicated shapes, in order to avoid subsequent grinding or machining, the die containing the article or articles to be pressed enclosed in a rubber casing, may be immersed in water or other liquid in a closed container and hydrostatic pressure applied thereto, whereby the pressure is uniform over the entire mold area. Although this method does not adapt itself to large automatic production, especially of small articles, yet for such purpose, molds can be used with multiple cavities to give large output. The dies or molds need not be made to withstand from one side only the strain of the high pressures, since in use the pressure is uniform from all sides.

In accordance with one embodiment of our invention, we take metal powder and press it in a die to make a blank for the finished article desired. The powder is pressed, as by a plunger, so that upon removal it may be satisfactorily handled. In some instances, as where a porous product is desired, the pressure employed need not be more than just enough for satisfactory handling.

Blanks 12 so produced may be passed through a treating furnace 14, illustrated in Fig. 1, wherein they are fired by being subjected to a relatively mild temperature while protected against oxidation by a reducing atmosphere, such as hydrogen or hydrogen-containing reducing mixture, preferably humidified with water vapor, so that sufficient strength is given to said blanks to withstand shaping, as by machining or other working operations, but not high enough to cause actual sintering to the finished condition. In some instances it may be desirable to fire at temperatures so low that the articles produced have not much more than just sufficient strength to withstand the contemplated shaping operation.

This can be determined by noting at what temperature shrinkage begins and keeping the heat just below that temperature. In the case of molybdenum this is from 1100° C. to 1200° C. when the treating period is from ten to twenty minutes, or about 1100° C. when the treating period is about an hour. In the case of tungsten, temperatures higher than 1300 C. as from 1300° to 1400° C., are employed for from ten to twenty minutes, temperatures in the low part of this range requiring longer periods of time.

The furnace 14 illustrated comprises a middle or intermediate hot zone part 15 comprising any suitable heating means, such as resistance wire 16 around a heating tube 17, and the whole enclosed in suitable insulating means such as alumina or magnesia 18. At the front end is a relatively cool vestibule portion 19, and at the rear or exit end there is a relatively cool tunnel 20, the length of which, for effecting the desired cooling of the treated material, may be shortened by surrounding, at least part thereof, with a water-cooling jacket 21. Valves or doors 22 and 23 are provided at the entering and exit ends. The treating atmosphere, which is preferably hydrogen or hydrogen-containing gas such as water gas, a gas as defined in the Rennie Patent No. 2,402,084, and owned by the assignee of the present application, or cracked illuminating gas, is introduced through the pipe 24, exhausted through pipes 25 and 26, and may be humidified to the desired extent prior to entering said pipe. However, if more convenient or desirable, the hydrogen may be admitted in a relatively dry condition and humidified in the furnace, as by admitting water by a pipe (not shown). The hydrogen is, however, desirably admitted near the exit end, or at least somewhat remote from the entrance end, so that the exit end of the hot zone 15 has a strong concentration of such protective atmosphere.

After the pressed blanks 12 have been moved through the furnace, as by means of an endless belt or chain passing over pulleys (not shown), or a pusher element 25, as described in the Rennie patent, above referred to, and have moved through or been held in any desired manner for a desired period in such a preliminary firing furnace, the same are removed therefrom and subjected to desired machining or similar working operations. The material removed during such operations is substantially powdered metal and may be used over again, although it is best to mix it with at least about 50% new powdered metal before pressing.

The machined or otherwise worked blanks are then passed through a sintering furnace, which, if the blanks are of molybdenum, may correspond generally with the furnace 14 of Fig. 1, except that in this furnace the shaped parts are fired in wet hydrogen at a higher temperature, that is preferably to between 1400° and 1700° C. at the appropriate schedule to give a desired finished object. In the case of tubes, they can be used at the produced size or drawn down by using standard drawing practice for the metal under consideration.

At the temperature it is desired to operate, that is at about 1600° C., practically all ceramics tend to wear rapidly if boats or slabs are used to hold the articles to be fired and slid thereover. We, therefore, find it preferable to use a track 27 of a refractory metal, such as molybdenum or tungsten, through the furnace 14, including the entrance vestibule 19 and the cooling chamber 20.

Such a track may be made in one piece or of several pieces riveted or otherwise suitably secured together, care being taken, if in several pieces, to lap them in the proper direction so that they give the least resistance to the passage of such boats or slabs over their surfaces. As holders for the articles being treated, we prefer to use molybdenum boats or skids 28. Since under the conditions of operation, there is welding of one surface of molybdenum to another, especially if many points of contact exist, it is desirable to use a powder such as magnesia, thoria, alumina, or other high-melting point oxide stable in reducing atmospheres at 1600° C. and over, to separate the article from the carrying boat or slab.

It is, of course, understood that the primary firing can be done in an atmosphere of dry hydrogen but that action is accelerated by the presence of moisture and the temperature and time factors reduced by its use. It is, however, necessary that the final firing be done in a moist atmosphere in accordance with the basic idea of our invention as previously described, in order to get articles of high density and strength at the temperature used. If molybdenum is being treated, the same furnace can be used for both operations, the only change required being in the treating temperature, and an increase in the length of treatment to about two hours.

If, however, the material is tungsten, then while the length of treatment may be the same as for molybdenum, it is necessary to use an induction furnace of high frequency type, adapting the frequency and coil spacing to the article being heated, or a furnace of the radiation type, such as described and claimed in the Hall et al. patent, previously referred to, for example, so as to get sintering temperatures of between 1600° and 2000° C.

Such production of the molded articles and finishing in final form by mere heat treatment in a furnace at relatively low temperature is believed to be a radical advance in the art of powder metallurgy. The making of such shapes by the old method, involving first baking or preliminary sintering and then final sintering between electrodes where the ends are gripped and the temperature of the sintering is nearly as high as the melting point of the metal, was not possible because said method is only applicable to ingots of uniform cross section and where it is permissible to discard the ends gripped in the sintering bottle as not being fully treated.

However, in accordance with our invention all parts of the ingot are treated to the same extent. Therefore, in pressing the article into shape there is no waste of untreated end portions and it is only necessary to make allowance for the shrinkage when the treating occurs. This, of course, is very simple and is well understood to those skilled in the art in connection with casting metal where a similar allowance is made.

The process of our invention can also be used to cement or weld the same or metals other than those mentioned to each other, provided they respond to the same reversible gas or vapor reaction within a common range of temperature and vapor pressure. Thus two standard ingots can be welded together end to end by heating to the sintering temperature while in close contact, 1400° C. to 1700° C. in the case of molybdenum, in wet hydrogen until the two have coalesced or practically welded together, thereby decreasing the number of pieces to be handled for swaging and drawing. In a like manner, because of the

time element permitting diffusion, non-metallic elements or metallic compounds may be incorporated into metal bodies and the crystalline structure of the resulting metal modified thereby.

The range of temperature for molybdenum has been reduced so low that furnaces of conventional design can be used, permitting the preparation of finished shapes which previously could not be treated but had to be fashioned from rod or bar. Our invention greatly increases the permissible size of the piece, as well as the variety of shapes that can be formed. Instead of a treating bottle limited to rods and bars of uniform cross-section and within the current-carrying capacity of the contacts, we can now make articles of any shape and size that can be contained in a furnace which can be heated to 1400° C. to 1600° C. and filled with a hydrogen-bearing gas desirably saturated at about 20° to 40° C. with water vapor. As an example, slabs of molybdenum for rolling can be pressed to any desired width, avoiding the necessity of cross rolling.

Our idea takes advantage of the crystallization induced by the water cycle to accelerate sintering or cementing the tungsten or molybdenum particles into a dense workable form. This can be carried on at any temperature above the minimum, but not for practical purposes at any temperature where this reaction takes place. For example, with molybdenum, this reaction takes place at 600° C. to 700° C. and with tungsten at a not very different temperature, but we have to raise the temperature high enough so that this effect is rapid enough to release large forces which pull the particles together. This is above about 1550° C. for tungsten and 1200° C. for molybdenum.

However, increase in temperature increases this force and decreases the time required for the maximum effect. Also, the greater the pressure used for pressing, the closer the metal particles are drawn together and the easier to get good workable metal at these low temperatures. It has, however, not been found necessary to increase the pressure over that normally used to obtain as dense an ingot as those obtained formerly, even though the treating or sintering temperature has been reduced 500° C. or more.

From the foregoing disclosure it will also be seen that the furnace of the Hall et al. patent referred to may be used to heat articles of tungsten or other refractory metal, to the high temperatures necessary to effect the final sintering operation, by radiation from an incandescent tungsten resistance element, the heat being conserved by polished and/or bright plated baffles, the whole enclosed in a water jacket, and the article during treatment being surrounded by a protective atmosphere, such as wet hydrogen, introduced through an upper pipe, controlled by a valve, and exhausted through a lower pipe.

By proper control of the material and processes used, it is possible to predetermine the shrinkage between the primary firing and the final size, and since there is no change in size between pressing and such primary firing, the size of the die or mold used for such pressing can be calculated with reasonable accuracy, making it possible to predetermine the die size for a definite finished size. The linear shrinkage in the final sintering is normally about 15% to 20% in the case of molybdenum, varying considerably with the particle size, pressure used, and previous history of the powdered metal. It is, therefore, essential to

have a uniform starting material if the relation between the pressed size and the finished size is to be accurately controlled.

Although we have described the process in connection with certain shapes, it is evident that any shape may be made by pressing as nearly as possible to that which, after sintering shrinkage, will produce the finished size, pre-firing as described, shaping, and then subjecting to the final sintering operation. If a higher degree of accuracy is desired, it is preferable to make slightly oversize and finish to definite limits thereafter, as by grinding.

As an example of what has been done in practicing the afore-disclosed process, tubes have been made 9" long, .9" outside diameter, and .5" inside diameter, by pressing blanks of molybdenum 24" long, 1½" square, using 4800 grams of powdered metal at a pressure of about 550 tons total. These bars were then cut to 12" lengths, and fired for from five to twenty minutes at approximately 1100° C. in moist hydrogen. Upon removal from the primary firing furnace, the bars were sufficiently strong to be clamped in a lathe, turned to 1¼" in diameter, and a ½" hole drilled the entire length of each piece.

The 12" untreated tubes were introduced into a furnace in an atmosphere of hydrogen saturated with water at 30° C. and heated to approximately 1600° C. for two hours. The shrinkage at the end of that time was of the order of 15% in all dimensions. The tubes were then clamped in a lathe and turned and drilled to the desired finished dimensions. Crucibles and rings have been pressed and made by the disclosed process.

From the foregoing disclosure, it will be seen that we have devised a process for making articles of refractory material, such as tungsten and molybdenum, in desired shapes before they are sintered to final hardness, whereby the forming of such articles is much easier than by methods heretofore used. Our process also makes practicable the manufacture of articles the formation of which has heretofore been difficult or impossible.

Although preferred embodiments of our invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims, in which the expressions "atmosphere of hydrogen" and "hydrogen-bearing" include such in which hydrogen is a diluted active ingredient, reference being made to the Rennie patent No. 2,402,084, for a disclosure of suitable "hydrogen-bearing atmospheres."

Although we have described our method as applied to the making of articles of molybdenum and tungsten, it will be understood that we use the same method in making articles of alloys of molybdenum and tungsten; and alloys of molybdenum, tungsten, and molybdenum-tungsten with other metals, in such small proportions, however, that the melting points of the molybdenum, tungsten or molybdenum-tungsten are not changed to an important extent. Therefore, in this specification and in the claims the words, "the group consisting of molybdenum and tungsten" include all of the above identified alloys, as well as the pure metals; and the words "molybdenum" and "tungsten" do not exclude such metals alloyed with such small proportions of other metals that the melting points are approximately the same as those of the unalloyed metals. "Alloying," in accordance with the pres-

ent application, is effected by mixing the constituent metals in powdered form, and in the proportion in accordance with that desired in the finished product, prior to performing the consolidating operations.

We claim:

1. The method of consolidating metal powder selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape for a relatively long period of time in a hydrogen-bearing reducing atmosphere, saturated between about 20° C. and 40° C. with water vapor, to a temperature, not higher than about 70% of that of fusion, as measured in degrees C., at which a reversible reaction between such materials occurs.

2. The method of consolidating metal powder selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising pressing to consolidate the powder, and then heating the entire pressed shape in a hydrogen-bearing reducing atmosphere containing water vapor, to a temperature between about 50% and 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

3. The method of consolidating powdered metal selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising subjecting the powdered metal to pressure to form a body in condition for handling, and then heating the body so formed for a relatively long period of time in an atmosphere of hydrogen saturated at a temperature between about 30° C. and 40° C. with water vapor, to a temperature above 1400° C. and between about 50% and 70% of that of fusion as measured in degrees C., until a strong coherent article is produced.

4. The method of consolidating molybdenum powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape for a relatively long period of time in a hydrogen-bearing reducing atmosphere saturated at between about 20° C. and 40° C. with water vapor, to a temperature, not higher than about 70% of that of fusion, as measured in degrees C., at which a reversible reaction between such materials occurs.

5. The method of consolidating molybdenum powder to form dense coherent metal, comprising pressing to consolidate the powder merely enough to be handled, and then heating the entire pressed shape in a reducing atmosphere containing at least a large proportion of hydrogen and some water vapor, to a temperature between about 50% and 70% of that of fusion, as measured in degrees C., for a relatively long period of time until the particles thereof sinter together.

6. The method of consolidating molybdenum powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape in an atmosphere of hydrogen, saturated at about 40° C. with water vapor, to a temperature of about 1630° C. for about two hours.

7. The method of consolidating tungsten powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape for a relatively long period of time in a hydrogen-bearing reducing atmosphere saturated at between about 20° C. and 40°

C. with water vapor, to a temperature, not higher than about 70% of that of fusion, as measured in degrees C., at which a reversible reaction between the associated materials occurs.

8. The method of consolidating tungsten powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape in hydrogen saturated between about 20° C. and 40° C. with water vapor, to a temperature ranging between about 1600° C. and 2000° C., for a relatively long period of time.

9. The method of consolidating tungsten powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating the pressed shape in hydrogen saturated at about 40° C. with water vapor, to a temperature of about 2000° C. for about two hours.

10. The method of making metal articles of consolidated refractory metal selected from the group consisting of molybdenum and tungsten, comprising pressing the metal while in the form of powder, firing the pressed powder in a protective atmosphere at a temperature only high enough to give it sufficient strength to withstand shaping, shaping said fired article, and finally heating said article for a relatively long period of time in a hydrogen-bearing reducing atmosphere saturated at between about 20° C. and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., at which a reversible reaction between said materials occurs, until a strong coherent article is produced.

11. The method of making articles of consolidated refractory metal selected from the group consisting of molybdenum and tungsten, comprising die pressing the metal while in the form of powder, firing the pressed powder in a protective atmosphere at a temperature only high enough to give it sufficient strength to withstand shaping, shaping said fired article, and finally heating said article in a hydrogen-bearing reducing atmosphere containing water vapor, to a temperature between about 50% and 70% of that of fusion, as measured in degrees C., for a relatively long period of time, until a strong coherent article is produced.

12. The method of making articles of consolidated refractory metal selected from the group consisting of molybdenum and tungsten, comprising die pressing the metal while in the form of powder, firing the pressed metal in moist hydrogen to a temperature of between 1100° C. and 1400° C. long enough to give it sufficient strength to withstand machining and other desired working, shaping the fired article, and finally heating said article in an atmosphere of hydrogen saturated at between about 30° C. and 40° C. with water vapor, to a temperature between 1400° C. and 2000° C. for a relatively long period of time until a strong coherent article is produced.

13. The method of making articles of consolidated molybdenum, comprising die pressing molybdenum powder, firing the pressed molybdenum in moist hydrogen to a temperature of about 1100° C. for about one hour to give it sufficient strength to withstand machining and other desired working, shaping said fired article, and finally heating said article in an atmosphere of hydrogen saturated at about 40° C. with water vapor, to a temperature of about 1630° C. for about two hours to cause the particles of molybdenum to sinter to the desired strength.

14. The method of making an article of consolidated molybdenum, comprising subjecting

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powdered molybdenum to pressure, firing the pressed molybdenum in moist hydrogen for from five to twenty minutes at a temperature of approximately 1100° C., shaping said fired article, and finally heating said article in an atmosphere of hydrogen saturated at about 30° C. with water vapor to a temperature of about 1600° C. for about two hours.

15. The method of making articles of consolidated tungsten, comprising die pressing tungsten powder, firing the pressed tungsten in moist hydrogen to a temperature of about 1300° C. for about twenty minutes to give it sufficient strength to withstand machining and other desired working, shaping said fired article, and finally heating said article in an atmosphere of hydrogen saturated at about 40° C. with water vapor, to a temperature of about 2000° C. for about two hours to cause the particles of tungsten to sinter to the desired strength.

16. The method of consolidating metal powder selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising pressing to consolidate the powder, and then heating the pressed powder in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature between about 50% and 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

17. The method of consolidating powdered metal selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising subjecting the powdered metal to pressure to form a body in condition for handling, and then heating the body so formed in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

18. The method of consolidating molybdenum powder to form dense coherent metal, comprising pressing, and then heating the pressed powder in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature between about 50% and 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

19. The method of consolidating molybdenum powder to form dense coherent metal, comprising pressing to consolidate the powder, and heating in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

20. The method of making an article of molybdenum comprising pressing molybdenum powder to consolidate it into a body of sufficient strength for handling, and then heating the pressed body in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature between about 1500° and 1700° C., for a relatively long period of time until a strong coherent article is produced.

21. The method of treating tungsten powder

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to form dense coherent metal, comprising pressing to consolidate it into a body of sufficient strength for handling, and heating the pressed body in a hydrogen-bearing reducing atmosphere containing water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

22. The method of treating tungsten powder to form dense coherent metal, comprising pressing to consolidate it into a body of sufficient strength for handling, and heating the pressed body in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time until a strong coherent article is produced.

23. The method of making articles of refractory metal selected from the group consisting of molybdenum and tungsten, comprising pressing the metal as a powder, firing the pressed powder in a protective atmosphere to a non-sintering temperature not lower than about 1100° C. for a long enough period to give it sufficient strength to withstand machining and other desired working, shaping the fired article, and finally heating the article in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time to produce a strong coherent article.

24. The method of making articles of molybdenum, comprising pressing molybdenum powder, firing the pressed powder in a reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a non-sintering temperature not lower than about 1100° C. for a long enough period to give it sufficient strength to withstand machining and other desired working, shaping the fired article, and finally heating the article in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time to produce a strong coherent article.

25. The method of making articles of tungsten, comprising pressing tungsten powder, firing the pressed powder in a reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a non-sintering temperature not lower than about 1100° C. for a long enough period to give it sufficient strength to withstand machining and other desired working, shaping the fired article, and finally heating the article in a hydrogen-bearing reducing atmosphere saturated at a temperature between about 20° C. and 40° C. with water vapor, to a temperature not higher than about 70% of that of fusion, as measured in degrees C., for a relatively long period of time to produce a strong coherent article.

26. The method of consolidating metal powder selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising pressing to shape, and heating the pressed shape in a hydrogen-bearing reducing atmosphere to a temperature not higher than about 70% of that of fusion as measured

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in degrees C., during which heating said atmosphere contains enough water vapor to provide at said temperature for a reversible oxidation-reduction reaction with respect to said metal, and continuing said heating for a relatively long period of time.

27. The method of consolidating metal powder selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising subjecting the powdered metal to pressure to form a body in condition for handling, placing said body in a hydrogen-bearing reducing atmosphere containing a large enough proportion of water vapor to provide for a reversible oxidation-reduction reaction with respect to said metal at the temperature of treatment, and exteriorly heating said atmosphere and through it said body, to a temperature not higher than about 70% of that of fusion as measured in degrees C., but high enough so that the reaction takes place rapidly, the treatment being continued for a relatively long period of time.

28. The method of consolidating metal particles selected from the group consisting of molybdenum and tungsten to form dense coherent metal, comprising pressing said particles to form a body in condition for handling, placing the body in a chamber, providing said chamber with a hydrogen-bearing reducing atmosphere, and treating said body by heating in said atmosphere to a temperature not higher than about 70% of the fusion temperature of the metal as measured in degrees C., but sufficiently high to sinter the particles composing the body, while maintaining a proportion of water vapor in the atmosphere large enough to provide at said temperature for a reversible oxidation-reduction reaction with respect to said body, in order to allow for low temperature sintering thereof, and continuing said treatment for a relatively long period of time to produce a strong coherent article.

29. A fully sintered and unworked body of coherent metal formed from at least one of the powdered metals selected from the group consisting

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of molybdenum and tungsten, said body having a high density imparting forging and rolling workability thereto, and having a uniform and small grain size, said density, grain size and uniformity of grain size extending throughout the body over its entire length and cross-section.

30. A fully sintered and unworked body of coherent metal formed from powdered molybdenum, said body having a density approximating 9.6 to 10 gm./cc., a uniform grain size, and a grain count per square millimeter of surface, not less than 8,000 and up to about 28,000, said density, grain size, and uniformity of grain size extending throughout the body from one end to the other and cross-sectionally.

31. A fully sintered and unworked body of coherent metal formed from powdered tungsten, said body having a high density imparting forging and rolling workability thereto, and having a uniform and small grain size, the density, grain size and uniformity of grain size extending throughout the body over its entire length and cross section.

32. A fully sintered and unworked body of non-uniform transverse section, consisting of coherent metal formed from at least one of the powdered metals selected from the group consisting of molybdenum and tungsten, said body having a high density imparting forging and rolling workability thereto, and having a uniform and small grain size, said density, grain size and uniformity of grain size extending throughout the body over its entire length and cross-section.

ROY D. HALL.
JOHN H. RAMAGE.

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