Oct. 19, 1954 R. F. BAKER 2,692,216

METHOD OF MANUFACTURING DUCTILE MOLYBDENUM AND ALLOYS THEREOF

Filed Oct. 10, 1951

Fig. 1.

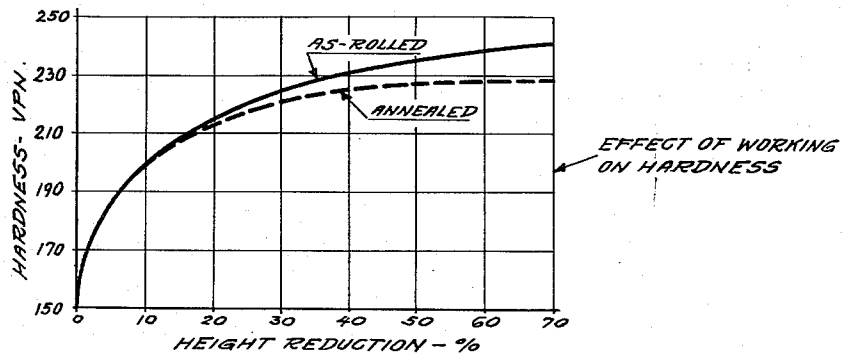


Fig. 2.

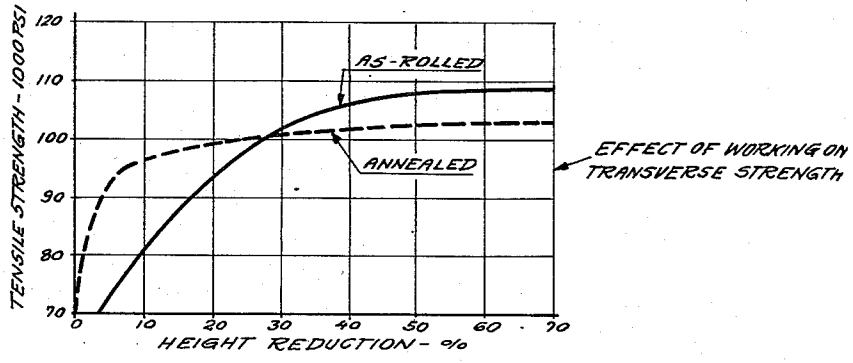


Fig. 3.

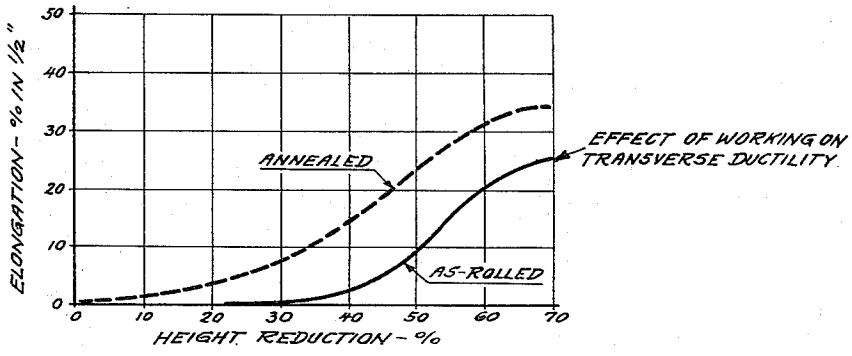
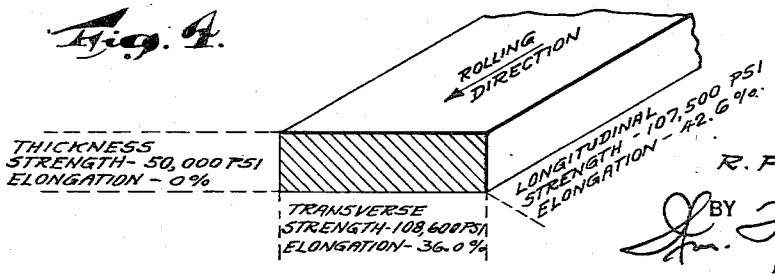


Fig. 4.



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Patented Oct. 19, 1954

2,692,216

UNITED STATES PATENT OFFICE

2,692,216

METHOD OF MANUFACTURING DUCTILE MOLYBDENUM AND ALLOYS THEREOF

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Application October 10, 1951, Serial No. 250,780

10 Claims. (Cl. 148—11.5)

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This invention relates to molybdenum and its alloys and, more particularly, to such that are ductile and methods of manufacturing the same.

The principal object of my invention, generally considered, is to manufacture molybdenum, and alloys thereof with small proportions of other metals such as cobalt, nickel, iron and tungsten, in order to produce material which is harder, stronger, and more ductile than the usual factory product.

Another object of my invention is to work molybdenum and alloys thereof at a proper temperature, that is, one between about 1150° and 1250° C., by a series of rolling operations, reducing the cross sectional area about 15% on each operation, annealing between operations to relieve stress without allowing recrystallization, and finally annealing and cooling slowly to a relatively low temperature to get hard, strong and ductile material.

A further object of my invention is to roll molybdenum and alloys thereof at a temperature of about 1200° C. in a series of, preferably four, steps, with limited stress-relieving periods between steps, and a final anneal and slow cooling, in order to increase hardness and strength.

A still further object of my invention is to effect the working of molybdenum and alloys thereof in a series of steps, without bringing the grains to a more or less equiaxed condition by recrystallization.

An additional object of my invention is to roll molybdenum in a series of steps, effecting a total reduction in area of about 50% or more, with a mere stress relief anneal between steps, and a final anneal and slow cooling, say at a rate between 60° C. and 120° C. per hour, to a relatively-low temperature, in order to produce metal with the desired characteristics.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Figure 1 is a graph showing the effect of working on hardness of molybdenum.

Figure 2 is a graph showing the effect of working on transverse strength of molybdenum.

Figure 3 is a graph showing the effect of working on transverse ductility of molybdenum.

Figure 4 is a perspective view of one end of a rolled bar of molybdenum, showing comparative strengths and elongations in various directions.

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The properties of molybdenum and molybdenum alloys are dependent primarily upon the grain structure of the rolled ingot. In order to obtain an ultimate tensile strength of 115,000 p. s. i. (pounds per sq. inch) in a bar which has been reduced approximately 50% in cross-sectional area, it is necessary to control the grain structure of the ingot during the rolling procedure. When an ingot is reheated after being worked there are three reactions which occur: The first, a stress relief, the second, recrystallization, and the third, grain growth. At 1600° C. or higher all three of these reactions occur almost instantaneously, resulting in a coarse-grained material which has low strength. At 1400° C. the stress relief is instantaneous, the period during which recrystallization takes place is about two or three minutes depending upon the degree of work strain, and then grain growth begins. However, by lowering the rolling and annealing temperature to about 1200° C., the time for stress relief and recrystallization is lengthened to about 15 minutes before grain growth begins.

In order to eliminate variables present in repeated fabricating and annealing cycles, data were obtained on molybdenum wedges, whereby the reduction could be varied in a single rolling pass at a given temperature. The use of such wedges machined from solid ingots allows varying reductions to be made on material possessing initially the same grain size, density and rolling temperature.

Solid ingots of unalloyed molybdenum were first prepared by pressing metal powder and sintered. Two wedges 13" long by 1½" wide by ⅜" thick at the thinner end were machined with a taper of .106" per inch of length, and lines were inscribed at ½ intervals on both sides along the length. These were rolled to ⅜" thickness at 1200° C. in a single pass in a 21" x 42" rolling mill. One wedge was allowed to simply cool in air after rolling, while the other was annealed for one hour at 950° C. before being allowed to cool.

Measurements of the height of the wedge after rolling at each of the scribed marks, when compared with the original height at the same points, gave a measure of the degree of height reduction. Hardness measurements were made across the surface of the rolled wedges at posi-

tions located by the previously scribed lines. Using the lines as centers, round tensile specimens 1⅛" long by .187" diameter were prepared and tensile tests made of the properties transverse to the rolling direction.

In order to show what relation these transverse properties would have to the properties in the longitudinal rolling direction, and to the properties in the thickness of compressive direction, round tensile specimens, ⅛" in diameter by 1" long, were cut from a factory rolled slab 1" by 2½" cross section. Six specimens were tested in each of the three directions; longitudinal, transverse, and thickness.

The sintered wedges, prior to rolling, had a hardness of 150 V. P. N., a strength of 60,000 to 70,000 p. s. i. and were quite brittle. After a single rolling pass, the initial hardness, transverse strength, and transverse ductility had increased with increasing reduction in both the as-rolled and annealed conditions, as shown by Figs. 1, 2 and 3, respectively.

In each case, the hardness increased rapidly at first with increasing reduction, up to about 25%. Above 25% reduction the hardness increased more slowly. The hardness of the annealed and as-rolled materials are substantially the same at the lower reduction values, but the hardness of the annealed material approached a lower maximum value than that of the as-rolled material, as shown in Figure 1.

The transverse strength of the annealed material approached a substantially constant value at a reduction of about 25%. The strength of the as-rolled material, on the other hand, increased much slower with increasing reduction, approaching a substantially constant value at about 40%, as shown in Fig. 2. The curve shown in said Fig. 2, illustrating the as-rolled tensile strength, has a lower value at the low percent height reductions due to the extreme brittleness of molybdenum in the as-rolled state. Theoretically, the as-rolled curve should be above the annealed curve at all points, but due to said brittleness under these conditions, the as-rolled tensile specimens break prematurely.

The ductility of molybdenum, expressed in percent elongation, is shown by the S-shaped curves of Figure 3. Ductility first increased slowly, suddenly increased greatly, and then slowly rose as reduction is increased. The curves for the as-rolled and annealed material are generally parallel with higher amounts of reduction. At low reductions, the annealed material possesses some ductility, whereas the as-rolled material is brittle. The points at which ductility begins to increase rapidly correspond to the points at which the tensile strength begins to approach a constant value; namely 25% reduction for the annealed material and 40% reduction for the as-rolled material.

The elongation-reduction curves show essentially the effect of working on the lowering of the transition temperature of molybdenum during a slow tensile test. To obtain maximum ductility at room temperature, it would be necessary to reduce the height of the ingot by 60% to 70%, whether in the as-rolled or annealed condition. With intermediate reductions of 30%–60%, however, some ductility can be obtained. Below 30% reduction, material is not produced which would be considered ductile.

The curves of Figures 1, 2 and 3 are average ones drawn through values of single tensile tests and, therefore, do not indicate exact values but trends. As the amount of working in a given piece is increased, the recrystallization temperature is decreased. Thus, for high values of reduction some instantaneous recrystallization may occur at the rolling temperature used and result in some variation of properties. Also, a roll slippage and lifting may occur in rolling wedges, causing some variation in the properties of the finished piece. The test results on these wedges have all been given in the transverse or width direction.

Figure 4 shows a factory-rolled unalloyed molybdenum slab reduced 56% in height by four passes at 1200° C., with reheating between passes in accordance with my invention, illustrating the variations in properties in the three directions. The longitudinal and transverse strengths are substantially equal, whereas the strength in the thickness direction is more like the strength of a merely sintered ingot. However, the elongation is greater in the longitudinal direction than in the transverse direction and the elongation in the thickness direction is zero.

Between flat rolls, an ingot elongates considerably, widens to some extent, and is decreased in thickness. The grains of the material are elongated both in longitudinal and transverse directions. They are, however, compressed in the thickness direction. It is thus apparent that working molybdenum develops strength and ductility in the directions in which the grains are elongated, or in the directions of metal flow. No increase in strength or ductility is noted in the direction along which only compressive force is applied.

The rolling schedule presently used consists of several, preferably four, rolling passes of approximately 15% area reduction per pass in flat rolls of a say 21" x 42" rolling mill. The temperature throughout the rolling procedure is maintained at about 1200° C., or between 1150° and 1250° C. Between passes the ingots are allowed to soak for a short period of say ten minutes at about 1200° C., or between five and twenty minutes at temperatures between 1250° and 1150° C., the lower the temperature the longer the time. During this anneal, the stresses of the previous rolling pass are relieved and there is a partial recrystallization which is necessary to prevent failure in the succeeding pass. Grain growth does not occur during this rolling schedule and the resulting bar has a fine-grain structure which is necessary for high strength.

The four-pass schedule has been selected as a convenience to stay within limitations of the rolling mill with about 21" diameter rolls which was employed. If a larger rolling mill were available, it would be possible to take a greater reduction per pass on bars, of the size referred to, such as 2¼" by 2¼", and perhaps make the same total reduction in two or three passes as presently made in the four-pass schedule. With the present 21" by 42" rolling mill it is possible to roll bars of the size 1⅝" by 1¾"—factory 7 kilogram size, to the same total reduction in area of 50% in three passes of approximately 20% each, using the same temperature and annealing times. In other words, if the reduction were made in three passes, approximately 20% reduction in area of the existing bar would be effected each time.

With the present rolling mill, it would be possible to effect the same total reduction in more than four passes by taking a lower reduction per pass, such as approximately 10%. Actually it is

quicker and more effective to accomplish the desired total reduction of 50% or greater in as few number of passes as possible. On rolling mills smaller than the 21" x 42", it is necessary to reduce the reduction per pass in order to prevent mill damage.

Examples of rolling schedules embodying my invention are as follows:

[A—Starting bar size, 2¼" x 2¼", Mo alloyed with .1% Co (although this same schedule could be used for Mo alloyed with not more than .2% Co or for pure Mo).]

Pass	Roll Spacing, inches	Pass Temperature, ° C.	Remarks
1	1⅝	1,200	Annealed 10 min. at 1,200° C.
2	1⅜	1,200	Do.
3	1 3/16	1,200	Do.
4	1	1,200	Given slow-cooling treatment, after about one hour anneal at about 990° C. Cooling rate about 60° C. per hour to a relatively-low temperature.

By the term "relatively-low temperature," I mean one below minimum visible redness, from which further slow cooling will yield only a very slight increase in ductility, say about 2% elongation as measured in a tensile test. In other words, removal of the metal from this slow-cooling furnace at visible redness or 700° C. involves a loss of not more than 10% of the ductility which might be obtained.

[B—Starting bar size 1⅝" x 1¾"—factory 7 kg. size Mo alloyed with .1% Co.]

Pass	Roll Spacing, inches	Pass Temperature, ° C.	Remarks
1	1¼	1,200	Annealed 10 min. at 1,200° C.
2	1	1,200	Do.
3	¾	1,200	Do.
4	⅝	1,200	Given slow-cooling treatment, after about one hour anneal at about 990° C. Cooling rate about 60° C. per hour to a relatively-low temperature.

The above rolling schedules will produce material with an ultimate tensile strength of about 115,000 p. s. i. By proper slow cooling it is possible to obtain approximately 20% elongation without appreciable loss in strength. Maximum strength obtainable under previous rolling schedules was 100,000 p. s. i.

[C—Starting bar size 2¼" by 2¼", unalloyed molybdenum.]

Pass	Roll Spacing, inches	Pass Temperature, ° C.	Remarks
1	1⅝	1,200	Annealed 10 min. at 1,150° C.
2	1⅜	1,150	Annealed 10 min. at 1,100° C.
3	1 3/16	1,100	Annealed 10 min. at 1,050° C.
4	1	1,050	Given slow-cooling treatment, after about one hour anneal at about 990° C. Cooling rate about 60° C. per hour to a relatively-low temperature.

The foregoing rolling schedule produced material with ultimate tensile strength of slightly less than that of the molybdenum alloy of Examples A and B. By proper slow cooling it is possible to obtain greater than 20% elongation without appreciable loss in strength.

[Starting bar size 1⅝" x 1¾"—factory 7 kg. size. Mo + .1%, or between .1% and .2%, Co.]

Pass	Roll Spacing, inches	Pass Temperature, ° C.	Remarks
1	1⅛	1,200	Annealed 10 min. at 1,200° C.
2	⅞	1,200	Do.
3	⅝	1,200	Given slow-cooling treatment, after about one hour anneal at about 990° C. Cooling rate about 60° C. per hour to a relatively-low temperature.

The above rolling schedule is to illustrate, what was previously mentioned, that the reduction prior to final annealing and slow cooling may be effected in a number of passes different from four.

From the foregoing, it will be seen that I have discovered an improved rolling schedule for molybdenum and alloys thereof, whereby metal with a fine grain structure and high strength, as well as good ductility, is produced. By the expression alloys of molybdenum with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, I mean such in which the proportion of any of the first three mentioned alloying metals is not greater than ½%, and in which the proportion of the alloying tungsten is not greater than 20%. Although cobalt is preferred as the alloying metal, the others mentioned have similar effects on the properties of molybdenum.

When I refer to finally annealing and cooling slowly to a low or nearly to room temperature, or to a temperature below 700° C., I am referring to the annealing and slow cooling schedule described and claimed in the co-pending application entitled "Ductilizing Molybdenum and Alloys Thereof," which I filed jointly with Edgar S. Byron under date of September 14, 1951, Ser. No. 246,654. In accordance with this schedule, the metal article, after working at a temperature near and desirably not higher than 1200° C., is brought in a protective atmosphere to a slightly lower stress relieving temperature, such as 1000° C. or between 1070° and 990° C. and held for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then slowly cooling, defined as at a rate in the range of 60° C. to 120° C. per hour, the article to room temperature or one not higher than 700° C.

Although preferred embodiments of my invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

I claim:

1. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross-sectional area while heated to a temperature between 1150° and 1250° C., annealing at about the same temperature, repeating such rolling and annealing, finally repeating such rolling, until the article has been reduced as much at 50% in cross-sectional area, heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° for from 1 to 30 minutes, the lower the temperature the longer

the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

2. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross-sectional area about 15% while heated to a temperature near and not higher than 1200° C., annealing at about the same temperature, repeating such rolling and annealing twice more, finally repeating such rolling, heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

3. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of nickel, cobalt, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross sectional area while heated to a temperature between 1150° and 1250° C., annealing it at about the same temperature for between 20 and 5 minutes, the higher the temperature, the shorter the time, repeating said rolling and annealing, finally repeating such rolling until the article has been reduced as much as 50% in cross-sectional area, heating in a protective atmosphere to a slightly lower stress-relieving temperature higher than 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress relief without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

4. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of nickel, cobalt, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross sectional area about 15% while heated to a temperature between 1150° and 1250° C., annealing it at about the same temperature for between 20 and 5 minutes, the higher the temperature, the shorter the time, repeating said rolling and annealing twice more, finally repeating such rolling, heating in a protective atmosphere to a slightly lower stress-relieving temperature higher than 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress relief without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

5. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross sectional area while heated to a temperature of about 1200° C., annealing at about the same temperature for about 10 minutes, repeating such rolling and annealing, finally repeating such rolling until the article has been reduced as much as 50% in cross-sectional area, heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get strong, hard, ductile material by stress relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

6. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross sectional area about 15% while heated to a temperature of about 1200° C., annealing at about the same temperature for about 10 minutes, repeating such rolling and annealing twice more, finally repeating such rolling, heating in a protective atmosphere to a stress-relieving temperature between about 1070° and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get strong, hard, ductile material by stress relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

7. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross-sectional area while heated to a temperature of about 1200° C., annealing at about the same temperature, repeating such rolling and annealing, finally repeating such rolling until the article has been reduced as much at 50% in cross-sectional area, heating in a protective atmosphere to a slightly lower stress-relieving temperature higher than 990° C. for from 1 to 30 minutes, the lower the temperature, the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

8. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, pressed and sintered, comprising rolling said article to reduce its cross-sectional area, while heated to a temperature near and not much higher than 1200° C., annealing at about the same temperature, repeating such rolling and annealing, finally repeating such rolling until the article has been reduced as much as 50% in cross-sectional area, heating in a protective atmosphere to a temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a

rate between 60° C. and 120° C. per hour to a temperature not higher than 700° C.

9. The method of manufacturing ductile metal from powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, comprising pressing the particles to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, rolling said article to reduce its cross sectional area while heating to a temperature between 1150° and 1250° C., annealing at about the same temperature, repeating such rolling and annealing, finally repeating such rolling until the article has been reduced as much as 50% in cross-sectional area, heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a relatively-low temperature not higher than 700° C.

10. The method of manufacturing ductile metal from powdered particles of molybdenum, comprising pressing the particles to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, rolling said article to reduce its cross sectional area while heated to a temperature of about 1200° C., annealing at a slightly lower temperature, repeating such rolling and annealing, but at slightly lower temperatures, finally repeating such rolling until the article has been reduced as much as 50% in cross-sectional area, heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, the lower the temperature the longer the time, to get hard, strong and ductile material by stress-relief, without allowing the grains to become equiaxed by recrystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a relatively-low temperature not higher than 700° C.

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