Jan. 19, 1954 J. H. BECHTOLD ET AL 2,666,721

PROCESS OF PRODUCING DUCTILE MOLYBDENUM

Filed March 20, 1951 4 Sheets-Sheet 1

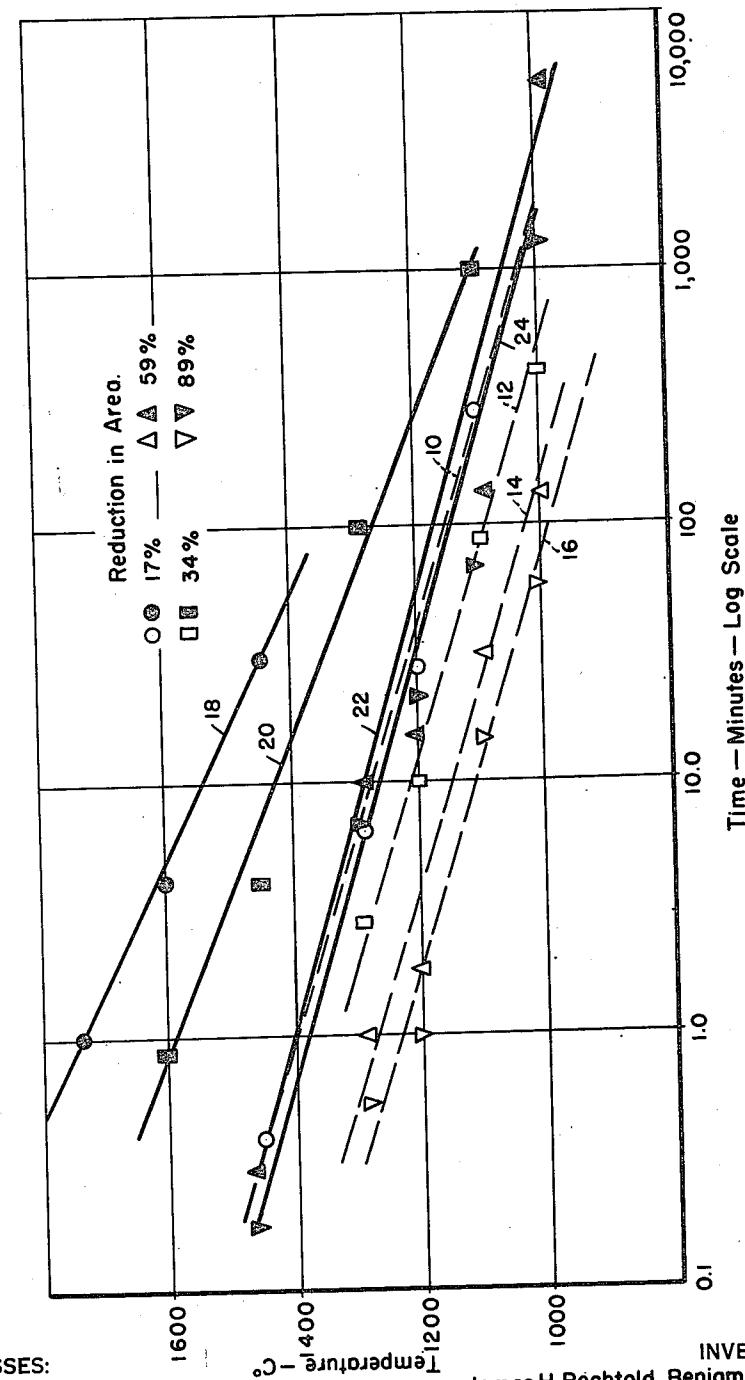


Fig. 1.

WITNESSES:

E. A. McCloskey.

Wm. L. Groome

INVENTORS

James H. Bechtold, Benjamin Lustman and Howard Scott.

BY

James R. Ely

ATTORNEY

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PROCESS OF PRODUCING DUCTILE MOLYBDENUM

Filed March 20, 1951 4 Sheets-Sheet 2

Fig.2.

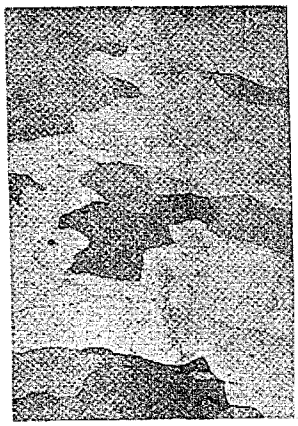


Fig.3.



Fig.4.

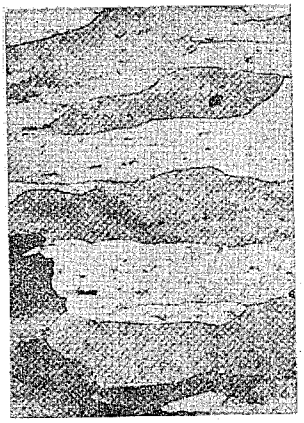


Fig.5.



Fig.6.



Fig.7.

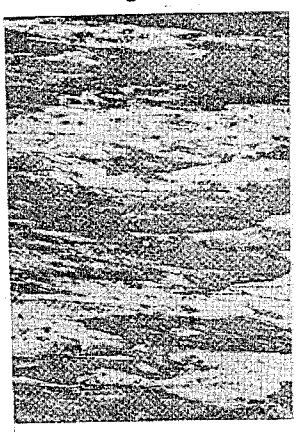


Fig.8.

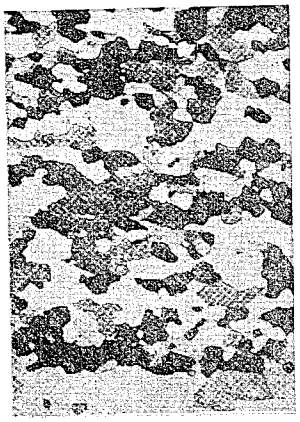
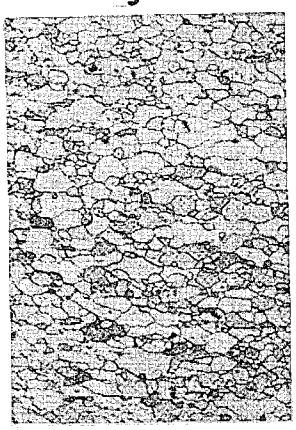


Fig.9.



*INVENTORS*
James H. Bechtold,
Benjamin Lustman
and Howard Scott.

*BY* James H. Ely
*ATTORNEY*

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PROCESS OF PRODUCING DUCTILE MOLYBDENUM

Filed March 20, 1951 4 Sheets-Sheet 3

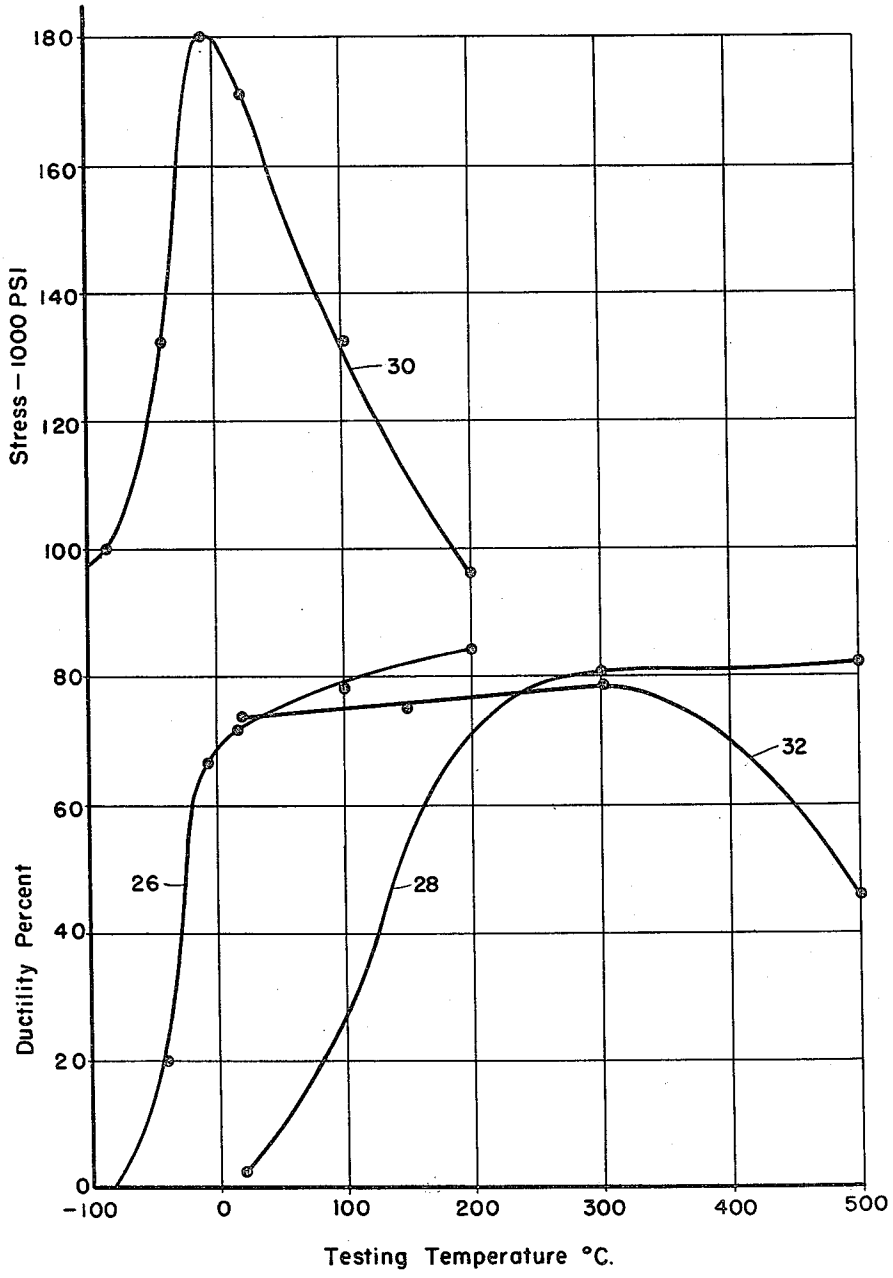


Fig.10.

WITNESSES:
E. A. McCloskey.
Wm. L. Groome

INVENTORS
James H. Bechtold, Benjamin Lustman
and Howard Scott.
BY
James R. Ely
ATTORNEY

Jan. 19, 1954 J. H. BECHTOLD ET AL 2,666,721

PROCESS OF PRODUCING DUCTILE MOLYBDENUM

Filed March 20, 1951 4 Sheets-Sheet 4

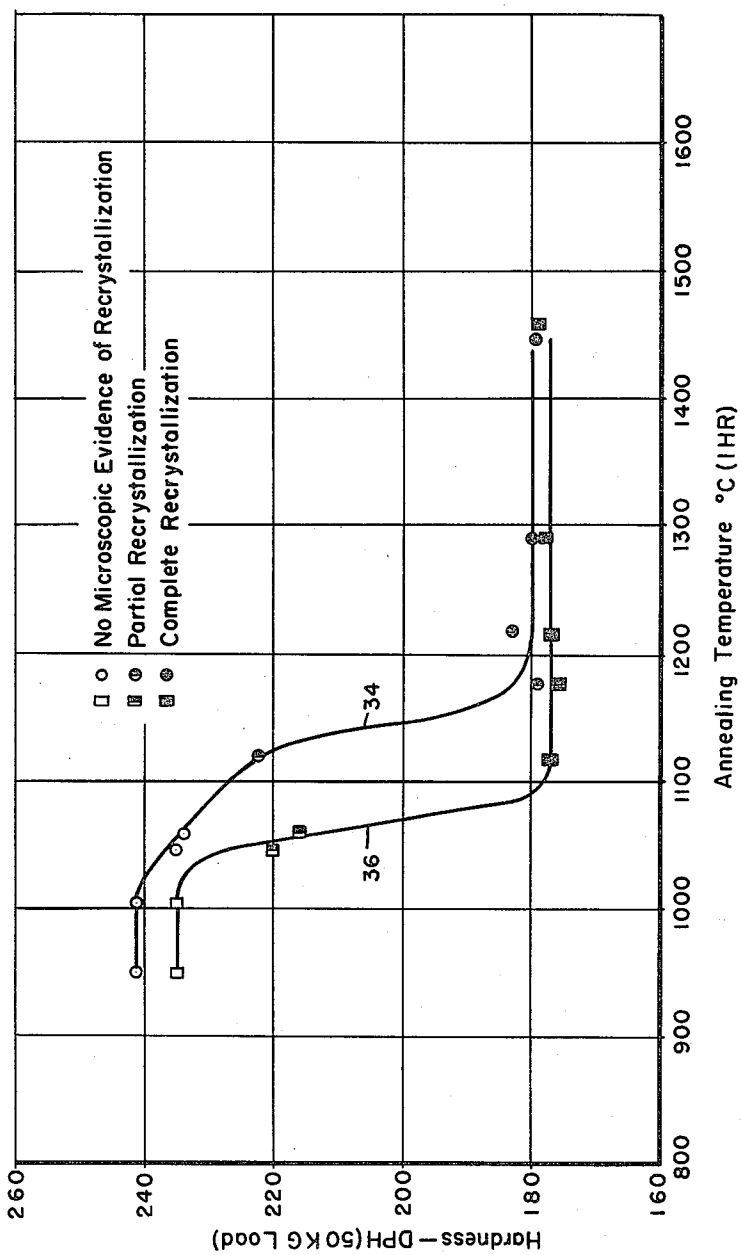


Fig. 11.

WITNESSES:

E. A. McAuley.

Wm. L. Boone

INVENTORS
James H. Bechtold, Benjamin Lustman
and Howard Scott.

BY

James M. Ely
ATTORNEY

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# UNITED STATES PATENT OFFICE

2,666,721

## PROCESS OF PRODUCING DUCTILE MOLYBDENUM

James H. Bechtold, Benjamin Lustman, and Howard Scott, Pittsburgh, Pa., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Application March 20, 1951, Serial No. 216,496

5 Claims. (Cl. 148—11.5)

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This invention relates to the process of producing ductile molybdenum base metal.

Pure molybdenum and the known molybdenum base alloys, such as 5% tungsten and 95% molybdenum, have many useful properties particularly at elevated temperatures of 900° C. and higher but their practical application is severely limited by their brittleness at room temperature and up to 150° C. Where alloying elements are employed to effect an increase in the hardness, and in particular, the creep and rupture strength at temperatures above 900° C. of molybdenum and its alloys, it is found that such alloys have poor cold ductility.

Heretofore attempts have been made to improve the cold ductility of molybdenum and its alloys by applying a moderate work hardening, as by rolling, thereto at room or slightly elevated temperatures. In such cases, however, it has been found that any gain in cold ductility is obtained only in the rolling direction. If cross rolling is employed then an improvement is obtained in the transverse direction but the cold ductility of rods or plates so treated remains poor in the thickness direction of the plate. In addition, work hardening of such metal with or without a preferred orientation in the direction of rolling appears to introduce objectionable directional properties.

An examination of molybdenum base metal plates produced by conventional hot or cold rolling reveals that the directional characteristics of such working is clearly evident after annealing the metal, for the metal has a coarse elongated grain structure. In most metals, the elongated grain structure found in a severely reduced metal is converted into a substantially equiaxed grain structure when annealed. However, the molybdenum base metal produced by prior practice does not have a well-defined recrystallization temperature but instead recrystallizes more or less progressively as the annealing temperature is increased.

An object of this invention is to provide a process for producing completely recrystallized molybdenum base metal having excellent ductility at room temperature.

Another object of this invention is to provide for so processing molybdenum base metal as to produce a wrought metal fully recrystallized and

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having a substantially uniform fine grain size and an excellent cold ductility.

Other objects of this invention will become apparent from the following description when taken in conjunction with the accompanying drawing in which:

Figure 1 is a graph, the curves of which illustrate the time-temperature relationship for the start and completion of recrystallization of molybdenum metal.

Figs. 2 through 8 are photomicrographs of molybdenum taken at different stages of the process of this invention.

Fig. 9 is a photomicrograph of bar stock produced from a sintered molybdenum compact processed in accordance with this invention.

Fig. 10 is a graph, the curves of which illustrate the improvement in tensile strength and ductility at room temperature of metal processed in accordance with this invention as compared with prior art metal, and

Fig. 11 is a graph, the curves of which illustrate the hardness change of two different molybdenum base metals treated in accordance with this invention and as annealed at different temperatures.

In practice, the molybdenum base metal, such as pure molybdenum or molybdenum alloy containing tungsten or other alloying elements in contents not greatly exceeding their solid solubility content, is produced by either the well-known powder metallurgy processes or by melting and casting methods. In the former case, fine powders of the metal are pressed under high pressures into simple shapes (not shown) such as circular cylinders or rectangular shapes suitable for forging, swaging, rolling or extruding into bars or billets. The density of such pressed shapes or briquettes is only about 60 to 70% of the base metal and the pressed briquettes are quite fragile.

When the pressed briquettes are sintered, as at a temperature between 1650 and 1750° C. in hydrogen for a time of 3 to 48 hours, the density of the compact is increased to between 94 and 98% of the theoretical density with an accompanying increase in strength. Although considerable shrinkage occurs, objectionable porosity remains and must be removed by working. Such sintered compacts are found to have a grain size

of from No. 7 to No. 11 ASTM which is quite favorable to working.

On the other hand, if the molybdenum base metal is produced by the casting method, it is found that in the "as cast" condition, the grain structure is quite coarse, grains a half inch or more in length often being observed. In order to break down the grain structure, the cast molybdenum base metal must be forged or rolled at a temperature above at least 1450° C. in cycles amounting to a 15 to 50% reduction in area, each of the working steps being followed by a reheat at substantially the initial heating temperature for a period of time sufficient to effect at least a partial recrystallization. Several such cycles, usually 2 to 5, are sufficient to break down the larger "as cast" grain structure to a mixed grain size of approximately No. 1 to No. 3 ASTM. Such metal is then in a favorable condition to be further processed as described hereinafter to obtain additional grain refinement and improve the cold ductility of the molybdenum base metal.

In order to produce the metal having a substantially uniform fine grain size and good cold ductility, the metal, whether sintered compacts or forged cast metal as referred to hereinbefore is subjected to a cyclic treatment comprising repeated alternate heating and working of the metal at temperatures below the recrystallization temperature of the metal. The recrystallization temperature of the metal will depend upon the initial grain size, composition and purity of the metal as well as the degree of work hardening but not necessarily the temperature at which the metal is worked. Such recrystallization temperature can be readily determined as shown hereinafter.

As representative of such a determination, reference may be had to Figure 1 of the drawing, the curves of which represent the time-temperature relationship for the beginning and ending of the recrystallization of cast molybdenum metal which had been forged to break up the initial large "as cast" grains to a mixed grain size of about No. 1 to No. 3 ASTM as described hereinbefore. Curves **10**, **12**, **14** and **16** shown in dotted line are representative of the start of recrystallization at different time and temperatures for the metal which has had 17%, 34%, 58% and 89%, respectively, of a reduction in area and curves **18**, **20**, **22** and **24**, respectively, are representative of the completion of recrystallization of the metal having 17%, 34%, 59% and 89%, respectively, of a reduction in area applied thereto, the reduction in areas being obtained by rolling from a starting temperature of 1000° C. As the rolling temperature is increased, the time of reheating between passes must be decreased to prevent recrystallization between passes. Also the maximum rolling temperature or the time of reheating or both must be decreased as the amount of deformation applied to the metal increases.

In general the process includes the heating of the molybdenum base metal to a substantially uniform temperature between 800° C. and the temperature at which recrystallization starts, which latter temperature in this application and in the claims is termed the recrystallization temperature, to thereby lower the resistance of the metal to deformation. The initial heating is preferably at a temperature of 1000° C. to 1300° C., but at all times below the recrystallization temperature of the metal and is applied for a sufficiently long time to develop a substantially uniform temperature throughout the mass of metal.

When the mass of metal is thus heated, the heated metal is worked, as by rolling, to effect a reduction in area of from 5 to 50%. The worked metal is again heated to a temperature not in excess of the initial temperature for from 3 to 15 minutes after which the reheated metal is again worked to effect a further reduction in area of from 5 to 50%. The alternate steps of heating at a temperature below the recrystallization temperature of the metal and working the heated metal are repeated until a total deformation equivalent to a reduction in area between 60% and 90% is effected. After such a reduction in area is obtained, the metal is then annealed at a temperature above the recrystallization temperature and preferably at 1150 to 1675° C. for a period of time of from a minimum of ½ hour at the lower temperature to a minimum of one minute at the higher temperature to effect the complete recrystallization of the metal to a substantially uniform grain size as fine as No. 6 ASTM. Such resulting completely recrystallized metal will have a room temperature ductility on tensile test in excess of 60% as measured by reduction in area.

As a specific example of the process of this invention reference may be had to the following table giving the schedule of treatment as applied to a 1¼ inch square hot forged billet of cast molybdenum having a grain size of No. 1 ASTM to work the billet to a ⅝ inch diameter round bar.

| Pass No. | Temp., ° C | Reheat time, min. | Reduction in area, percent | Total reduction in area, percent |
|---|---|---|---|---|
| 1–3 | 1,300 | | 25 | 25 |
| 4–5 | 1,300 | 5 | 15 | 36 |
| 6–8 | 1,150 | 15 | 20 | 49 |
| 9–11 | 1,150 | 5 | 23 | 60 |
| 12–14 | 1,000 | 15 | 27.5 | 72 |
| 15–17 | 1,000 | 10 | 27 | 81 |

Referring to Figs. 2, 3, 4, 5, 6 and 7 of the drawing, there are shown photomicrographs at magnifications of 100 times of the molybdenum metal in the "as received" condition, and after the 25%, 36%, 61%, 72% and 81% reduction in area as recorded in the foregoing table. These photomicrographs reveal that no recrystallization has occurred during the working of the metal.

After working the metal in this manner, the reduced metal was annealed at a temperature of 1150° C. for 1 hour to completely recrystallize the metal to a uniform fine grain size. The resulting recrystallized metal had a fine grain size of No. 6 to No. 7 ASTM or about 1000 grains per square millimeter as clearly shown in the photomicrograph at 100 times magnification of Fig. 8 of the drawing. When subjected to tensile testing, the completely recrystallized metal was found to have 55% elongation and 70% reduction in area at room temperature.

The process is equally applicable to the production of completely recrystallized molybdenum base metal having cold ductility from sintered compacts produced by powder metallurgy. For example, a 2⅛ inch diameter "as sintered" ingot of molybdenum having an initial grain size "as sintered" of No. 9 to No. 10 ASTM was satisfactorily rolled to a ⅝ inch diameter round by heating the "as sintered" ingot to a uniform tem-

perature of 1050° C. and thereafter alternately working and reheating at progressively lower temperatures with the final working at a temperature of 900° C. and at all times below the recrystallization temperature of the metal until a reduction of about 92% had been applied to the bar. When the worked bar was annealed at a temperature of 1150° C. for one half hour the metal of the bar was completely recrystallized to a substantially uniform grain size of No. 8 ASTM as shown in the photomicrograph, taken at a magnification of 100 times, of Fig. 9 of the drawing.

In order to clearly demonstrate the improvement in cold ductility of the molybdenum base metal which has been completely recrystallized as just described in accordance with this invention to a substantially uniform grain size of No. 8 ASTM as opposed to prior art hot swaged molybdenum base metal having a coarse and mixed grain size averaging about No. 3 ASTM, reference may be had to Fig. 10 of the drawing. In this figure, curve 26 represents the reduction in area obtained on the completely recrystallized fine grained metal of Fig. 9 whereas curve 28 represents the reduction in area obtained on the coarse grained hot swaged molybdenum. The lowering of the temperature of transition from ductile to brittle material obtained by the process of this invention is quite evident by comparing curves 26 and 28. The exceptionally good ductility at room temperature of molybdenum metal subjected to the new process is evidenced by curve 26. The improvement in room temperature breaking strength of the completely recrystallized fine grain molybdenum over that of the coarse grained hot swaged molybdenum is also clearly shown by curves 30 and 32, respectively, these curves being based on true breaking stress tests.

In practicing this invention it has been found necessary in all cases to apply a total reduction of from 60 to 90% without effecting recrystallization, if the grain size after the recrystallization anneal is to be as fine as No. 6 ASTM and if the metal is to have the improved cold ductility. This is true even though the initially "as sintered" metal had a grain size as fine as No. 10 to No. 11 ASTM.

In effecting the reduction in area, reductions of from 5 to 50% between reheats and preferably 10 to 25% are applied. In practice it is found that two to four passes of the metal may be made between reheats with a total reduction of from 10 to 25% reduction in area per reheat. Such large reductions in area between reheats and below the recrystallization temperature effect an increased uniformity of the grain size in the cross sectional area of the metal being worked.

Where the process is applied to molybdenum base alloys, higher temperatures or longer times are required to effect recrystallization thereby permitting higher rolling temperatures or longer reheating time between passes. In the molybdenum alloys smaller grain sizes are obtained by equivalent reductions in area than are obtained with pure molybdenum metal. This is evident from the curves of Fig. 11 in which curve 34 is representative of the hardness vs. annealing temperature for a molybdenum base alloy containing 5.13% tungsten and which had an initial grain size of No. 6 ASTM and curve 36 is representative of the hardness vs, annealing temperature for a pure molybdenum having an initial grain size of No. 7 ASTM, both metals being processed in a like manner as to the alternate reduction in area and reheat cycles and then annealed at the temperatures indicated.

While different variations of the reheating temperatures, time and reduction in area are contemplated as long as the alternate heating and working is below the recrystallization temperature of the molybdenum base metal, in practice, the following schedule has been found to produce excellent results when applied to sintered molybdenum base metal compacts and to cast molybdenum base metal which has been hot forged to break up the "as cast" coarse grain structure to No. 1 or No. 2 ASTM size.

| Reheat No. | Total prior reduction, percent | Reheat temperature, ° C. | Reheat time, min. | Reduction in area per reheat, percent | Number of passes per reheat |
|---|---|---|---|---|---|
| 0 | 0 | 1,000–1,300 | 10–60 | 5–50 | 1–8 |
| 0 | 0 | 1,150 | 30 | 15 | 2 |
| 1 | 5–50 | 1,000–1,300 | 3–15 | 5–50 | 1–8 |
| 1 | 15 | 1,150 | 5 | 15 | 2 |
| 2 | 9.5–75 | 1,000–1,250 | 3–15 | 5–40 | 1–8 |
| 2 | 27.5 | 1,150 | 5 | 15 | 2 |
| 3 | 14.5–85 | 900–1,200 | 3–15 | 5–30 | 1–8 |
| 3 | 38.5 | 1,100 | 5 | 15 | 2 |
| 4 | 18.5–89.5 | 900–1,200 | 3–15 | 5–30 | 1–8 |
| 4 | | 1,100 | 5 | 15 | 2 |
| 5 | 22.5–92.5 | 900–1,100 | 3–15 | 5–30 | 1–8 |
| 5 | 55.5 | 1,050 | 5 | 15 | 2 |
| 6 | 26–94.6 | 900–1,100 | 3–15 | 5–30 | 1–8 |
| 6 | 62.2 | 1,050 | 5 | 15 | 2 |
| 7 | 30–96.2 | 800–1,050 | 3–15 | 5–30 | 1–8 |
| 7 | 68 | 1,000 | 5 | 15 | 2 |
| 8 | 33.5–97.3 | 800–1,050 | 3–15 | 5–30 | 1–8 |
| 8 | 73 | 1,000 | 5 | 15 | 2 |
| 9 | 37.0–98 | 800–1,050 | 3–15 | 5–30 | 1–8 |
| 9 | 77 | 1,000 | 5 | 15 | 2 |
| 10 | 40–98 | 800–1,050 | 3–15 | 5–30 | 1–8 |
| 10 | 80.5 | 950 | 5 | 15 | 2 |
| 11 | 43–98 | 800–1,000 | 3–15 | 5–30 | 1–8 |
| 11 | 83.5 | 950 | 5 | 15 | 2 |
| 12 | 46–98 | 800–1,000 | 3–15 | 5–30 | 1–8 |
| 12 | 86 | 950 | 5 | 15 | 2 |
| 13 | 49–98 | 800–1,000 | 3–15 | 5–30 | 1–8 |
| 13 | 88 | 950 | 5 | 15 | 2 |
| 14 | 52–98 | 800–1,000 | 3–15 | 5–30 | 1–8 |
| 14 | 90 | 950 | 5 | 15 | 2 |

When the foregoing schedule of working is followed by an anneal above the recrystallization temperature and preferably at a temperature in the range of 1150° C. to 1650° C. for 15 minutes to 1 hour it is found that the resulting metal is completely recrystallized to a substantially uniform grain size as fine as No. 6 ASTM and in most cases to a grain size of No. 7 or 8 ASTM or finer. In all cases the tensile properties at room temperature have been improved as is evident from the curves of Fig. 10. From the showing of Fig. 10 it is evident also that the transition from ductile to brittle behavior on tensile test has been lowered approximately 150° C. and that very high elongation and reduction in area values are obtained at room temperature for the molybdenum base metal when processed in accordance with this process. In addition a more uniform ductility in all directions in the metal is obtained because of the substantially uniform fine and more nearly equiaxed grain structure.

We claim as our invention:

1. In the process of producing completely recrystallized ductile molybdenum base metal from the group consisting of molybdenum and alloys of molybdenum and tungsten in solid solution, the steps comprising, subjecting the molybdenum base metal to a temperature between 800° C. and the recrystallization temperature of the metal to reduce the resistance of the metal to deformation, applying deformation to the heated metal in an amount equivalent to a reduction in area between 5% and 50%, repeating the alternate steps of heating the metal below the recrystallization

temperature and above 800° C. and deforming the metal to effect a total deformation equivalent to a total reduction in area in excess of 60%, the time of heating at any given temperature being determined by both the temperature and the reduction in area in accordance with the showing in Figure 1 of the drawing, wherein for a given reduction in area indicated by a dashed line curve, the time of heating employed at any given temperature is below the dashed line, and similarly in proportion thereto for a reduction in area other than shown by the dashed lines, and thereafter annealing the deformed metal at a temperature for a period of time comprising a minimum of ½ hour at 1150° C. to one minute at 1675° C. above the recrystallization temperature to completely recrystallize the metal to a substantially uniform grain size not coarser than No. 6 ASTM, the recrystallized metal having a ductility in excess of 60% reduction in area at room temperature.

2. In the process of producing completely recrystallized ductile molybdenum base metal from cast molybdenum base metal from the group consisting of molybdenum and alloys of molybdenum and tungsten in solid solution, the steps comprising, working the cast metal at a temperature between 1450° C. and 1650° C. to effect a reduction in area of 15% to 50%, reheating the metal to substantially the initial heating temperature to effect complete recrystallization thereof and thereafter again work the heated metal to effect a reduction in area of 15% to 50%, repeating the cycles of heating and working until a substantially uniform grain size of between No. 1 and No. 3 ASTM is obtained, subjecting the metal to a temperature between 800° C. and the recrystallization temperature of the metal, working the heated metal an amount equivalent to a reduction in area of between 5% and 50%, repeating said later alternate steps of heating the metal below the recrystallization temperature and working the heated metal to effect a total deformation equivalent to a total reduction in area in excess of 60% without effecting recrystallization, the time of heating at any given temperature being determined by both the temperature and the reduction in area in accordance with the showing in Figure 1 of the drawing, wherein for a given reduction in area indicated by a dashed line curve, the time of heating employed at any given temperature is below the dashed line, and similarly in proportion thereto for a reduction in area other than shown by the dashed lines, and thereafter annealing the worked molybdenum base metal at a temperature above the recrystallization temperature to completely recrystallize the metal to a substantially uniform grain size as fine as No. 6 ASTM for a period of time comprising a minimum of ½ hour at 1150° C. to one minute at 1675° C., the recrystallized metal having a room temperature ductility in excess of 60% reduction in area.

3. In the process of producing completely recrystallized ductile molybdenum base metal from the group consisting of molybdenum and alloys of molybdenum and tungsten in solid solution, the steps comprising, heating the molybdenum base metal to a temperature between 800° C. and the recrystallization temperature of the metal, working the heated metal an amount equivalent to a reduction in area between 5% and 50%, repeating the alternate steps of heating and working the metal to effect a total working thereof equivalent to a reduction in area between 60% and 90%, the successive heating steps being at a temperature not in excess of the previous step and at all times being at a temperature below the recrystallization temperature of the molybdenum base metal, the time of heating at any given temperature being determined by both the temperature and the reduction in area in accordance with the showing in Figure 1 of the drawing, wherein for a given reduction in area indicated by a dashed line curve, the time of heating employed at any given temperature is below the dashed line, and similarly in proportion thereto for a reduction in area other than shown by the dashed lines, and thereafter annealing the worked metal at a temperature above the recrystallization temperature to completely recrystallize the metal to a substantially uniform grain size as fine as No. 6 ASTM for a period of time comprising a minimum of ½ hour at 1150° C. to one minute at 1675° C., the recrystallized metal having room temperature ductility in excess of 60% reduction in area.

4. In the process of producing completely recrystallized ductile molybdenum base metal from the group consisting of molybdenum and alloys of molybdenum and tungsten in solid solution, the steps comprising, heating the molybdenum base metal to a temperature between 800° C. and the recrystallization temperature of the metal, working the heated metal an amount equivalent to a reduction in area between 5% and 50%, repeating the alternate steps of heating and working the metal to effect a total working thereof equivalent to a reduction in area between 60% and 90%, the successive heating steps including a plurality of series of steps of heating at the same temperature but below the recrystallization temperature of the molybdenum base metal, each series of heating steps being at a progressively lower temperature, the time of heating at any given temperature being determined by both the temperature and the reduction in area in accordance with the showing in Figure 1 of the drawing, wherein for a given reduction in area indicated by a dashed line curve, the time of heating employed at any given temperature is below the dashed line, and similarly in proportion thereto for a reduction in area other than shown by the dashed lines, and thereafter annealing the worked metal at a temperature above the recrystallization temperature to completely recrystallize the molybdenum base metal to a substantially uniform grain size as fine as No. 6 ASTM, for a period of time comprising a minimum of ½ hour at 1150° C. to one minute at 1675° C., the recrystallized metal having a room temperature ductility in excess of 60% reduction in area.

5. In the process of producing completely recrystallized ductile molybdenum base metal from the group consisting of molybdenum and alloys of molybdenum and tungsten in solid solution, the steps comprising, heating the molybdenum base metal to a temperature between 900° C. and 1200° C. to reduce the resistance of the metal to deformation, working the heated metal an amount equivalent to a reduction in area between 5% and 50%, repeating the alternate steps of heating and working the metal to effect a total deformation equivalent to a total reduction in area between 60% and 90%, the steps of heating between the working steps being applied to develop predetermined temperatures in the worked metal that are below the recrystallization temperature of the worked metal and are lowered in a predetermined step schedule within the

range of 900° C. and 1200°, the time of heating at any given temperature being determined by both the temperature and the reduction in area in accordance with the showing in Figure 1 of the drawing, wherein for a given reduction in area indicated by a dashed line curve, the time of heating employed at any given temperature is below the dashed line, and similarly in proportion thereto for a reduction in area other than shown by the dashed lines, and thereafter annealing the worked metal at a temperature within the range of 1150° C. and 1650° C. for a minimum period comprising ½ hour at 1150° C. to one minute at



1650° C. to completely recrystallize the molybdenum base metal to a substantially uniform grain size as fine as No. 6 ASTM, the recrystallized metal having a room temperature ductility in excess of 60% reduction in area.

JAMES H. BECHTOLD.
BENJAMIN LUSTMAN.
HOWARD SCOTT.

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