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J. W. MARDEN ET AL
LOW TEMPERATURE FABRICATION OF
MOLYBDENUM AND ALLOYS THEREOF
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2,667,435

Fig. 1.

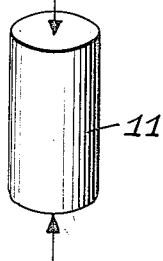


Fig. 2.

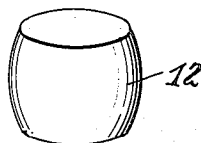


Fig. 3.

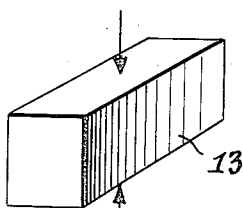


Fig. 4.

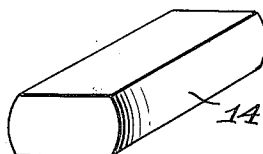


Fig. 5.

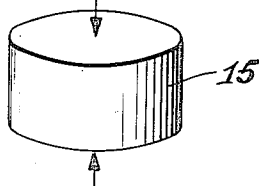


Fig. 6.

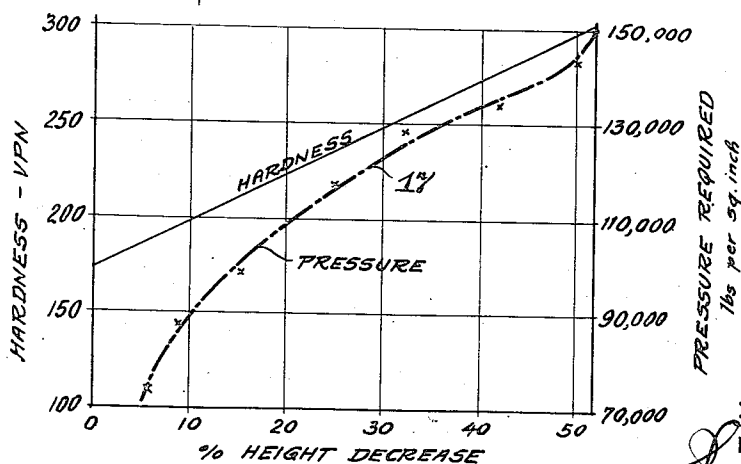
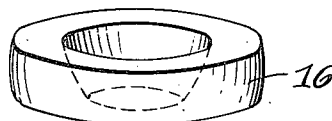


Fig. 7.

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LOW TEMPERATURE FABRICATION OF
MOLYBDENUM AND ALLOYS THEREOF

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Application September 21, 1951, Serial No. 247,652

9 Claims. (Cl. 148—11.5)

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This invention relates to molybdenum and, more particularly, to its fabrication at low temperatures.

The principal object of our invention, generally considered, is to work molybdenum under compressive stress at low temperatures, terminating the treatment with a stress-relieving anneal from a temperature below that of grain growth.

Another object of our invention is to work molybdenum by compression at a slow rate when approximately at room temperature.

A further object of our invention is to work molybdenum under compression at a slow rate of speed, and finally stress relieve it by treatment at about 1200° C., allowing it to cool nearly to room temperature, or to as low as 200° C., for about 24 hours, or at a rate of 60° C. or less per hour.

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

Referring to the drawing:

Fig. 1 is a perspective view of a cylinder of pressed and sintered metal prior to treatment in accordance with our invention.

Fig. 2 is a similar view of the same cylinder after cold working at a slow rate.

Fig. 3 is a perspective view of a bar of pressed and sintered metal prior to working.

Fig. 4 is a similar view of the same bar after cold working in accordance with our invention.

Fig. 5 is a perspective view of a cylinder of pressed and sintered metal prior to working.

Fig. 6 is a similar view of said cylinder after formation of a pocket therein by cold working at a slow speed.

Fig. 7 is a diagram showing how hardness of pressed and sintered molybdenum increases when compressed at room temperature to various degrees.

Molybdenum, prior to being worked, is brittle and, prior to the present invention, there has been no known method of fabricating at room temperature ingots thereof which were merely sintered after pressing the powder. Tensile tests of such merely heat-treated molybdenum, prior to working such as hot rolling and annealing which would develop its strength, show that it as well as alloys thereof containing small percentages of metal such as cobalt, nickel, iron and tungsten, have no appreciable ductility under tension and an ultimate strength of only about 50,000 lbs. per square inch.

By the expression alloys of molybdenum with small proportions of metal selected from the

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group consisting of cobalt, nickel, iron and tungsten, we mean such in which the proportion of any one of the first three mentioned alloying metals is not greater than ½%, and in which the proportion of alloying tungsten is not greater than 20%.

When a block of such merely pressed and sintered molybdenum powder, for example, is struck a sharp blow while at room temperature, the block shatters. So it is impossible to roll or forge such heat-treated unworked metal at such low temperatures. The experience of workers in the art indicates that rolling, forging, or other working must start at or above 1200° C.

In accordance with our invention, however, we take a piece of unworked molybdenum, or such containing small percentages of another metal as enumerated above, and deform it while cold, that is, at room temperatures which we have defined as those between 15° and 35° C., or merely slightly warmed but still at a relatively cold temperature and one not above 200° C., by compressing at a slow rate of speed. Under such treatment, a cylinder 11 of pressed and sintered powder, shown in Figure 1, on slow compression deforms to the generally barrel shape 12 of Fig. 2. A bar 13, as shown in Fig. 3, on slow compression deforms to the bulged shape 14 of Fig. 4. In pressing a pocket in a shape 15, shown in Fig. 5, by slow action on an article of pressed and sintered molybdenum powder, we get a shape 16 such as shown in Fig. 6.

In effecting such compression, a selected piece of molybdenum is placed between hardened steel platens in a hydraulic press and slowly but uniformly compressed. The press preferably closes at a rate of about ½" or less per minute to decrease the height of the sample a desired amount, or otherwise deform it, for example, as shown in Fig. 6. After such compression, which may warm the article slightly due to the conversion of work into heat, the article is placed in a furnace at a desired stress-relieving temperature below that of grain growth such as, for example, about 1200° C. The power to the furnace is then cut off and the sample allowed to cool nearly to room temperature at a rate of cooling, for example, such as described in the co-pending application of Baker and Byron, Serial No. 246,654, filed September 14, 1951, "Ductilizing Molybdenum and Alloys Thereof," and owned by the assignee of the present application or; for example, the furnace may be cooled nearly to room temperature, or as low as 200° C. in about 24 hours or at the rate of 60° C. or less per hour.

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The pressure required for deforming pieces of molybdenum is shown by the curve 17 in Fig. 7. From this it appears that to decrease the height about 6% takes approximately 75,000 lbs. per square inch. However, as the piece is compressed, it works strains so that to compress it as much as 50% in height, a pressure of about 150,000 lbs. per square inch is required. Of course, the pressure required decreases as the working temperature is increased and vice versa. Many samples in several sizes have been cold worked in this fashion and the following table is merely an example to indicate the pressure required at approximately 25° C.

Table I

[Original sample: Mo + .1% Co, length .750", diam. .625", hardness 173 VPN.]

Load Required, lbs.	Length, inches	Diameter, inches	Area, Sq. in.	Pressure Required, lbs. per sq. inch	Height Decrease, Percent
25,000.....	.707	.645	.324	76,500	5.7
30,000.....	.681	.659	.329	87,800	9.2
40,000.....	.623	.695	.380	105,000	16.9
50,000.....	.567	.725	.413	121,500	24.4
60,000.....	.505	.770	.466	129,000	32.7
75,000.....	.436	.830	.542	138,500	41.8
90,000.....	.383	.883	.609	146,500	48.9
100,000.....	.353	.921	.665	151,000	53.0

The physical properties obtained on rectangular pieces of molybdenum compressed 33% in height is indicated by the following table.

Table II

Sample No.	PL1	PL9	PL10	PL11	PL12	PL13	PL14
Pressed Side, VPN.....		261	256	263	265	255	263
Hardness Top, VPN.....	171	248	254	252	268	259	283
Annealing Temperature, °C.....		1,200	1,220	1,215	1,200	1,130	1,100
Time at Temperature, Minutes.....		20	10	5			
Annealed Hardness, VPN.....		156	169	215	221	242	254
Elongation in 1/2", Percent.....	0.0	0.2	2.3	22.4	10.3	1.1	0.6
Yield Strength, 10 ³ p. s. i.....	50.0	71.7	66.9	71.8	78.8	104.3	108.2
Ultimate Strength, 10 ³ p. s. i.....	50.0	71.7	67.3	94.3	97.3	105.6	108.2

The amount of work strain is indicated in accordance with the above table but the hardness of the original samples, PL1, was about 171 VPN while after compression the hardness varied from 255 to 265 VPN on the side, and from 248 to 283 VPN on the top, that is, the surface on which pressure was applied. Time, temperature, hardness, elongation and strength have been recorded after annealing and slow cooling.

Thus, we have discovered that working molybdenum and its alloys enumerated may be accomplished by cold compression, followed by annealing, so that hardness, strength and ductility may be obtained without the use of hot rolling or forging. While it is old in the art to cold work ordinary common, soft, ductile metal like copper and iron, these show ductility under tension at room temperature. However, refractory metals such as molybdenum, which show no appreciable ductility in tensile tests, have heretofore needed to be worked at elevated temperatures.

We have, therefore, discovered an entirely new method for fabricating molybdenum and alloys thereof which has never heretofore been known or resorted to for such metals. In accordance with our invention, such may now be worked from the start, after merely pressing and sintering the powder, at temperatures below that of recrystal-

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lization. We have also discovered that extremely high density, indicating well-treated material, is not required in starting the process. Also, it makes little difference in the working schedule, in accordance with our invention, whether pure molybdenum or such alloyed with cobalt, for example, in the amount of .1%, .2% or .3%, is used.

The strength and elongation values of Table II are those where the tensile specimens were cut across the sample, that is, at right angles to the direction of pressing or in the direction in which metal flow takes place during the cold compression of our invention. These figures are comparable to those obtained by cutting tensile specimens from samples along the direction of rolling, if hot rolling is resorted to. The ductilities obtained were found to be far superior to those obtainable by a similar amount of reduction in normal factory practice. The utility and desirability of our method of obtaining good ductility in special sizes and diameters, will, therefore, be apparent.

Although a preferred embodiment of our invention has been described, it will be understood that modifications may be made within the spirit and scope of the invention.

We claim:

1. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of

metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at room temperature at a rate of speed of not more than 1/2" per minute until deformed not less than about one-third, heating to a stress-relieving temperature between about 1100° C. and 1220° C., and finally allowing said article to cool from that temperature to one not higher than 200° C. in a length of time not shorter than 24 hours.

2. The method of manufacturing ductile metal from a merely pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing said article within the range of temperature between about 15° and 35° C. at a rate of speed of not more than 1/2" per minute until deformed not less than about one-third, heating to a stress-relieving temperature above about 1100° C. and below that of grain growth, and finally allowing said article to cool slowly to a temperature not higher than 200° C. in a length of time not shorter than 24 hours.

3. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum

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and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at room temperature at a rate of about $\frac{1}{2}$ " per minute until deformed to the desired extent but not less than about one-third, heating to a stress-relieving temperature below that of grain growth but above about 1100° C., and finally allowing said article to cool slowly to a temperature not higher than 200° C. in a length of time not shorter than 24 hours.

4. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at room temperature at a rate of speed not greater than $\frac{1}{2}$ " per minute until deformed not less than about one-third, heating to a temperature of about 1200° C., and finally allowing said article to cool slowly to a temperature not higher than 200° C. in a length of time not shorter than 24 hours.

5. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at room temperature at a rate of speed not greater than $\frac{1}{2}$ " per minute until deformed not less than about one-third, heating to a stress-relieving temperature above about 1100° C. and below that of grain growth, and finally allowing said article to cool at a rate not higher than 60° C. per hour to a temperature not higher than about 200° C.

6. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at room temperature at a rate of speed not greater than $\frac{1}{2}$ " per minute until substantially deformed, heating to a stress-relieving temperature below that of grain growth but higher than 1100° C., and finally allowing said article to slowly cool to a temperature not higher than about 200° C. a length of time not shorter than 24 hours.

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7. The method of manufacturing ductile metal from a pressed and sintered article of powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron and tungsten, comprising compressing the article at a temperature between about 15° and 35° C. at a rate of speed not higher than $\frac{1}{2}$ " per minute until deformed not less than about one-third, heating to and holding at a temperature of between about 1100° C. and 1220° C. for from about 5 to 20 minutes, and finally allowing said article to cool at a rate not higher than about 60° C. per hour to a temperature not higher than about 200° C.

8. The method of manufacturing ductile metal from powdered particles of the group consisting of molybdenum and alloys thereof with small proportions of metal of the group consisting of cobalt, nickel, iron, and tungsten, comprising pressing the powdered material to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, pressing the article at room temperature at a rate of speed not greater than $\frac{1}{2}$ " per minute until substantially deformed, heating to a stress-relieving temperature below that of grain growth but higher than 1100° C., and finally allowing said article to cool slowly to a temperature not higher than 200° C. in a length of time not shorter than 24 hours.

9. The method of manufacturing ductile metal from powdered molybdenum comprising pressing the powdered material to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, pressing the article at room temperature at a slow rate of speed of about $\frac{1}{2}$ " per minute until decreased in height at least one-third, heating to a stress-relieving temperature of about 1200° C., and finally allowing said article to cool slowly from that temperature to one not higher than 200° C. in a length of time not shorter than 24 hours.

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