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R. H. SCHNITZEL ET AL

2,921,875

MANUFACTURE OF MOLYBDENUM AND ALLOYS THEREOF

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Fig. 1.

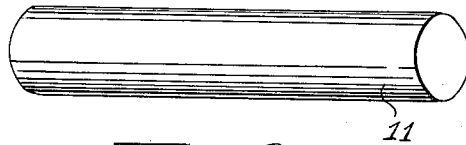


Fig. 2.

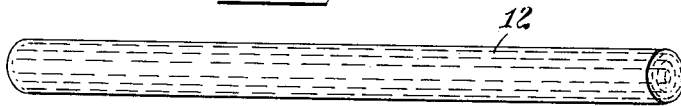


Fig. 3.

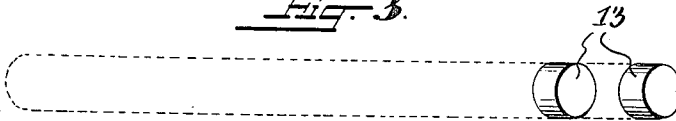


Fig. 4.

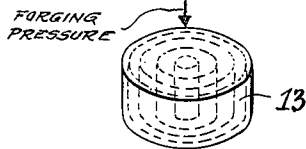


Fig. 5.

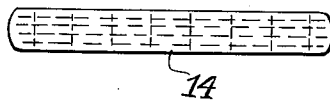


Fig. 6.

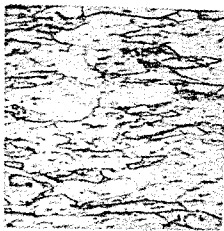


Fig. 7.

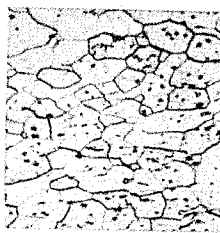


Fig. 8.

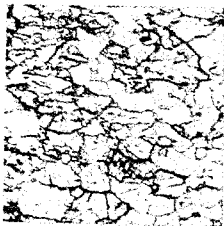
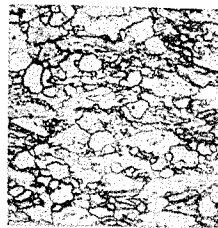


Fig. 9.

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1

2,921,875

MANUFACTURE OF MOLYBDENUM AND ALLOYS THEREOF

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Application November 12, 1953, Serial No. 391,520

9 Claims. (Cl. 148—11.5)

This invention relates to molybdenum and its alloys and, more particularly, to improving the grain and fiber structure of articles made therefrom.

An object of our invention is to manufacture molybdenum, and alloys thereof with small proportions of other metals such as cobalt, iron, nickel and tungsten, in order to produce material in which the structure is substantially equalized in all directions, by diffusing the laminations produced by working in one direction with those produced by working in another direction.

Another object of our invention is to produce molybdenum and alloys thereof having an improved structure, by swaging sintered ingots thereof to produce fibers extending in an axial direction, followed by forging axially of the swaging fibers to effect a diffusing of the laminations and general improvement in the structure of the metal.

A further object of our invention is to improve the strength of molybdenum and alloys thereof with small proportions of cobalt, nickel, iron or tungsten, pressed and sintered, comprising swaging to elongate the article, and then forging to compress it in a direction along its axis, thereby working the metal not only longitudinally but also transversely of its initial axis.

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

In the drawing:

Fig. 1 is a perspective view of a pressed and sintered ingot of metal to be processed in accordance with our invention.

Fig. 2 is a perspective view of the ingot of Fig. 1 after swaging to a desired extent and showing the way in which the fibers or laminations extend in the metal bar so produced.

Fig. 3 is a perspective view of sections cut from the swaged ingot of Fig. 2.

Fig. 4 is a perspective view on a larger scale of one of the sections cut from the bar of Fig. 2, positioned with its axis vertical and in position to be forged.

Fig. 5 is an elevational view on a still larger scale of one of the sections as shown in Fig. 4, but after final forging has taken place, and showing the lines along which the fibers extend throughout the metal.

Fig. 6 is a photomicrograph showing enlarged 500 times the grains at a section taken vertically through the center of an ingot such as illustrated in Fig. 5, after being forged in accordance with standard practice without prior swaging.

Fig. 7 is a photomicrograph corresponding to Fig. 6, but showing the grains at the edge of such an ingot.

Fig. 8 is a photomicrograph corresponding to Fig. 6, but showing the grains at the center of an ingot swaged and forged in accordance with our invention.

Fig. 9 is a photomicrograph corresponding to Fig. 8, but showing the grains at the edge of an ingot embodying our invention.

It has been shown by numerous tests and investigations that the vertical tensile strength or that in the line of the

2

pressure exerted during working, is exceedingly low as compared to the longitudinal and transverse tensile strengths. That is, the strength in both the direction in which the ingot is elongated and the transverse tensile strength or that in the direction in which the ingot widens during rolling or other working is higher than that in the thickness or other direction. The primary reason given for the low strength is the existence of laminations or fibering in the molybdenum or alloy thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten. By such an expression, we mean to include in addition to pure molybdenum, alloys thereof in which the proportion of cobalt is not greater than .3%, in which the proportion of either nickel or iron is not greater than ½%, and in which the proportion of alloying tungsten is not greater than 25% by weight. However, cobalt is preferred as the alloying metal, and in the specific embodiment to be described, that is what is used. However, the other alloying materials have effects which will be described hereinafter.

We now propose to show that the laminations above referred to can be used to advantage in improving the vertical tensile strength. It must be remembered that such laminations are developed by working, as is common in physical metallurgy.

The vertical tensile strength, or that in the direction of working pressure, can be improved as follows:

(a) Line up the laminations by working at high temperatures.

(b) Follow the line-up of laminations at high temperatures by working at a lower temperature and in the direction perpendicular to that which in the previous operation yielded the highest tensile strength.

(c) Cancel the previous strains by different methods of working and finally obtain an article having approximately the original size.

(d) Working some areas that are usually not worked under ordinary procedures. For example, we may swage where the metal is subjected to strong side pressures. It is known that in operations involving strong side pressures residual stresses are greater than in pure tension, compression and torsion where side pressures are not employed. By obtaining these residual stresses in certain areas not normally worked, the structure and mechanical properties which are desired can be obtained upon annealing. Of course, working is accompanied with proper heat treatment in order to obtain the desired results.

For example, by using different methods of working, such as swaging followed by forging, increased vertical tensile strength may be obtained. In a normal forging operation the laminations or fibers are lined up in a direction transverse to the forging pressure, the highest tensile strength being in the direction of the laminations so produced, and the lowest tensile strength being in the direction of forging pressure. From this, it may be seen that laminations occur in a direction perpendicular to the direction of working or forging. In this direction, higher tensile strengths are obtained, as contrasted with the lowest tensile strength across the laminations.

In a normal swaging operation, the laminations are lined up parallel to the direction in which the article is elongated. Our idea, therefore, is to combine these two methods of working, swaging and forging, or any other two similar methods of working, keeping in mind the desire to equalize the fibers or grain elongations which are obtained during the working. Operating on a molybdenum bar about 1" in diameter and containing about .15% of cobalt (or from .05% to .3% of cobalt), swaging desirably takes place at temperatures between 1400° and 1450° C., with a reduction in cross-sectional

area of approximately 34% to 42%, and an increase in length of approximately 67%, the laminations extending longitudinally of the article and in the direction in which it is elongated. Following the specified reduction in cross-sectional area by swaging, the article is forged in the direction of the laminations or grain elongation, corresponding to a reduction of about 50% in height at a temperature of about 950° C.

The diameter of a typical specimen or ingot may now be approximately 1", or a recovery of the 34% to 42% in cross-sectional area initially lost and an increase in section to approximately that of the original slug or specimen which was swaged. By this combination of different kinds of working, the principal strains are canceled, obtaining essentially an article of a size approximately that at which the working started, but in which the laminations produced are diffused and extend, not only longitudinally, but also transversely and in the direction of thickness.

Since swaging is at a high temperature, the mobility of formation of the laminations is greater than at a lower temperature, and it can be expected that these swaging laminations will persist in the forging and post forging operations. Residual stresses are probably higher in the swaging operation than in forging. Areas unworked are now worked in the forging operation, and consequently the grain size and the subsequent mechanical properties can be controlled with properly-applied heat treatment and annealing.

Referring now to the drawing in detail, the article 11 of Fig. 1 represents a bar or ingot of molybdenum, with which .15% of cobalt has been alloyed, said bar having been formed by pressing and sintering the powder in accordance with conventional procedures. Such a round bar, originally about 1 inch in diameter, was swaged to a finished size of about .81" diameter, as represented at 12 in Fig. 2, corresponding to a reduction in cross-sectional area of from about 34% to 40%, at a temperature of approximately 1400°-1450° C.

The swaged rod was then cut to proper lengths, as indicated at 13 in Fig. 3, and forged in a direction axial of the original bar as represented in Fig. 4, to produce a flattened disk 14 as illustrated in Fig. 5. The material was given a half hour stress-relief soak at the forging temperature of about 950° C. before the finish forging at such a temperature. The forged button or disk was then given a stress relief anneal for about 40 minutes at a temperature of about 1000° C., the higher the annealing temperature the shorter the annealing time and vice versa, followed by slow cooling in a furnace. Said annealing and slow cooling operations are more fully described and claimed in the Baker et al. application, Ser. No. 246,654, filed Sept. 14, 1951, now U.S. Patent No. 2,721,138, dated October 18, 1955. From Fig. 5 it will be seen that the laminations, which were swaged to extend vertically as viewed in Fig. 5, have now been diffused with laminations produced by forging, and which extend generally horizontal as viewed in that figure.

The following data show the mechanical properties obtainable from material processed in the above manner. Similar data are given for material processed by the best present or conventional techniques.

Table 1

Technique	Hardness (DPN)	Ultimate Strength (p.s.i.)	Total Elongation (percent)
Present.....	331	128,600 (A)	35.0
Proposed.....	331	124,200 (A)	41.6
Present.....	331	46,600 (B)	0
Proposed.....	331	107,100 (B)	0

(A) Measured in the tangential direction.
(B) Measured in the vertical direction.

The photomicrographs designated Figs. 6 to 9, incl. show the excellent consistency of grain size and structure throughout the material produced in accordance with our invention, as compared with the best present or conventional techniques.

Although the data above given has been restricted as to the combination of swaging and forging processes, since these are the most readily adaptable to mass production techniques, yet we do not wish to be limited to this combination as the material may be worked by other combinations such as rolling and forging. The finished swaged diameters are easily made correct for the forging operation, so there is no additional machining required. The swaged rod need only be cut off to proper length and fed directly to a continuous type furnace to be stress-relieved and finish-forged.

When rolling and forging are combined the following procedure may be followed. Standard rolling flats of molybdenum, 2 1/4" square in section, alloyed with .15% of cobalt were reduced 50% in height in four passes using standard procedures. After a stress relief and slow cooling in a furnace, the bars were split and turned round or cylindrical to proper forging size. Forging was at about 950° C. with no holding time, followed by an anneal of about 1/2 hour at about 1000° C.

Table 2

Technique	Tangential Direction		Vertical Direction	
	Ultimate Tensile Strength, p.s.i.	Elongation, percent	Ultimate Tensile Strength, p.s.i.	Elongation, percent
Forged.....	128,600	35.0	46,600	0.0
Swaged and Fgd.....	124,200	41.6	107,100	0.0
Rolled and Fgd.....	129,500	29.6	112,600	2.5

Although the foregoing examples are specific to molybdenum alloyed with .15% of cobalt by weight, yet similar temperatures may be employed in operating on molybdenum alloyed with proportions of cobalt within the range of .05% to .3% and proportions of either nickel or iron within the comparable range of .1% to .5%. In operating on pure molybdenum, or such containing alloying material less than the minima above specified or less than 1% of tungsten, the swaging and rolling temperatures are desirably slightly higher, or approximately 1450° to 1475° C., as compared with 1400° to 1450° C., for the molybdenum-cobalt alloys. Likewise, the forging temperature for pure molybdenum, and such including the minima in alloying ingredients above specified, is desirably increased to about 1050° C. as compared with 950° C. for the molybdenum-cobalt alloys. The working temperatures for molybdenum-tungsten alloys, within the specified range of up to 25% tungsten (or from 1% to 25%), are desirably about the same as those for pure molybdenum. Likewise, the annealing temperature after forging is desirably increased to about 1075° C. for pure molybdenum and such including the minima in alloying ingredients above specified, as well as for molybdenum alloyed with tungsten within the specified range.

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

We claim:

1. The method of manufacturing refractory metal of improved structure from an article of powdered particles thereof, pressed and sintered, comprising working said article to elongate it, and then working said article in a direction along its longitudinal axis to produce a diffused pattern of fibrous laminations within said article.

2. The method of manufacturing metal of improved structure from an article of powdered particles of the group consisting of molybdenum and alloys thereof with

5

small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, such small proportions by weight being up to .3% of cobalt, up to .5% of nickel, up to .5% of iron, and up to 25% of tungsten, pressed and sintered, comprising swaging said article to elongate it about 67%, with a reduction in cross-sectional area of between about 34% and 42%, and then forging said article to compress it about 50% in a direction along its swaging axis and effect a diffused pattern of fibrous laminations within said article.

3. The method of manufacturing metal of improved structure 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, such small proportions by weight being up to .3% of cobalt, up to .5% of nickel, up to .5% of iron, and up to 25% of tungsten, pressed and sintered, comprising swaging said article at a temperature between about 1400° and 1475° C. to elongate it about 67%, with a reduction in cross-sectional area of between about 34% and 42%, and then forging said article at a temperature between about 950° C. and 1050° C. to compress it about 50% in a direction along its swaging axis and effect a diffused pattern of fibrous laminations within said article.

4. The method of manufacturing metal of improved structure from an article of powdered particles of the group consisting of molybdenum alloyed with a small proportion of cobalt, comprising swaging said article at a temperature between about 1400° and 1450° C. to elongate it to about 67% with a reduction in cross-sectional area of between about 34% and 42%, cutting said elongated article into sections on planes transverse to its length, and then forging said sections at a temperature about 950° C. to compress them about 50% in a direction along their swaging axes and effect a diffused pattern of fibrous laminations therein.

5. The method of manufacturing refractory metal of improved structure from an article of powdered particles of molybdenum alloyed with between about .05% and .3% by weight of cobalt, pressed and sintered, comprising swaging a cylindrical bar about 1" in diameter to about .81" in diameter, at a temperature of approximately 1400° to 1450° C. to elongate it, cutting said elongated bar to sections along planes transverse to its length, and then forging said sections at a temperature of about 950° C. to compress them about 50% in the direction along their swaging axes and effect a diffused pattern of fibrous laminations therein, subjecting said forged sections to a stress-relief anneal for about 40 minutes at a temperature of about 1000° C., and then slowly cooling them to room temperature.

6. The method of manufacturing refractory metal of improved structure from an article of powdered particles of molybdenum alloyed with between about .1% and .5% by weight of material selected from the group consisting of nickel and iron, pressed and sintered, com-

6

prising swaging a cylindrical bar about 1" in diameter to about .81" in diameter, at a temperature of approximately 1400° to 1450° C. to elongate it, cutting said elongated bar to sections along planes transverse to its length, and then forging said sections at a temperature of about 950° C. to compress them about 50% in the direction along their swaging axes and effect a diffused pattern of fibrous laminations therein, subjecting said forged sections to a stress relief anneal for about 40 minutes at a temperature of about 1000° C., and then slowly cooling them to room temperature.

7. The method of manufacturing refractory metal of improved structure from an article of powdered particles of the group consisting of molybdenum and alloys thereof with a proportion of tungsten up to 25% by weight, pressed and sintered, comprising swaging a cylindrical bar about 1" in diameter to about .81" in diameter, at a temperature of approximately 1450° to 1475° C. to elongate it, cutting said elongated bar to sections along planes transverse to its length, and then forging said sections at a temperature of about 1050° C. to compress them about 50% in the direction along their swaging axes and effect a diffused pattern of fibrous laminations therein, subjecting said forged sections to a stress relief anneal for about 40 minutes at a temperature of about 1075° C. and then slowly cooling them to room temperature.

8. The method of manufacturing refractory metal of improved structure from an article of powdered particles thereof, pressed and sintered, comprising working said article to elongate it and effect a predetermined reduction in its cross-sectional area, and then compressing said worked article in a direction along the initial working axis to restore said article to approximately its original size and produce a diffused pattern of fibrous laminations therein.

9. The method of manufacturing metal of improved structure 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, such small proportions by weight being up to .3% of cobalt, up to .5% of nickel, up to .5% of iron, and up to 25% of tungsten, pressed and sintered, comprising rolling said article to reduce its height by about 50% and form a flattened bar, splitting said flattened bar along the direction of rolling into sections, and then forging said sections to compress them about 50% in the direction along which they were rolled and effect a diffused pattern of fibrous laminations therein.

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