Oct. 18, 1955 R. F. BAKER ET AL 2,721,138

METHOD OF DUCTILIZING MOLYBDENUM AND ALLOYS THEREOF

Filed Sept. 14, 1951

Fig. 1.

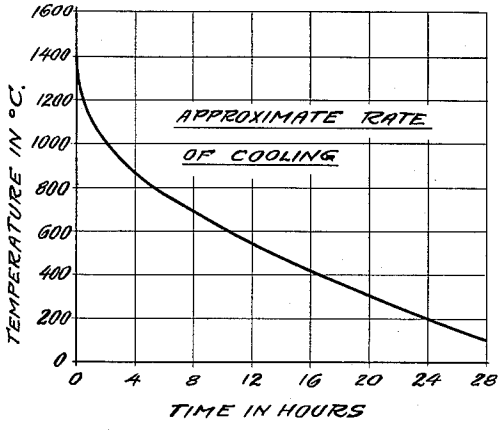


Fig. 2.

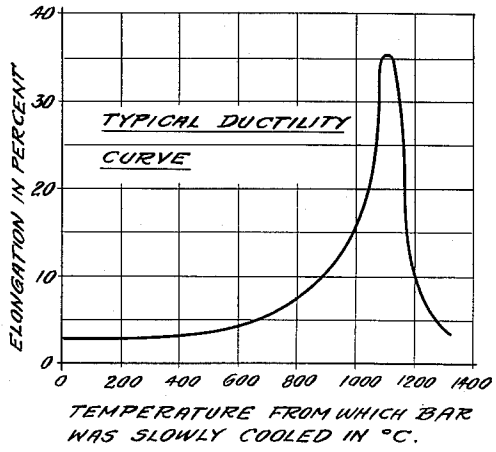
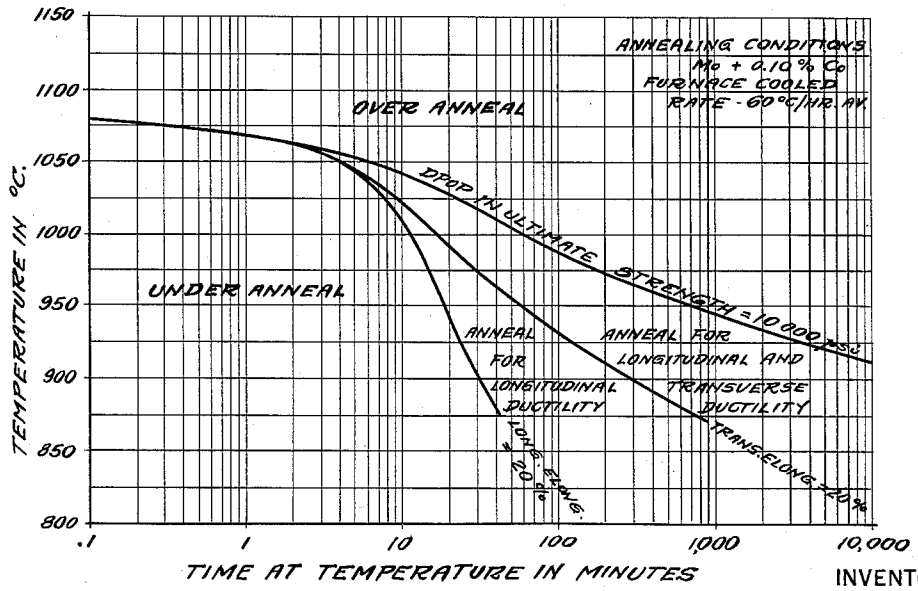


Fig. 3.



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METHOD OF DUCTILIZING MOLYBDENUM AND ALLOYS THEREOF

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11 Claims. (Cl. 75—214)

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 our 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 our invention is to work molybdenum and alloys thereof at the proper temperature, relieve the stress therein, and slow-cool to get hard, strong and ductile material.

A further object of our invention is to work molybdenum and alloys thereof at or below 1200° C., with limited reheating periods between working steps, and a final slow-cooling in order to increase hardness and strength.

A still further object of our invention is to effect grain elongation in molybdenum and alloys thereof, without recrystallization to a more or less equiaxed condition.

An additional object of our invention is to place molybdenum and the like, strained by work at or below 1200° C., in a cooling furnace at some predetermined temperature, such as about 1050° C., and allow it to cool at a slow rate so as to effect desired properties therein.

Another object of our invention is to treat molybdenum and the like in two steps: first, effect stress relief and, second cool slowly, as without stress relief the desired ductility is not producible.

A further object of our invention is to eliminate the critical nature of the stress relief step by using a longer time at a lower temperature, the cooling from said stress relief treatment being at the rate of between 60° C. and 120° C. per hour in order to avoid seriously affecting the properties of the metal.

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

In the drawing:

Fig. 1 is a curve showing the approximate rate of cooling in the practicing of one embodiment of our invention.

Fig. 2 is a curve indicating the critical nature of the stress relief step for producing the desired ductility in worked material loaded into a furnace at temperatures shown and slow cooled without soaking at such temperatures.

Fig. 3 is a chart with curves indicating the annealing times required for molybdenum with different temperatures of treatment to produce the desired results.

In the application of Marden and Wroughton, Serial No. 743,000, filed April 22, 1947, and now abandoned, there is disclosed a method of producing ductile molybdenum of relatively large diameters or thicknesses. Until recently, the largest bars of molybdenum commercially fabricated were about 1 inch square. At present, much larger ingots are being worked and the handling and

fabrication of such when composed of molybdenum or alloys thereof with small proportions of metal selected from the group consisting of cobalt, nickel, iron and tungsten, is far more difficult and requires new fabrication procedures not used for the fine sheet and wire previously produced. By the expression alloys of molybdenum with small proportions of metal selected from the 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%.

We have discovered that by placing work-strained molybdenum, in pieces of considerable mass obtained from the rolling mill, in a furnace at a predetermined temperature and allowing the furnace to cool slowly to a relatively-low temperature, say nearly to room temperature or to temperatures below 700° C., a new and unexpected result is obtained. We found that if the work-straining of molybdenum during rolling or forging was at temperatures above 1250° C., the metal had a tendency to recrystallize, with accompanying rapid grain growth, and the hardness and strength did not change much during working. However, when we worked the metal at or slightly below 1200° C., with limited reheating periods between working steps, the hardness and strength increased. During working, the grains were elongated but did not recrystallize nor grow rapidly to become more or less equiaxed, as they did during high temperature fabrication.

When this work-strained material is placed in a cooling furnace at some predetermined temperature, such as about 1050° C., and the furnace allowed to cool at a slow rate, we found that recrystallization did not take place, that the hardness was reduced only a relatively small amount, but that the ductility, as measured by elongation when subjected to tensile test, increased greatly.

We call our process stress-relief and slow-cooling. A preferred rate of furnace cooling is shown in Figure 1. The critical nature of the slow cooling process is indicated by Figure 2 which essentially shows the ductility produced in worked material when slowly cooled from various temperatures. To obtain points on this curve, worked material was loaded into a furnace at various temperatures between about 250° C. and 1300° C. and, without allowing any soaking time for stress relief effects to occur, cooled slowly to room temperature. The peak ductility shown in this figure corresponds with conditions at the starting point on the curve of Fig. 3. Since the stress relief process, however, is a rate process and dependent upon both temperature and time at temperature, a chart such as shown in Figure 3 is required to define the limits of our process. This chart consists of curves indicating the proper time-temperature relationships required to produce the desired results. To produce material of high hardness, strength and ductility, a specification was set on the process that the loss in ultimate strength must not exceed 10,000 p. s. i. and that both the longitudinal and transverse elongations must exceed 20%. The terms longitudinal and transverse refer to the direction of rolling and to the direction at right angles to the rolling direction, but in the plane of rolling, respectively.

In connection with the specification set on the process, it should be pointed out that at a given temperature, for example, 1000° C., the hardness and strength of the material gradually decreases as time at temperature is increased up to a certain point. At this time, the hardness and strength fall off rapidly. The elongation gradually increases with increasing time to a maximum value which remains more or less constant. The top curve in the chart (Figure 3) shows the time necessary at any temperature

between 900° C. and 1080° C. for a loss in ultimate strength of 10,000 p. s. i. The middle curve depicts the time necessary to produce a transverse elongation of 20% in the same temperature range and the bottom curve shows the time necessary to produce a longitudinal elongation of 20%.

The time-temperature relationship expressed by any point below the bottom curve does not produce either a longitudinal or a transverse ductility greater than 20%. When the time temperature relations fall between the bottom and middle curve, the material will have a longitudinal elongation exceeding 20% but the transverse elongation will still be below 20%. As the time is increased for a given temperature, the point expressing the relationship falling between the top and the middle curves, the material will have elongations in both the longitudinal and transverse directions exceeding 20% and still suffer a loss in ultimate strength of less than 10,000 p. s. i. Whenever such a point falls above the top curve, the material will lose more than 10,000 p. s. i. in ultimate strength. It was further found that stress relief without slow cooling did not produce as high ductility as the combined operation referred to, as shown in columns 4 and 5 of Table II, later shown.

In practicing our process, pieces of work-strained metal are placed in a furnace at a predetermined temperature and the furnace allowed to cool. Much of the critical nature of the stress-relief portion of the process may be eliminated by using a longer time at a lower temperature for the stress relief. Referring to Figure 3, it is seen that is is possible to stress-relieve a properly rolled piece of molybdenum in 20 or 30 minutes at 990° C., while only 1 or 2 minutes are required at 1065° C. or 1070° C. The lower the temperature the longer the period required for stress-relief. For example, an hour or longer periods of time might be used at lower temperatures, as indicated in said figure.

As an example of a specific process embodying our invention, a furnace was heated to 1100° C. and sufficient rolled metal put in it so that the temperature dropped to 990° C. This latter temperature was maintained for ½ hour, after which the furnace was allowed to cool at the approximate rate of 60° C. per hour, as by shutting the power off, to a temperature of 700° C. or lower. It is possible to then remove the material and allow it to air cool, without seriously damaging the properties of the metal. Also, it is possible to cool at a higher rate, that is, one up to about 120° C. per hour, without seriously damaging the properties of the metal. The above process, is not only suitable for rolled slab 1" thick and 2½" wide prepared on the 1200° C. rolling schedule, but also for metal swaged or rolled at higher temperatures, such as, 1400° C. to 1500° C.

Summarizing, we have discovered that by this process of stress relief without recrystallization, followed by slow cooling, a high degree of ductility and strength is obtainable with molybdenum containing .1% of cobalt, as above described. The increase in ductility obtained in this process is clearly evident from a comparison of the elongation values of the as-rolled versus ductilized material shown in the following table:

If the temperature is too high during stress relief, recrystallization takes place in part at least with a loss of both strength and ductility. If the stress relief step is attempted at too low a temperature, the metal remains hard and strong but does not develop ductility to any large extent.

As will be seen from Figure 3, the time required for proper stress relief is dependent upon the temperature. That is, the higher the temperature the shorter the permissible time. The basic reason for this behavior is not at present clearly understood. The result is similar to that obtained with steel, where the retention of carbides is responsible for the hardening effect when cooled rapidly, and where by slow cooling the carbon precipitates and the compounds thereof are no longer present to maintain the hardness. In the case of molybdenum, however, the metal is relatively pure and even with small percentages of other metals, such as cobalt, there is no indication of any such precipitation, nor is it any indication of such phase modifications in molybdenum as those commonly designated as alpha, beta and gamma occurring in steels.

It is possible, however, that the effect may be explained from the basis of thermal strains. Experiments have shown molybdenum to possess poor ductility as measured by tensile tests when the test samples are cut in the direction in which compressive stresses have been applied during working.

During cooling, thermal stresses set up between the exterior and interior of the bar result in high compressive stresses in all directions, the magnitude of such stresses depending on the rate of cooling. Thus, by cooling slowly, such stresses are diminished. Calculated values of the probable compressive stresses set up by rapidly cooling from various temperatures, when plotted against those temperatures show a break in the curve. Experiments on cooling from various temperatures show an increase in ductility at the same point. The temperature at which the break occurs is between approximately 800° C. and 900° C. when working with a bar 2½" wide and 1" thick. Although a specific example has been given showing the critical nature of the temperature of the furnace used for slow cooling experiments, it must be understood that this temperature will vary with the size of the piece which is slow cooled, the rate of cooling of the furnace, and the amount and kind of working to which the piece had been subjected.

Although thin sheet and fine wire are commercially made today with high ductility, yet the thermal gradient set up in such is small compared to that in the larger pieces, so that thermal strains are not sufficient to affect the ductility of such fabricated product. It will be understood that the above is simply an explanation and is not relied on for validity of the appended claims. Although a thin sheet of wire is highly ductile in the direction in which it is rolled or drawn, no experimenters have heretofore been able to obtain ductility, as measured by percent elongation, in relatively-thick pieces of metal with only approximately 50% reduction in cross-sectional area, of such high magnitude as measured in tensile tests. Although our method has been applied principally to material worked at or near 1200° C., it is also applicable

TABLE I

Examples of ductilities obtainable at right angles to the direction of rolling

Description	⅝" x 2" Flat	⅝" x 2" Flat	1" x 2½" Flat	1" x 2½" Flat
Material, Mo plus	.1% Co	.1% Co	.1% Co	.1% Co.
Method of Mfg	Flat Rolled	Flat Rolled	Flat Rolled	Flat Rolled.
Slow Cool Ductilization	No	Yes	No	Yes.
Reduction in Cross-Sectional Area	55%	55%	45%	45%.
Hardness	260 VPN	225 VPN	250 VPN	225 VPN.
Elongation	2.0%	32.0%	2.0%	30.0%.
Field Strength, p. s. i.	102,000	89,000	97,000	85,000.
Ultimate Strength, p. s. i.	110,000	102,000	108,000	101,000.

to molybdenum and its referred-to alloys produced at other working temperatures, as in the factory at from 1400° to 1500° C. Note, for example the data on ½" diameter molybdenum rod, set forth in the following table:

TABLE II

Examples of advantages of slow cooling ductilization process

Description	½" dia. Rod	½" dia. Rod	1" x 2½" Flat	1" x 2½" Flat	1" x 2½" Flat.
Material, Mo plus			.1% Co	.1% Co	.1% Co.
Method of Mfg	Swaged and Drawn at 1,400°–1,500° C.	Swaged and Drawn at 1,400–1,500° C.	Flat Rolled at about 1,200° C.	Flat Rolled at about 1,200 ° C.	Flat Rolled at about 1,200° C.
Slow Cool Ductilization	No	Yes	No	Annealed ½ hr. at 990° C. and air cooled.	Yes.
Reduction in Cross-Sectional Area.	65%	65%	45%	45%	45%.
Hardness	210 VPN	200 VPN	252 VPN	225 VPN	226 VPN.
Elongation	4.5%	15.2%	7.4%	10.5%	34.9%.
Yield Strength, p. s. i.	90,500	89,000	99,100	90,000	82,400.
Ultimate Strength, p. s. i.	96,500	96,500	106,200	100,000	99,000.

From the foregoing, it will be seen that we have discovered how to fabricate and heat-treat large pieces of molybdenum and the like so as to get both high strength, high hardness, and high ductility, without an excessive amount of fabrication, thus greatly simplying the process of reduction of pieces of large size which might, for example, be used for structural purposes.

It will also be noted from the tabulated data that we have produced sintered and worked bodies as large or larger than ¼" in transverse and thickness dimensions, of coherent metal from pressed 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, treated so that the ductility, as measured by elongation, is increased from about 2% to over 20% without loss of strength of more than 10,000 pounds per square inch, and with hardness averaging above 200 VPN. In other words, the improved material has a ductility, as measured by elongation, of over three times that of material otherwise similar but produced by previous methods.

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

We claim:

1. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with proportions of metal selected from the group consisting of cobalt, nickel and iron up to ½%, and tungsten up to to 20%, pressed and sintered, comprising working said article at a temperature from near but not higher than 1200° C. to 1500° C., heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 975° C. for from 1 to 60 minutes within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

2. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with proportions of cobalt up to ½%, pressed and sintered, comprising working said article, at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 975° C. for from 1 to 60 minutes within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, to get hard, strong, and ductile material by stress-relief, without allowing the grains to become equiaxed by re-

crystallization, and then cooling the article at a rate between 60° C. and 120° C. per hour to a relatively-low temperature.

3. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with proportions of metal selected from the group consisting of cobalt, nickel and iron up to ½%, and tungsten up to 20%, pressed and sintered, comprising working said article, at a temperature between 1400° C. and 1500° C., heating in a protective atmosphere to temperature between about 1070° C. and 975° C. from 1 to 60 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strengthen and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

4. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of the molybdenum and alloys thereof with proportions of metals selected from the group consisting of cobalt, nickel and iron up to ½%, and tungsten up to 20%, pressed and sintered, comprising working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a temperature between about 1070° C. and 975° C. for from 1 to 60 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

5. The method of manufacturing ductile metal from an article of powdered particles of the group consisting of molybdenum and alloys thereof with proportions of metal selected from the group consisting of cobalt, nickel and iron up to ½%, and tungsten up to 20%, pressed and sintered, comprising working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at

least 20%, 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.

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 and iron up to ½%, and tungsten up to 20%, pressed and sintered, comprising working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a temperature between about 1070° C. and 990° C. from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

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 cobalt up to ½%, pressed and sintered, comprising working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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 powdered particles of the group consisting of molybdenum and alloys thereof with proportions of metal selected from the group consisting of cobalt, nickel and iron up to ½%, and tungsten up to 20%, comprising pressing the material to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, working said article at a temperature from near but not higher than 1200° C. to 1500° C., heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 975° C. for from 1 to 60 minutes within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

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 and iron up to ½%, and tungsten up to 20%, comprising pressing the material to a desired shape, heating the

pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

10. The method of manufacturing ductile metal from powdered particles of the group consisting of molybdenum comprising pressing the material to a desired shape, heating the pressed shaped in a protective atmosphere until the particles are sintered into a strong coherent article, working said article at a temperature between 1400° C. and 1500° C., heating in a protective atmosphere to a stress-relieving temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

11. The method of manufacturing ductile metal from powdered particles of the group consisting of molybdenum and alloys thereof with proportions of cobalt up to ½%, comprising pressing the material to a desired shape, heating the pressed shape in a protective atmosphere until the particles are sintered into a strong coherent article, working said article at a temperature near and not higher than 1200° C., heating in a protective atmosphere to a temperature between about 1070° C. and 990° C. for from 1 to 30 minutes, within the limits of a time-temperature relationship as shown in Fig. 3 of the drawing accompanying the specification and constituting the area below the upper curve representing drop in ultimate strength and above the middle curve representing a longitudinal and transverse elongation of at least 20%, 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.

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