Title: Method for Extruding Molybdenum and Tungsten

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Diagram:

[Diagram showing a process involving extrusion with labeled parts 1 through 12.]

Force direction indicated by an arrow pointing to the right.
METHOD FOR EXTRUDING MOLYBDENUM AND TUNGSTEN

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Filed Nov. 6, 1964, Ser. No. 409,620
6 Claims. (Cl. 72—38)

This invention relates generally to extrusion processes and more particularly to an improved method for extruding molybdenum and tungsten metals and alloys thereof. While the present invention is applicable to preparing any type extruded product, such as T-shape, tube hollow and/or round rods, it will be hereinafter described in detail as a method for preparing tube shells from hollow billets.

Owing to their various physical and mechanical properties, the refractory metals are generally quite difficult to work mechanically. As a class of metals they can be extruded, but not without some difficulty. Due to their lack of plasticity at low temperatures, these metals generally require that the extrusion be carried out at an elevated temperature, as well as requiring some type of lubricant. Various types of lubricants, such as graphite, graphite in oil, glass, and highly ductile metals, have been tried, but have not been found to be successful with these high melting metals. To illustrate, molybdenum and tungsten melts require such high extrusion temperatures (2800°—3200° F.) that most glass and metal compound lubricants have been found to be ineffective, probably due to the lack of adherence at the extrusion temperature. Also, highly ductile metal sheeting materials have been found undesirable in many such applications due to poor boundary layer lubrication properties at elevated temperatures, expense of sheeting materials and causing operation, and also due to the likelihood of a reaction between the sheeting and the extrusion billet. It may thus be seen that it would be highly desirable to find a lubricant which is compatible with carrying out high temperature extrusions of metals like molybdenum and tungsten.

It is therefore a general object of the present invention to provide a method for extruding metals which form volatile oxides at the extrusion temperature without the use of additive lubricants.

Another object is to provide an improved method for extruding molybdenum and tungsten metals and alloys thereof at elevated temperatures wherein the resulting product is essentially free of all contaminants.

Still another object is to provide an improved method for fabricating molybdenum and tungsten metal tube shells which have a finish superior to that normally obtained by prior art methods.

Other objects and advantages of this invention will become apparent from the following detailed description thereof when read in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view of one embodiment of the assembled extrusion apparatus.

In accordance with the present invention there is provided an improved method for extruding metals which form volatile oxide bearing surfaces at the extrusion temperature comprising the steps of heating the metal to the extrusion temperature, exposing the heated metal to an oxidizing atmosphere immediately preceding the extrusion operation to thereby cause the metal to undergo a surface oxidation and thereafter extruding the metal. Applicants have found, quite unexpectedly, that the refractory metals molybdenum and tungsten, as well as their alloys, can be extruded at elevated temperatures without any additive lubricant, using instead the volatile oxide, which is formed by exposing such oxidizing environments as air, as a lubricant. Whereas with usual lubricants there is a contamination problem after the extrusion, the present process is essentially free of any such problem inasmuch as the oxide formed with molybdenum and tungsten is volatile at the extrusion temperature and is removed almost as fast as it is formed. Furthermore, the resulting tube shells are amenable to subsequent drawing into metal tubing.

Preparation of the metal billet may be accomplished by any suitable manner such as by powder metallurgy techniques or arc-casting. For example, tungsten metal billets may be prepared by pressing tungsten metal powder into compacts and sintering the compacts. After cooling, the sintered product may be ground to the desired dimensions of the billet. On the other hand, molybdenum may be prepared in wrought form by arc-casting the metal into a suitable form and then hot-rolling the metal to the desired dimensions. While the finished dimensions of the billet are not critical and may be varied over a wide range to meet the requirements of the extrusion press, applicants have found certain dimensions to be preferred. Cylindrical metal billets (3"—6" O.D. x 5"—12" long) within a one-inch axial bore therethrough have been found to be quite suitable for extruding metal tube shells and thus are preferred.

The extrusion of the metal billets into tube shells may be carried out with any conventional extrusion apparatus. Referring to FIG. 1, the apparatus may comprise a cylindrical billet container 1 adapted to receive the refractory metal billet 2 which has an axial bore therethrough. A thin-walled metal liner 3 is removable mounted within the billet container 1. A die assembly 4 consisting of a 90° conical die 5, die holder 6, and die bolster block 7 is mounted to one end of the billet container 1. A floating mandrel 8 which has its terminal end threaded is adapted to be centered in the billet container 1 so as to extend therethrough the axial bore of the refractory metal billet 2 and axially aligned with the die 4. This centering of the floating mandrel 8 may be accomplished by screwing the threaded end of the mandrel into a dummy block 9 which is slidably retained within the billet container 1. A follower block 10 having an axial bore therethrough may be slid over the mandrel in abutting relation with the dummy block 9 and the tail end of the billet 1. An extrusion ram 11 is adapted to be slidably received in the billet container 1 in abutting relation with the dummy block 9. Suitable heater means 12 may be placed around the billet container 1 to heat the liner, container, and die assembly to a maximum temperature of about 1000° F., which is below the temperature at which the steel components would soften. The extrusion ram 11, die 5, and mandrel 8 should be made of hardened alloy steel, such as H-12, and the die, mandrel, and follower block should be coated with suitable insulating material, such as zirconia, to insulate these parts from the heated metal billet, thus precluding melting and/or reacting of these parts during the extrusion.

In carrying out the practice of this invention, the conditioned metal billet is heated to the extrusion temperature in a suitable furnace. For this an argon atmosphere induction furnace has been found to be quite suitable. It will be appreciated that the extrusion temperatures for the refractory metals, molybdenum and tungsten as well as their alloys, may vary over a wide range. As is known in the extrusion art it is essential that the extrusion be carried out within a range of temperatures in which the metal has sufficient plasticity to allow the shaping process to be conducted within the capacity of the available press. Also, it should be carried out within a range of temperatures in which the effects of the deformation...
are dissipated rapidly enough to prevent the resistance of the material from being affected to any serious extent by work-hardening such as occurs at lower temperatures. Such a temperature range will depend, for example, not only upon the particular metal, but also upon the reduction ratio employed and the capacity of the extrusion press.

After the metal billet is heated to the extrusion temperature, it is removed from the furnace and inserted immediately in the billet chamber of the extrusion press. Upon contact with room air the molybdenum metal, for example, was found to undergo rapid oxidation, evolving white clouds of molybdenum oxide from the billet surface. This is also observed in the case of tungsten metal when exposed to ambient air after being heated to the extrusion temperature. Upon completion of the transfer of the billet to the extrusion press, the billet is extruded into metal tubes shells which could then be fabricated into metal tubing by conventional metal fabrication techniques, as for example, by warm drawing. Inasmuch as the oxidation of the metal tubes took place almost instantaneous upon contact with an oxidizing atmosphere, the length of exposure of the heated metal to oxidizing environments is not critical. Applicants have found that the time lapse between the removal of the billet from the furnace and completion of the extrusion was about 10 seconds. It will be appreciated that the time lapse should not be too great or the metal billet might have to be reheated to insure maintaining a desired temperature during the extrusion operation. The extrusion press parameters are not critical in the practice of the invention. For example, reduction ratios employed varied from 6 to 1 for tungsten metal billets to 9 to 1 for molybdenum metal billets and the ram speeds were in both cases 300 inches/minute. The press capacity was 700 tons and the press had a stroke of 18 inches.

It is not completely understood how the volatile oxide affords good lubrication of the metal billet during extrusion. However, it is believed that the oxides, to wit—molybdenum and tungsten—undergo surface oxidation at a rate sufficient to provide a suitably lubricated bearing surface for extrusion. To insure a suitably lubricated bearing surface, it is believed important that the oxide be liquid during the extrusion. While the extrusion should be carried out at a temperature above the melting point of the particular oxide, the extrusion temperature should be selected to insure that the oxide present is at an optimum amount throughout the extrusion. Applicants have found that too little oxide will provide no lubricating bearing surface and too much oxide may result in surface defects and inferior surface finishes.

Inasmuch as the oxide is volatile it will be appreciated that the evaporation rate of the oxide has a significant effect upon the effectiveness of the oxide bearing surface as a lubricant during extrusion. Applicants have found, for example, that when a tungsten billet was extruded at a temperature of about 3400° F. the breakthrough pressure was 480 tons, whereas when a tungsten billet was extruded at 3200° F. the breakthrough pressure was significantly lower (~405 tons). It further was noted that the rate of evaporation of WO$_3$ at 3400° F. was about 7½ times as great as that at 3200° F. Thus, it is believed that at the high extrusion temperature (3400° F.) the rate of evaporation of the oxide was too great to afford an adequate bearing surface. However, even at 3400° F. the surfaces of the resulting billets were found to be far superior to those produced with such lubricants as glass.

Further illustration of the quantitative aspects and procedures of the present invention is provided in the following examples. Examples I-III demonstrate the applicability of this invention to fabricating molybdenum and molybdenum alloy tube shells and/or metal tubing from tube hollows.

### Example I

A wrought unalloyed molybdenum metal billet which had been arc-cast was machined to 3" O.D. x 5" long billet and had a 3/4” axial bore therethrough. One end of the billet was machined to a cone shape having a 90° included angle. All finished surfaces were polished to a finish of better than 64 R.M.S.

The extrusion press utilized for extruding the molybdenum metal billet into a tube shell had a press capacity of 700 tons and consisted of hardened H-12 tool steel, zirconia-coated floating mandrel and 90° conical die. The press had a ram speed of 300 inches/minute and an 18° stroke length. Heating coils were placed around the billet container to heat the liner, container and die assembly to a temperature of 1000° F. Prior to the insertion of the billet in the billet container, the die and mandrel were sprayed with colloidal graphite and the excess wiped off.

The molybdenum metal billet was placed in an induction furnace and heated in an argon atmosphere to an extrusion temperature of 3000° F. When the billet was at temperature, it was removed from the furnace and inserted immediately into the billet container. Upon contact with the room air, white clouds of molybdenum oxide were evolved from the billet. The billet was extruded at a reduction ratio of 8.8 to 1 into a molybdenum tube shell (11/4" O.D. x 40° long) with the time lapse between removal of the billet from the furnace and completion of the extrusion being about nine seconds.

Visual inspection of the tube shell indicated a honed appearance with good finishes, and essentially no trace of contaminants. Subsequent ultrasonic inspection of the billet indicated no significant defects in the tube shell.

After the tube shell was inspected for defects it was placed on a warm-draw bench and drawn to 3/4" O.D. molybdenum tubing having a wall thickness of 0.035 inch by conventional warm-drawing techniques.

### Example II

A wrought molybdenum alloy-TM (Mo-0.5% Ti) metal tube hollow billet was prepared and extruded into a tube shell (11/4" O.D. x 40° long) as in Example I. The extrusion was carried out at a temperature of 3500° F., ram speed of 300 inches/minute, and a reduction ratio of 8.8 to 1. The resulting tube shell was visually examined for contaminants, ultrasonically checked for defects, and was found to be free of both. The tube shell was then warm drawn into 3/4" O.D. metal tubing having a wall thickness of 0.035 inch. This is the first known defect-free molybdenum alloy-TM tubing to be drawn from an extruded tube shell.

### Example III

A wrought molybdenum alloy-TZM (Mo-0.5% Ti-0.1% Zr-0.08% C) metal tube hollow billet was prepared and extruded into a tube shell (11/4" O.D. x 40° long) as in Example I. The extrusion was carried out at a temperature of 3700° F., ram speed of 300 inches/minute, and a reduction ratio of 8.8 to 1. The resulting tube shell was visually examined for contaminants, ultrasonically checked for defects, and was found to be free of both. The tube shell was then warm drawn into 3/4" O.D. metal tubing having a wall thickness of 0.035 inch. Examples IV and V demonstrate the applicability of the present process for extruding tungsten tube shells from tube hollows.

### Example IV

A sintered tungsten billet, 3" O.D. by 5" long having an axial bore 11/4" in diameter and a conical nose with a 90° included angle, was prepared for extrusion as in Example I. The billet was heated to a temperature of 3400° F. in an argon atmosphere. When the billet reached temperature, it was transferred immediately to the billet container. Upon coming in contact with ambient air, a white cloud of WO$_3$ formed around the billet. The billet...
was extruded at 3400° F. with a 5.88 to 1 reduction ratio to form a tube shell approximately 18” long and 1%” O.D. The billet had a breakthrough pressure of 480 tons and a running load of 405 tons and a ram speed of 300 inches/minute.

After extrusion the tube shell was visually examined and the outside surface was found to have areas of roughened appearance with a surface finish which was only of average appearance.

The resulting tungsten tube shell was then warm drawn into 3¾” O.D. tungsten tubing having a wall thickness of 0.035 inch.

**Example V**

A sintered tungsten billet, 3” O.D. x 5” long having an axial bore 1¼” in diameter and a conical nose with a 90° included angle, was extruded as in Example I, except it was extruded at 3200° F. The billet had a breakthrough pressure of 405 tons and a running load of 380 tons. The resulting tube shell (18” x 1¾” O.D.) was visually examined and all of the extruded surfaces were found to be of superior appearance. Subsequent non-destructive evaluation indicated no significant defects in the tube shell. The tube shell was then warm drawn into 3¾” O.D. tungsten tubing having a wall thickness of 0.035 inch.

Examples VI and VII demonstrate that solid tungsten billets may be extruded with the present invention to produce wrought tungsten bar stock.

**Example VI**

A sintered powder metallurgy solid tungsten billet (6” O.D. x 11” long) having a conical nose with a 90° included angle was extruded bare as in Example I, except it was extruded at 2850° F. with a reduction ratio of 4:1. The extruded bar stock (3” O.D. x 44” long) was visually examined and found to have an excellent surface with no nose burst, and ultrasonically checked and found to be essentially free of any defects. This wrought bar stock may be subsequently conditioned to tube hollow billets for ultimate tube shell production.

**Example VII**

A sintered powder metallurgy solid tungsten billet (6” O.D. x 11” long) having a conical nose with a 90° included angle was extruded bare as in Example I, except it was extruded at 3200° F. with a reduction ratio of 4:1. The extruded bar stock (3” O.D. x 44” long) was visually examined and found to have a good surface with minimum nose burst. This wrought bar stock may be subsequently conditioned to tube hollow billets for ultimate tube shell production.

From the results shown, it appears that the extrusion of tungsten metal billets utilizing the surface oxidation of the tungsten metal to provide an oxide bearing surface is better carried out at the lower temperature. The breakthrough pressure at the lower temperature was found to be less than that at the higher temperature which is the reverse of what might be expected.

It is to be understood that the foregoing examples are merely illustrative and are not intended to limit the scope of this invention, but the invention should be limited only by the scope of the appended claims.

What is claimed is:

1. An improved method for extruding a metal selected from the class consisting of molybdenum, tungsten, and alloys thereof which comprises the steps of heating said metal to an extrusion temperature within the range of 2850°–3700° F., exposing said heated metal to an oxidizing atmosphere immediately preceding the extrusion operation thereby forming a volatile oxide bearing surface and thereinafter extruding said metal.

2. The method of claim 1 wherein said metal is molybdenum, said extrusion is carried out at a temperature of 3000° F., and said oxidizing atmosphere is ambient air.

3. The method of claim 2 wherein said molybdenum metal is an arc-cast tube hollow billet.

4. The method of claim 1 wherein said metal is tungsten, said extrusion is carried out at a temperature of 2850° F., and said oxidizing atmosphere is ambient air.

5. The method of claim 4 wherein said tungsten metal is a sintered tube hollow billet.

6. The method of claim 4 wherein said tungsten metal is a sintered solid tungsten billet.

**References Cited**

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