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APPLYING PROTECTIVE METAL COATINGS ON MOLYBDENUM

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Fig. 1.

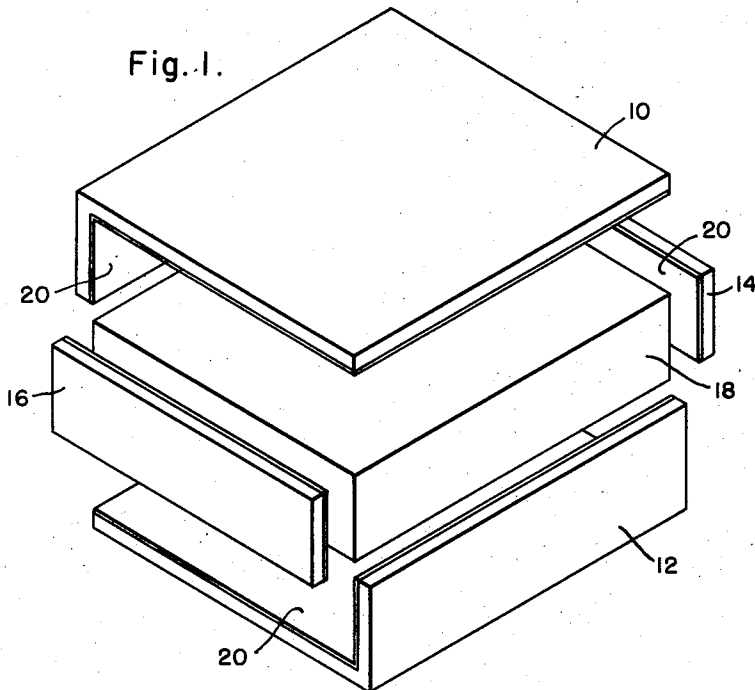


Fig. 2.

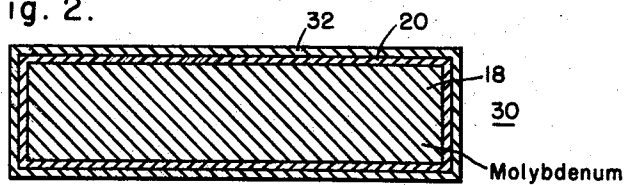
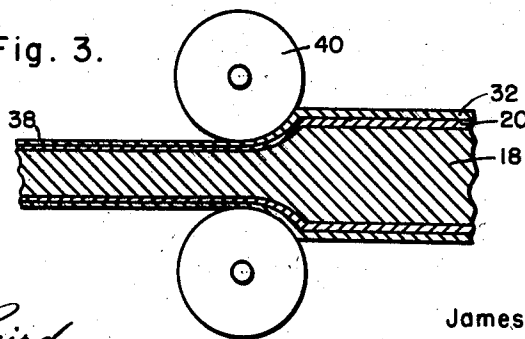


Fig. 3.



WITNESSES

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## APPLYING PROTECTIVE METAL COATINGS ON MOLYBDENUM

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This invention relates to the application of protective metal coatings on molybdenum with improved bond strength therebetween.

Components suitable for use as buckets, blades, valves, nozzles, and the like, in gas or steam turbines, jet engines and devices having similar atmosphere and temperature conditions, must possess high hot tensile strength, hot fatigue strength, and high resistance to creep at elevated temperatures.

The refractory metal molybdenum possesses certain desirable characteristics which make it highly adaptable for structural materials exposed to high temperatures. However, molybdenum is readily oxidized when exposed to an oxygen-bearing atmosphere at elevated temperatures. Thus, while molybdenum melts at 2625° C. in a non-oxidizing atmosphere, if the molybdenum metal is heated to 500° C. and higher in contact with air, oxygen, or other oxidizing gas, it forms a readily volatile oxide. Thus, when in contact with air at 700° C., for example, the molybdenum metal gives off dense dark clouds of smoke consisting of molybdenum oxides and in a short time it is consumed.

It has been proposed to coat the surface of molybdenum metal with a protective layer of chromium or other oxidation-resistant metal which would prevent access of oxygen or other oxidizing vapor to the molybdenum metal and in this way enable the use of molybdenum metal at temperatures above 500° C. However, such coatings have not always been entirely satisfactory.

For making components for high temperature applications as in gas turbines, jet engines and other highly heated applications demanding great strength, it is not only essential that the molybdenum metal be provided with a coating of a metal resistance to oxidation at the elevated temperatures of use, but it is also essential that a strong bond exist at the interface between the molybdenum metal and the coating of oxidation-resistant metal. Thus, a poor bond will result in separation of the oxidation-resistant coating from the molybdenum metal during fabrication of a component, thereby rendering the component useless for high temperature operation. Furthermore, components for use at high temperature are often subjected to great stress in service which could cause separation of the oxidation-resistant coating from the molybdenum metal should a weak bond exist. Such a separation would expose the molybdenum metal to high temperature oxidation, resulting in premature failure of the component in service.

The object of this invention is to provide for applying to a body of molybdenum metal a well bonded coating of a metal possessing good resistance to oxidation at high temperatures by first preparing an assembly comprising a body of molybdenum metal, a casing of an oxidation-resistant metal enclosing the molybdenum body and an intermediate layer of a bonding metal disposed between the molybdenum body and the casing, and then subjecting the assembly to heat and pressure to reduce the cross-

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sectional area of the assembly and firmly bond together the components.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter. For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawing, in which:

Fig. 1 is an exploded perspective view showing a molybdenum body, an intermediate layer of a bonding metal and a casing of an oxidation-resistant metal.

Fig. 2 is a cross-section through an assembly of a molybdenum body having applied to its outer surface an intermediate layer of a bonding metal and an exterior casing of an oxidation-resistant metal.

Fig. 3 is a view illustrating the rolling and reduction of the assembly of Fig. 2 to form the final protected molybdenum product.

In accordance with this invention, a method has been discovered for producing on bodies of molybdenum metal a highly protective surface coating, which coating is so well bonded and adherent to the molybdenum body that it will withstand elevated temperatures and will protect the metal from oxidizing atmospheres at such elevated temperatures under service conditions for prolonged periods of time. Briefly, the method comprises providing on a clean, oxide-free molybdenum body a relatively thin intermediate coating of a bonding metal. The coated molybdenum body is then completely encased and sealed in a casing of an oxidation resistance metal to provide a three component assembly. The assembly is then heated to a temperature of from 870° C. to 1320° C. and rolled under pressure to reduce the cross-sectional area of the assembly at least 30%, whereby to effect a strong bond between the components comprising the assembly. The resulting coating is so well bonded to the molybdenum body that it will not crack open or separate therefrom during fabrication of components therefrom or during extreme conditions of service of the fabricated components, under which conditions previously prepared molybdenum members failed.

The invention will be detailed hereinafter specifically by reference to molybdenum metal but it will be understood that similar procedures may be applied to high temperature alloys in which molybdenum constitutes at least 50% by weight. Such alloys may comprise tungsten, niobium, and titanium as minor components. Thus, the invention may be applied to members comprising 99% molybdenum and 1% titanium.

The thin intermediate coating comprises a bonding metal selected from the group consisting of chromium, palladium, copper and an alloy comprising, by weight, from 60% to 70% nickel and the balance being substantially all copper. The application of the intermediate coating can be made either to the surface of the molybdenum body or to that one side of the casing that is placed in contact with the molybdenum body. The application of the bonding metal can be made by dipping, spraying, electroplating or simply by sandwiching thin sheets of the intermediate metal between the molybdenum body and the casing metal. It is not essential that the entire surface of the molybdenum body or that all surfaces of the casing metal that come into contact with the molybdenum body be thus completely coated initially. It is essential, however, that after preparation of the assembly, an intermediate layer of the bonding metal is so disposed between the molybdenum body and the casing that the intermediate layer is subjected to the direct pressure of the rollers during the rolling procedure.

To effect a strong bond between the casing metal and the molybdenum it is preferred to employ a thickness of the bonding metal of the order of from 1 mil to 10 mils.

The casing metal which provides the protection against high temperature oxidation may be one of the metals of the group of nickel, cobalt or various heat resistant alloys comprising at least 50% of nickel or cobalt, or both, with chromium or iron or both. Such latter alloys are well known in the art. Examples of suitable alloy compositions are an alloy comprising, by weight, 80% nickel, 12% chromium, and the balance being substantially all iron, an alloy comprising, by weight, 80% nickel and 20% chromium, and an alloy composed of 60% nickel, 20% cobalt, 25% chromium and 5% iron. These oxidation-resistant casing metals exhibit poor bonding to molybdenum and base alloys thereof.

The thickness of the applied casing metal is such that when the assembly has been reduced to the desired cross-section and the bond effected, the resulting thickness will be that desired in accordance with the service intended. The resulting thickness being of the order of from 1 mil to 10 mils. Usually the thickness of the casing wall, that is applied, will be from 5% to 20% the thickness of the molybdenum. To prevent oxidation of the molybdenum body during the rolling procedure, which will be discussed more fully hereinafter, it is essential that the molybdenum body and the intermediate coating be completely enclosed and sealed in the casing metal.

The following example illustrates a method of preparing an assembly for use in this invention.

#### Example I

Referring to Fig. 1 of the drawing there is shown angle shaped members 10 and 12, and end members 14 and 16 which were prepared from  $\frac{1}{16}$  inch thick sheet of a metal comprising, by weight, 80% nickel, 12% chromium and the balance being substantially all iron, applied to a body 18 of molybdenum so as to closely fit the surfaces thereof when assembled. The molybdenum body is 6 inches long by  $1\frac{1}{4}$  inches wide by  $\frac{1}{2}$  inch thick. All surfaces of members 10 and 12 and end members 14 and 16 that make contact with the molybdenum body 18 are electroplated with one mil coating 20 of chromium metal. In preparing the assembly, a container is prepared by welding together the angle shaped members 10 and 12 and the end member 14 into an open ended casing. The container is so constructed that it is just large enough to permit the molybdenum body 18 to be inserted through the open end. After the molybdenum body 18 is inserted into the prepared container the other end member 16 is welded at the open end of the container so as to enclose completely and seal the molybdenum body 18, to form the assembly. It is important, in preparing the assembly that the surfaces of the molybdenum body 18 and the coating 20 be kept clean and free of oxides at all times. Any foreign particle or oxide present will prevent the attainment of a good bond between the components of the assembly.

Referring to Fig. 2 of the drawing there is illustrated a cross-section of an assembly 30 for use in practicing this invention. The assembly 30 comprises the molybdenum body 18, an intermediate metal coating 20, to function as a bonding layer and a complete casing 32 enclosing the molybdenum body 18 and coating 20.

The assembly 30 is heated to a temperature of from 870° C. to 1320° C. and then rolled to effect a reduction in the area of the cross-section and to produce a strong bond between the components of the assembly, as illustrated in Fig. 3 of the drawing. This produces a long continuous multi-layer strip 38 shown emerging at the left of rolls 40.

The following example is a rolling schedule that has been employed in carrying out this invention. The assembly used in this schedule was prepared in accordance with Example I and was approximately  $6\frac{1}{4}$  inches long,  $1\frac{1}{2}$  inches wide, and  $\frac{5}{16}$  inch thick. Prior to the first pass the assembly was heated to a temperature of 1024°

C. for 15 minutes and the assembly was reheated between each pass. A reduction in area of approximately 25% was obtained in each pass.

#### Example II

| Pass: | Pass temperature ° C. |
|-------|-----------------------|
| 1     | 1024                  |
| 2     | 1024                  |
| 3     | 1024                  |
| 4     | 1024                  |
| 5     | 1024                  |
| 6     | 1024                  |
| 7     | 1024                  |

The final thickness of the rolled assembly was approximately 50 mils. After the final pass the assembly was heated at 1024° C. for a period of about 5 minutes.

The schedule set forth in Example II provides for so processing the molybdenum body as to produce a wrought metal fully recrystallized and having a substantially uniform fine grain size and an excellent cold ductility. A more uniform ductility in all directions in the molybdenum metal is obtained because of the substantially uniform fine and more nearly equiaxed grain structure. A good bond between the components of the assembly is usually effected during the first or second pass, i. e., when 30% reduction is reached.

It will be obvious to those skilled in the art that many variations can be made in the rolling schedule of Example II depending on the original size of the assembly, the amount of reduction in cross-sectional area desired, and the desired room temperature ductility of the molybdenum. Other rolling schedules suitable for carrying out this invention are set forth in U. S. Patent No. 2,666,721 and assigned to the same assignee as the present invention.

#### Example III

The rolling schedule of Example II was employed to reduce the thickness of the assembly of Example I to about 50 mils. Six specimens  $0.32$  inch wide,  $1\frac{1}{4}$  inches long, and  $.050$  inch thick were cut from the rolled assembly. A small amount of the molybdenum was etched out at one end of each specimen. This permitted the casing and intermediate layer to be gripped in the jaws of a tensile test machine. The average load required by such a tear test to separate the casing metal from the molybdenum body was 27 pounds.

#### Example IV

An assembly was prepared in accordance with Example I except that palladium was employed as the intermediate coating instead of chromium. The rolling schedule of Example II was employed to reduce the thickness of the assembly to about 50 mils. Six specimens  $0.32$  inch wide,  $1\frac{1}{4}$  inches long, and  $0.050$  inch thick were cut from the rolled assembly. The tear strength of the six specimens was tested in the manner set forth in Example III. The average load required to separate the casing metal from the molybdenum body of the six specimens was 30 pounds.

#### Example V

An assembly was prepared using Monel metal as the intermediate layer. The assembly was prepared in a manner similar to that of Example I except that instead of electroplating, the Monel was applied by placing a 5 mil thick sheet between the molybdenum body and the casing metal. Monel designates a proprietary alloy comprising by weight from 60% to 70% nickel, from 25% to 35% copper, from 1% to 3% iron, from 0.25% to 2% manganese, from 0.02% to 1.5% silicon, and from 0.3% to 0.5% carbon. The assembly was rolled in accordance with the schedule of Example II and the thickness of the assembly reduced to about 50 mils. Four specimens  $0.32$  inch wide,  $1\frac{1}{4}$  inches long, and  $0.050$  inch thick were cut from the rolled assembly and tested

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for tear strength in the manner set forth in Example III. The average load required to separate the casing from the molybdenum body for the four specimens was 45 pounds.

#### Example VI

An assembly was prepared in accordance with Example I except that copper metal was employed as the intermediate coating instead of chromium. The rolling schedule of Example II was employed to reduce the thickness of the assembly to about 50 mils. Three specimens 0.32 inch wide, 1¼ inches long, and .050 inch thick were cut from the rolled assembly. The three specimens were tested for tear strength in the manner set forth in Example III. The average load of the three specimens was 18 pounds.

The excellent bond obtained by employing the method of this invention results from the application of the intermediate coating metal. This is shown by comparing the bond strength obtained in the following examples in which the intermediate coating of bonding metal is not present.

#### Example VII

An assembly was prepared in accordance with Example I using a body of molybdenum metal and a casing of nickel without any intermediate coating. The rolling schedule of Example II was employed to reduce the thickness of the assembly to about 50 mils. Two specimens 0.32 inch wide and 1¼ inches long were cut from the rolled assembly. The tear strength of the two specimens was tested in the manner set forth in Example III. The average load required to separate the casing from the molybdenum body was 12.5 pounds.

#### Example VIII

Five specimens were prepared in the manner set forth in Example VII except an alloy comprising 80% nickel, 12% chromium, and the balance substantially all iron was employed as the casing metal. The tear strength was tested in the same manner and the average of the five specimens was 11 pounds.

#### Example IX

Two specimens were prepared using a body comprising 99.7% molybdenum and 0.3% columbium and a metal casing comprising 80% nickel and 20% chromium. The specimens were prepared in the same manner of Example VII. The average load required to separate the two components was 4 pounds.

In general, the protected wrought members of the invention will comprise a core of molybdenum or molybdenum base alloy, an exterior layer or casing of from 1 to 10 mils of a heat resistant metal, and a substantially thinner intermediate bonding layer uniting the exterior layer to the core.

Since certain obvious changes may be made in the above procedures and different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above description and drawing shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. In the process of producing well bonded, oxidation-resistant coatings on a molybdenum body, the steps comprising (1) preparing an assembly comprising a molybdenum body completely enclosed and sealed in a relatively thick casing of at least one oxidation-resistant metal selected from the group consisting of nickel, cobalt and alloys comprising at least 50% thereof and the balance being at least one of the group consisting of iron and chromium and a relatively thin intermediate bonding layer disposed between the molybdenum body and the casing of a metal selected from the group consisting of palladium, copper, chromium and an alloy comprising, by weight, from 60% to 70% nickel and the balance being substantially all copper, (2) heating the

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assembly to a temperature of from 870° C. to 1320° C., and (3) rolling the heated assembly to effect a reduction of at least 30% in the cross-sectional area and to effect intimate bonding of the molybdenum body, the intermediate layer and the casing.

2. In the process of producing well bonded, oxidation-resistant coatings on a molybdenum body, the steps comprising preparing an assembly by completely enclosing and sealing a molybdenum body in a casing comprising an exterior layer of at least one oxidation resistant metal selected from the group consisting of nickel, cobalt, and alloys comprising at least 50% thereof and the balance being at least one of the group consisting of iron and chromium and an intermediate bonding layer of a metal selected from the group consisting of palladium, copper, chromium and an alloy comprising, by weight, from 60% to 70% nickel and the balance being substantially all copper, said intermediate layer being of a thickness of the order of from 1 mil to 10 mils, and said exterior layer being of a thickness of from 5% to 20% of the thickness of the molybdenum body, heating the assembly to a temperature of from 870° C. to 1320° C., repeatedly rolling the heated assembly to effect a reduction in its cross-sectional area and to produce an intimate bond between the molybdenum body and the intermediate layer and the exterior layer of the casing, with intermediate reheating, until the assembly has been reduced at least 30% in cross-sectional area.

3. In the process of producing well bonded, oxidation-resistant coatings on a molybdenum body, the steps comprising preparing an assembly by applying to a molybdenum body an intermediate bonding layer of a thickness of from 1 mil to 10 mils of a metal selected from the group consisting of palladium, copper, chromium and an alloy comprising, by weight, from 60% to 70% nickel and the balance being substantially all copper, and completely enclosing and sealing said molybdenum body with said applied intermediate bonding layer in a casing of at least one oxidation-resistant metal selected from the group consisting of nickel, cobalt, and alloys comprising at least 50% thereof and the balance being at least one of the group consisting of iron and chromium, said casing having a wall thickness of from 5% to 20% the thickness of the molybdenum body, heating the assembly to a temperature of from 870° C. to 1320° C., repeatedly rolling the heated assembly to effect a reduction in its cross-sectional area and to produce an intimate bond between the molybdenum body and the intermediate layer and the casing, with intermediate reheating, until the assembly has been reduced at least 30% in cross-sectional area.

4. A unitary wrought member comprising a core of a molybdenum base alloy, an exterior casing having a wall thickness of from 1 mil to 10 mils of at least one oxidation-resistant metal selected from the group consisting of nickel, cobalt and alloys comprising at least 50% thereof and the balance being at least one of the group consisting of iron and chromium, and a substantially thinner intermediate bonding layer uniting the casing to the core of a metal selected from the group consisting of palladium, copper, chromium and an alloy comprising, by weight, from 60% to 70% nickel and the balance being substantially all copper, the core, casing and bonding layer being united into a unitary body by hot rolling which effects a reduction of at least 30% in cross-sectional area.

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