

Sept. 20, 1960

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2,952,904

APPLYING PROTECTIVE METAL COATINGS ON MOLYBDENUM

Filed Jan. 15, 1957

Fig. 1

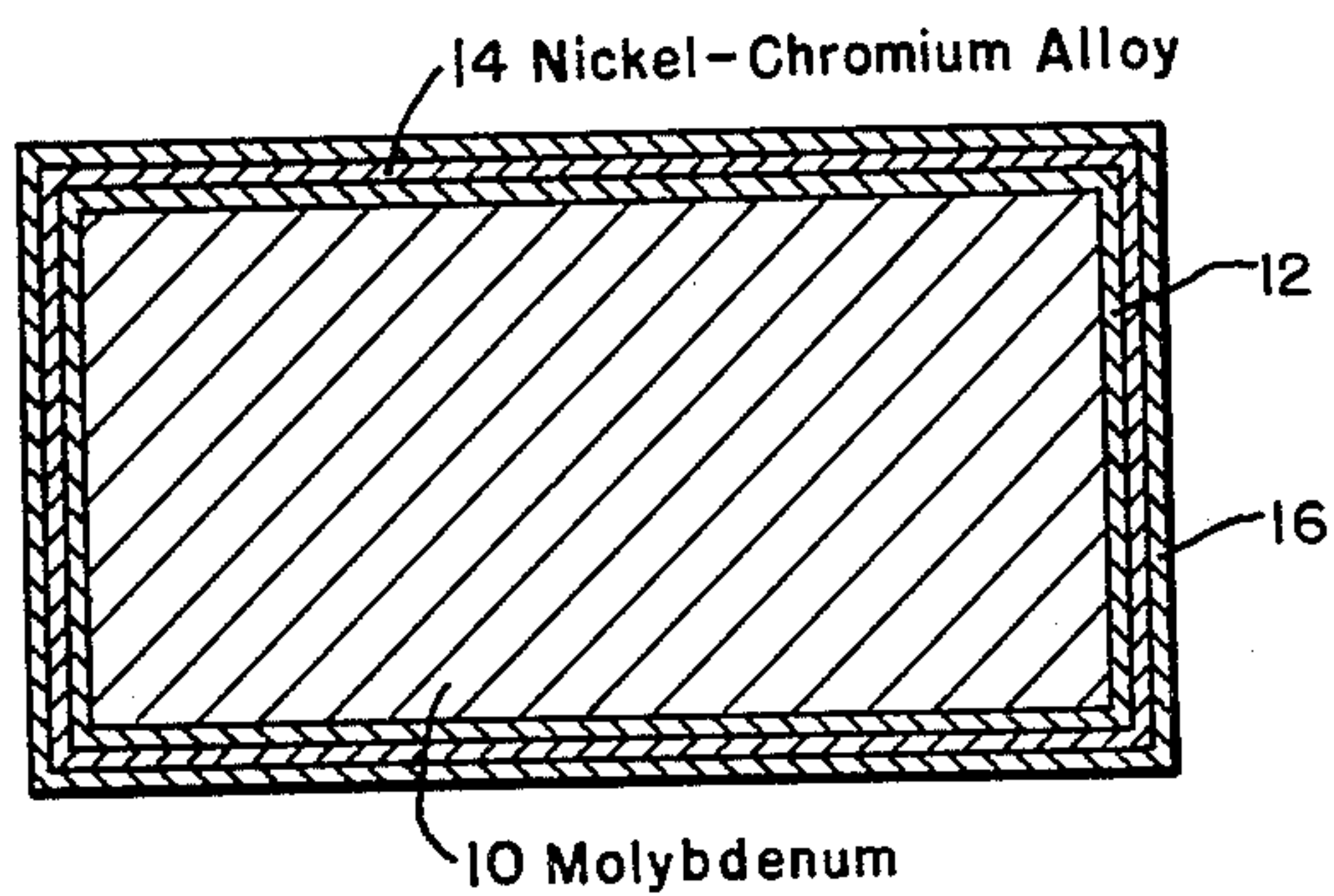
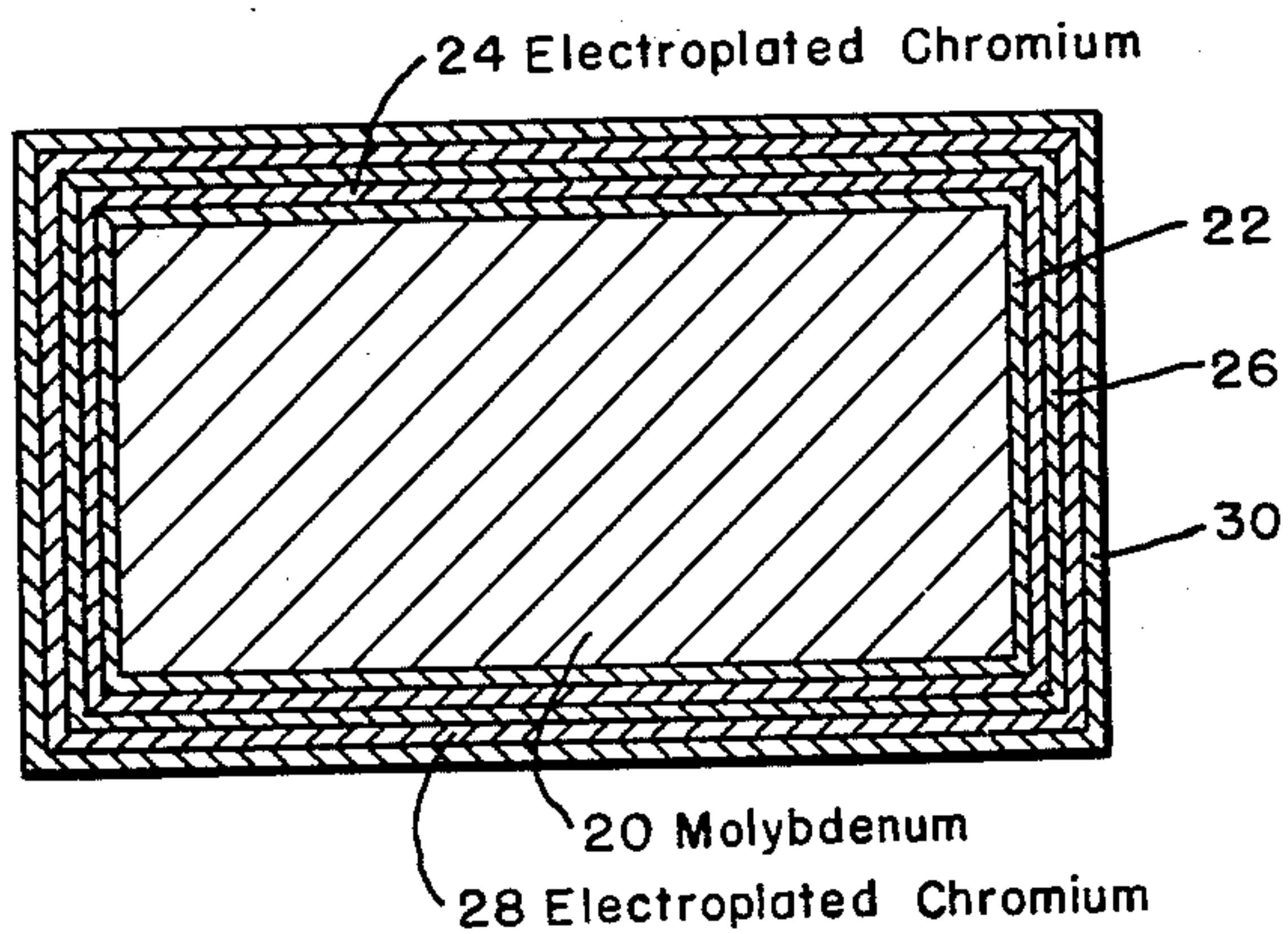


Fig. 2



WITNESSES

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2,952,904

## APPLYING PROTECTIVE METAL COATINGS ON MOLYBDENUM

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Filed Jan. 15, 1957, Ser. No. 634,365

6 Claims. (Cl. 29—194)

This invention relates to molybdenum metal with well bonded imperforate protective metal coatings applied to the surface thereof.

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, a piece of 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 and in this way enable the use of molybdenum metal at temperatures above 500° C. It is absolutely necessary that such applied protective layers be imperforate in order to be of any value. For example, electrodeposits of chromium have been plated on members of molybdenum and such coatings appeared to be sound and without pores. However, on heating such chromium plated member to 600° C. to 700° C., microscopic cracks and previously unnoted pinholes admitted oxygen to the molybdenum metal so that a stream of molybdenum oxide smoke issued from each of these openings and in only a short time substantial volumes of the molybdenum metal adjacent to each such opening had disappeared because it had oxidized and the resulting volatile oxide had escaped.

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 resistant to oxidation at the elevated temperatures of use, but it is also essential that the coating have good resistance to impact and shock under normally expected service conditions so as not to crack or spall and thereby expose the molybdenum body. Aviation gas turbine engine components are often subject to impact and shock from foreign particles, such as pebbles and the like being picked up and passed through the engine at high velocity. Should the impact of the foreign particles cause the coating metal to crack, the molybdenum body would thus become exposed to high temperature oxidation, this exposure resulting in premature failure of the component in service.

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The thickness of the applied protective coating is critical in that it must be of such a thickness to possess high impact resistance and at the same time adequately accommodate for differences in thermal expansion between the protective coating and the molybdenum body.

The object of this invention is to provide a body of molybdenum metal with a well bonded imperforate coating having good resistance to oxidation at elevated temperatures and good resistance to impact and shock, said coating comprising at least one layer of an oxidation-resistant metal sandwiched between at least two layers of a fused brazing alloy.

Another object of the invention is to provide a body of molybdenum with an imperforate coating of critical thickness to enable it to meet impacts and shock without being subject to failure due to differences in thermal expansion, said coating being bonded to the body of molybdenum by a nickel-chromium base brazing alloy.

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 a cross-section through a member comprising a body of molybdenum with an imperforate protective coating comprising three metal layers applied thereto; and

Fig. 2 is a cross-section through a member comprising a body of molybdenum with an imperforate protective coating comprising five metal layers applied thereto.

In accordance with this invention, a method has been discovered for producing on bodies of molybdenum metal, a highly protective surface coating of a critical thickness of the order of from 5 mils to 10 mils, which coating is highly resistant to impact and shock, and capable of accommodating differences in thermal expansion, and so well bonded and adherent to the metal that it will withstand elevated temperatures for prolonged periods of time. Briefly, the method comprises applying to the molybdenum body a layer of a finely divided brazing alloy to a thickness of the order of from about ½ mil to 2 mils and then heat-treating the molybdenum body with the applied brazing alloy to at least a temperature corresponding to the melting point of the brazing alloy in a reducing atmosphere. A relatively thin layer of the order of from about 1 mil to 3 mils of an oxidation-resistant metal is then applied to the entire surface of the fused brazing alloy. A third layer of a thickness of the order of about ½ mil to 2 mils of the brazing alloy is then applied to the entire surface of the oxidation-resistant metal layer and heat-treated in the same manner as the first layer. Additional alternating layers of the oxidation-resistant metal and the brazing alloy can be applied if desired.

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

The first layer that is applied to the body of molybdenum metal is a brazing alloy that is adherent to molybdenum and has good resistance to oxidation, said brazing alloy comprising, by weight, from 11% to 25% chromium, from 2% to 12% silicon, up to 8% iron, up to 3½% boron, and the balance being substantially all nickel with incidental impurities. The layer of brazing alloy can be applied in any convenient manner. It has been found that a convenient method of applying the layers of brazing alloy is to first prepare an aqueous slurry comprising



calcium chloride and finely divided brazing alloy. In preparing the slurry 12 parts to 55 parts by weight of finely divided brazing alloy is thoroughly admixed with each 10 parts by weight of a 10% aqueous calcium chloride mixture. The brazing alloy passes through a sieve having from 100 to 300 meshes per inch. The slurry is applied to the molybdenum body by dipping or brushing methods. The molybdenum body with the applied slurry is placed in a reducing atmosphere where it is heated to a temperature corresponding at least to the liquidus or melting point of the brazing alloy for a period of time of from about 5 minutes to 15 minutes. For small components of an area of a few square inches, such as jet engine blades, the heating time required is about 10 minutes. The brazing alloy fuses, thoroughly coats and firmly bonds to the molybdenum body. The calcium chloride serves as a flux during the brazing operation. Caution must be observed not to exceed too greatly the melting point of the brazing alloy. If the melting point is greatly exceeded, the brazing alloy will become too fluid and as a result will not be deposited in a layer of uniform thickness over the entire surface of the molybdenum body, but will tend to flow off elevated portions and gather at the bottom. A temperature range of from about 1050° C. to 1100° C. has been found to be a satisfactory melting range for the brazing alloys employed in this invention.

A second layer of an oxidation-resistant metal selected from the group consisting of chromium and chromium-nickel alloys melting above the melting point of the brazing alloy, is applied to the entire surface of the fused brazing alloy. The oxidation-resistant layer can be applied in any convenient manner. It is preferred, however, to apply chromium by electroplating means and to apply the chromium nickel alloys by spraying techniques or cladding methods. The second oxidation-resistant layer is applied in a thickness of from 1 mil to 3 mils.

A third layer of a brazing alloy is then applied to the entire surface of the oxidation-resistant layer in the same manner as the first layer of brazing alloy was applied to the molybdenum body. The second application of fused brazing alloy serves to fill any pinholes that may be present in the oxidation-resistant layer. The molybdenum body is thus provided with a well bonded imperforate coating of a total thickness of about 5 mils comprising a layer of a thickness of from 1 mil to 3 mils of an oxidation-resistant metal sandwiched between two layers of fused brazing alloy.

If desired, an additional layer of an oxidation-resistant layer and an additional layer of fused brazing alloy can be applied so as to provide a coating comprising two layers of oxidation-resistant metal alternately sandwiched between three layers of fused brazing alloy. Also, it is not essential that both layers of oxidation-resistant metal be of the same composition or that they be applied in the same manner. For example, one layer could be electroplated chromium and the second layer could be sprayed chromium-nickel alloy. Further, it is not essential that the layers of fused brazing alloy be of the same composition.

The following examples illustrate the method of applying to a molybdenum body an imperforate protective coating in accordance with this invention.

#### EXAMPLE I

A member of molybdenum metal is first sandblasted or otherwise treated to remove any impurities therefrom and also to roughen slightly the surface thereof. The entire surface of the molybdenum member is then brushed with a slurry of the following composition:

	Parts by weight
10% aqueous solution of calcium chloride	10
Finely divided brazing alloy comprising, by weight,	
16% chromium, 69% nickel, 5% silicon, 6% iron,	
3% boron, and 1% carbon	35

The slurry is so applied as to provide on the entire surface of the member a layer of the slurry of a thickness of about 1½ mils. The coated molybdenum member is then placed in a furnace provided with a hydrogen atmosphere and is heated slowly to a temperature of 1080° C. The temperature is held at 1080° C. for about 10 minutes. Heating is then terminated and the member cooled to room temperature in the hydrogen atmosphere. The entire surface of the molybdenum member with the applied fused layer is removed from the furnace and spray coated by means of a flame spraying operation with an oxidation-resistant metal alloy comprising, by weight, 80% nickel and 20% chromium. The alloy is applied in a thickness of about 2 mils. A second layer of a thickness of about 2 mils of brazing alloy of the same composition as that of the first applied layer is then applied to the entire surface of the oxidation-resistant layer and fused in a furnace in the same manner as the first layer.

Referring to Fig. 1 of the drawing, there is illustrated a cross section of a member produced in accordance with the process of this Example I. The body 10 of molybdenum metal has applied to all of its surfaces a layer 12 of the fused brazing alloy. The layer 12 has applied to all its surfaces a layer 14 of the 80% nickel, 20% chromium alloy, and to the layer 14 is applied a second layer 16 of the fused brazing alloy.

A ballistic impact test was carried out in which a test panel could be heated to elevated temperatures, then subjected to direct impact by copper coated steel pellets 0.175 inch in diameter projected at controllable muzzle velocity from an air pistol with the muzzle approximately 12 inches from the test panel which is held in position on a small anvil by clamping means. A Benjamin Air Pistol, Model 130-BB, is held in position by wooden gun rests. The gun rests are attached to the anvil by means of high temperature-resistant metal rods. The anvil with the attached test panel is placed in a furnace maintained at the test temperature. The pellets are fired at the test panel after the test panel has been heated to the desired temperature. The following table shows the test results employing test panels prepared by coating a body of molybdenum 1 inch x 0.38 inch x 0.05 inch in accordance with Example I.

Table I

Test Panel	Temperature of Panel, ° F.	Velocity of Pellet, ft./sec.	Results
1-----	1200	226	Continuous coating at impact area.
2-----	1200	341	Do.
3-----	1200	427	Do.
4-----	1500	226	Do.
5-----	1500	341	Do.
6-----	1500	427	Do.
7-----	1800	226	Do.
8-----	1800	341	Do.
9-----	1800	427	Do.

#### EXAMPLE II

A member of molybdenum metal is sandblasted to clean and roughen the surface thereof. An imperforate protective coating comprising five layers, each averaging about 1.5 mils thick, is then applied in the following manner. A first layer of fused brazing alloy comprising, by weight, 71.5% nickel, 11.5% chromium, 5.2% iron, 4.2% silicon, 2.5% boron, and 0.74% carbon, the balance being incidental impurities is applied to the entire surface of the molybdenum member in the same manner as set forth in Example I employing a slurry comprising 10 parts by weight of 10% aqueous calcium chloride and 35 parts by weight of the brazing alloy. A second layer comprising chromium is then electrodeposited over the entire surface of the first layer. A third layer comprising the fused brazing alloy is applied to the entire surface of



the second layer. Another layer of electrodeposited chromium is then applied to the entire surface of the third layer. A final layer of the fused brazing alloy is applied to the entire surface of the second chromium layer.

Referring to Fig. 2 of the drawing, there is illustrated a cross section of a member produced in accordance with the process of this example. The body 20 of molybdenum metal has applied to all its surface a layer 22 of the fused brazing alloy. The layer 22 has applied to all its surface a layer 24 of electrodeposited chromium to which is applied a second layer 26 of the fused brazing alloy. A layer 28 of electrodeposited chromium has been applied to the entire surface of the layer 26. A final layer 30 of the fused brazing alloy has been applied to the entire surface of the layer 28.

The following table shows the test results employing test panels prepared by coating a body of molybdenum 1 inch x 0.38 inch x 0.05 inch in accordance with Example II.

Table II

Test Panel	Temperature of Panel, ° F.	Velocity of Pellet, ft./sec.	Results
1-----	1200	226	Continuous coating at impact area.
2-----	1200	341	Do.
3-----	1200	427	Do.
4-----	1500	226	Do.
5-----	1500	341	Do.
6-----	1500	427	Do.
7-----	1800	226	Do.
8-----	1800	341	Do.
9-----	1800	427	Do.

It has been determined that the protective coatings of this invention should be at least about 5 mils in thickness so as to provide adequate resistance to impact. Furthermore, coatings of a thickness considerably in excess of 10 mils, for example 30 mils, are too thick. Massive molybdenum bodies can be provided with thicker coatings than relatively small bodies, such as jet engine blades, without being subject to failure due to differences in thermal expansion.

Molybdenum bodies coated in accordance with this invention have been subjected to continuous oxidation at temperatures up to 2000° F. for many hours without failure. Furthermore, the coated molybdenum members of this invention have shown good results in thermal cycling test between room temperature and temperatures as high as 2000° F.

Since certain obvious changes can be made in the above procedures and different embodiments of the invention can 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.

I claim as my invention:

1. A member comprising a molybdenum body and a well bonded imperforate coating applied to the entire surface of the body, the coating having good resistance to oxidation at elevated temperatures and good resistance to impact and shock so as not to expose the molybdenum body under normally expected service conditions, said coating comprising at least one continuous layer of an oxidation-resistant metal selected from the group consisting of chromium and nickel-chromium alloys sandwiched between at least two continuous layers of a fused brazing alloy comprising, by weight, from 11% to 25% chromium, from 2% to 12% silicon, up to 8% iron, up to 3½% boron, and the balance being substantially all nickel with incidental impurities, said layers of fused brazing alloy bonded together the layers to each other and to the molybdenum body, the said coating having a wall thickness of the order of from 5 mils to 10 mils.

2. A member comprising a molybdenum body and a well bonded imperforate coating applied to the entire surface of the body, the coating having good resistance to oxidation at elevated temperatures and good resistance to impact and shock so as not to expose the molybdenum body under normally expected service conditions, said coating comprising at least two continuous layers of an oxidation-resistant metal, each of said layers being selected from the group consisting of chromium and nickel-chromium alloys, alternately sandwiched between at least three continuous layers of a fused brazing alloy comprising, by weight, from 11% to 25% chromium, from 2% to 12% silicon, up to 8% iron, up to 3½% boron, and the balance being substantially all nickel with incidental impurities, said layers of fused brazing alloy bonding the layers to each other and to the molybdenum body and each of said layers being of a thickness of the order of from about ½ mil to 2 mils, each layer of said oxidation-resistant metal being of a thickness of the order of from about 1 mil to 3 mils, the said coating having a wall thickness of the order of from 5 mils to 10 mils.

3. A member comprising a molybdenum body and a well bonded imperforate coating applied to the entire surface of the body, the coating having good resistance to oxidation at elevated temperatures and good resistance to impact and shock so as not to expose the molybdenum body under normally expected service conditions, said coating comprising one continuous layer of a thickness of the order of from about 1 mil to 3 mils of an oxidation-resistant metal comprising, by weight, 80% nickel and 20% chromium sandwiched between two continuous layers of a thickness of the order of from about ½ mil to 2 mils of a fused brazing alloy comprising, by weight, from 11% to 25% chromium, from 2% to 12% silicon, up to 8% iron, up to 3½% boron, and the balance being substantially all nickel with incidental impurities, said layers of fused brazing alloy bonding the layers to each other and to the molybdenum body, the total wall thickness of the layers being of the order of from 5 mils to 10 mils.

4. The member of claim 3 wherein two continuous layers of the oxidation-resistant metal are alternately sandwiched between three continuous layers of the fused brazing alloy.

5. A member comprising a molybdenum body and a well bonded imperforate coating applied to the entire surface of the body, the coating having good resistance to oxidation at elevated temperatures and good resistance to impact and shock so as not to expose the molybdenum body under normally expected service conditions, said coating comprising one continuous electrodeposited layer of a thickness of the order of from about 1 mil to 3 mils of chromium sandwiched between two continuous layers of a thickness of the order of from about ½ mil to 2 mils of a fused brazing alloy comprising, by weight, from 11% to 25% chromium, from 2% to 12% silicon, up to 8% iron, up to 3½% boron, and the balance being substantially all nickel with incidental impurities, said layers of fused metal alloy bonding the layers to each other and to the molybdenum body, the total wall thickness of the layers being of the order of from 5 mils to 10 mils.

6. The member of claim 5 wherein two continuous electrodeposited layers of chromium are alternately sandwiched between three continuous layers of the fused brazing alloy.

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