ADDITION OF CARBON TO NICKEL COATINGS ON MOLYBDENUM Filed Aug. 1, 1958

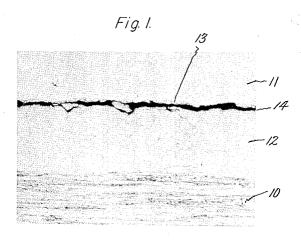
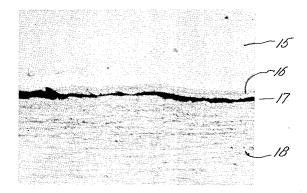


Fig. 2.



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## 2,983,035

## ADDITION OF CARBON TO NICKEL COATINGS ON MOLYBDENUM

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Filed Aug. 1, 1958, Ser. No. 752,599

4 Claims. (Cl. 29-198)

This invention relates to protective coatings for metal 15 bodies and more particularly to coating materials for protecting molybdenum bodies from oxidation and for reducing the formation of zones of recrystallized molybdenum in the region of the interface between the molybdenum body and the coating material.

Molybdenum and molybdenum alloys containing inclusions of a second phase hardening compound such as a carbide of titanium, zirconium, hafnium, or any of the other more reactive metals combined into a stable compound with a suitable non-metal, i.e., oxygen, nitrogen 25 and boron, have found increasing use in situations where high mechanical strength, creep resistance, etc., and resistance to oxidation at high temperature are important. For example, molybdenum is particularly useful in making blades for use in gas turbines which operate at high temperatures and which subject the metal parts to high centrifugal forces during operation.

While molybdenum has the desired mechanical properties, it does not satisfactorily resist oxidation at high temperatures. The principal existing method of overcoming 35 this difficulty is to cover the molybdenum body with a suitable oxidation resisting coating, nickel, chromium, and nickel and iron base alloys being the principal materials used. While these coatings have generally proven effective in preventing oxidation of the molybdenum base. they are subject to certain disadvantages, one of the principal disadvantages to the nickel coating occurring after diffusion of nickel into the molybdenum alloy base. The result of the diffusion is a lowering of the recrystallization temperature, within the diffused zone. The zone of recrystallized molybdenum is weak at high temperatures and tends to be brittle at low temperatures. Also, the diffused layer is always brittle and promotes poor adherence of the coating. Chromium is somewhat better in its resistance to the formation of an intermediate compound or compounds at the molybdenum-coating interface, although the layer still forms, but it also tends to be brittle and is more difficult to apply than nickel when roll cladding of sheet is an objective. Although the exact interaction between the coating and the basis metal is not fully developed, it is believed that the lowering of the recrystallization temperature results from removal of the non-metallic parts (carbon, boron, etc.) of the second phase hardening compound from the molybdenum body by the adjacent coating matrix material which acts as a sink. Even though the coating material has a lesser chemical affinity for the non-metallic part of the hardening compound than does the reactive metal with which it is combined it may still act as a diluent and cause removal of enough of the compound to result in lowering of the recrystallization temperature, thereby weakening the

It is therefor a principal object of this invention to provide a coating material for application to molybdenum bodies containing second phase hardening compounds which coating protects the molybdenum from oxidation and prevents the formation of a recrystallized zone.

final composite structure.

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It is another object of this invention to provide a molybdenum body having a coating material preventing the formation of recrystallized zone at the interface between the molybdenum base and the coating.

A further object of this invention is to provide a process for coating a molybdenum base which prevents the formation of a recrystallized zone at the interface between the coating and the body.

Other objects and advantages of this invention will be 10 in part obvious and in part explained by reference to the accompanying specification and drawings.

In the drawings:

Fig. 1 shows the weakening zone of recrystallized molybdenum resulting from the use of a plain coating; and

Fig. 2 shows the absence of the recrystallized zone when a coating made according to the present invention is used.

Briefly, the present invention concerns a coating ma-20 terial for use in protecting molybdenum bodies containing a dispersion of a second phase hardening compound of a reactive metal combined with a non-metal. The coating is made up of a desired metal having the proper oxidation resisting properties and a non-metal correspond-25 ing to that used in the hardening compound.

Turning now to a more specific discussion of the invention, the coating materials are, as already mentioned, particularly useful on molybdenum containing a predetermined amount of a selected second phase hardening compound. Each of these hardening compounds is made of a reactive metal selected from the group consisting of titanium, zirconium, hafnium, columbium and tantalum. Occasionally chromium, thorium and beryllium may also be used.

The non-metals with which the preceding metals are reacted to form suitable hardening compounds include boron, oxygen, nitrogen, and carbon. The principal requirement in selecting a particular non-metal for use is, to be certain that it has more affinity for the reactive metal than it does for the base metal, otherwise, the non-metal will combine primarily with the base metal.

The principal coating materials used in protecting molybdenum bodies are nickel, chromium, nickel base alloys and iron base alloys containing sufficient quantities of materials such as chromium, to render them oxidation resistant. Under special circumstances, special coatings such as tantalum and titanium are also used.

Since all of the non-metallic parts of the hardening dispersion are taken from the group carbon, boron, oxygen and nitrogen, one of these substances is included in the particular coating material to preclude the formation of the recrystallized zone. Prevention of the recrystallized zone is believed accomplished by promoting equilibrium between the coating and the molybdenum. That is, if the coating contains a sufficient amount of the non-metal being used, there is no tendency for the coating to act as a sink drawing the non-metal away from the reactive metal in the molybdenum base. Of course, the non-metal selected for addition to the coating corresponds to that forming part of the dispersed hardening phase.

To ascertain the value of the additions to the coating metal sample molybdenum bodies containing about 0.5 weight percent titanium and about 0.02 weight percent carbon were prepared for testing. It is generally accepted that the titanium and carbon in the molybdenum combine to form titanium carbide particles, which constitute the second phase hardening dispersion, although such particles are not easily identified metallographically.

Two diffusion couples were prepared by drilling axial 1/6" holes through 1/2 inch by 3/8 inch diameter pieces of the molybdenum and inserting a 2 inch by 1/8 inch diameter rod of a nickel alloy in each of the axial holes.

In one case the solid rod was nickel plus 5.0 weight percent titanium while in the other the solid rod was nickel plus 0.3 weight percent carbon.

The resulting couples were then annealed in dry hydrogen for 72 hours at 2100° F. to determine the effect of the carbon in preventing a recrystallized zone in the molybdenum.

The results are as follows:

Referring to Fig. 1 of the drawings which shows the couple between molybdenum body 10 and the nickel rod 11 containing 5.0 weight percent titanium, it is apparent that a rather large amount of recrystallization has occurred. The recrystallized zone is indicated by numeral 12. There is also a small zone 13 of a nickel-molybdenum compound and a void 14 where the two bodies separated somewhat upon cooling. By comparing Fig. 1 with Fig. 2 it will readily be seen that the recrystallized zone is absent, this being due to the fact that the coating 15 contains 0.3 weight percent carbon. Under coating 15 is a nickel-molybdenum compound layer 16, a slight void 17, and the molybdenum body 18. Although the nickel and molybdenum have separated slightly, this is due to the type of coupling arrangement used to test the effects of the non-metal additions to the coating. Had actual coatings been used rather than diffusion couples, the differ- 25 ences in expansion and contraction rates would have had little effect and no voids would occur.

Thus, by supplying a protective coating on a body of molybdenum which contains an amount of a non-metallic component coinciding with that used as the non-metallic 30 part of the dispersion hardening compound, it is possible to prevent the formation of a depleted zone beneath the alloy coating. If depletion of this zone of its dispersion hardening content is not effected, the recrystallization temperature of the molybdenum alloy will not be lowered 35 and the final body will be of substantially uniform mechanical ability throughout its entire temperature operat-

ing range.

Where a material such as titanium or zirconium carbide is used in the matrix of molybdenum, the coating metal, i.e., nickel, should contain an amount of carbon, that being the non-metallic part of the compound corresponding to the compound used in the molybdenum. Similarly, if a nitride compound is used as the dispersion hardening agent, nitrogen is added to the coating material to prevent 45 depletion of the nitride particles from the zone of the body immediately beneath the coating material. same, of course, will hold true where boron or oxygen is used as the non-metallic part of the hardening compound.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. An article of manufacture comprising a molybdenum body, a second phase dispersion of a hardening compound consisting of a nonmetal selected from the group consisting of nitrogen, oxygen, carbon and boron combined with a metal which is more reactive with the selected nonmetal than with said molybdenum, a protective coating comprising a desired metal, and an amount of a nonmetal identical in composition to the nonmetal in said hardening compound reducing removal of said nonmetal from said molybdenum body and preventing recrystallization of said molybdenum body.

2. An article of manufacture comprising a molybdenum body, a second phase dispersion of a hardening compound consisting of a nonmetal selected from the group consisting of nitrogen, oxygen, carbon and boron combined with a metal selected from the group consisting of titanium, zirconium, halnium, columbium tantalum, chromium, thorium and beryllium, a protective coating comprising a desired metal, and an amount of a nonmetal identical in composition to the nonmetal in said hardening compound reducing removal of said nonmetal from said molybdenum body and preventing recrystalliza-

tion of said molybdenum body.

3. In combination with a molybdenum body containing a second phase dispersion of a hardening compound consisting of a nonmetal selected from the group consisting of carbon, nitrogen, oxygen and boron combined with a metal which is more reactive with the selected nonmetal than with said molybdenum, a protective coating comprising a metal selected from the group consisting of nickel, chromium, nickel-base alloy, and oxidation-resistant iron-base alloys, and an amount of a nonmetal identical in composition with the nonmetal in said hardening compound reducing removal of said nonmetal from said molybdenum and preventing recrystallization of said molybdenum body adjacent said coating.

4. The combination as defined in claim 3 wherein said

40 coating is nickel.

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