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MULTIPLE COATED MOLYBDENUM BASE ARTICLE

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Fig. 1

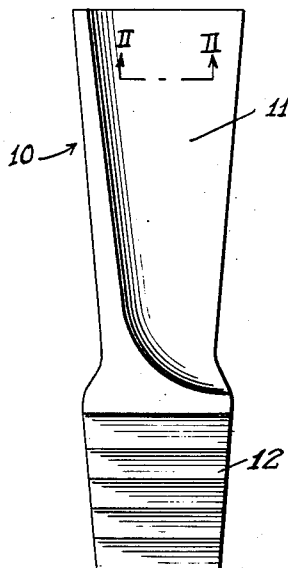


Fig. 2

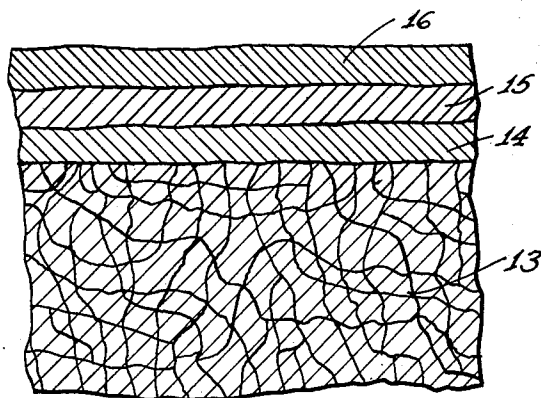
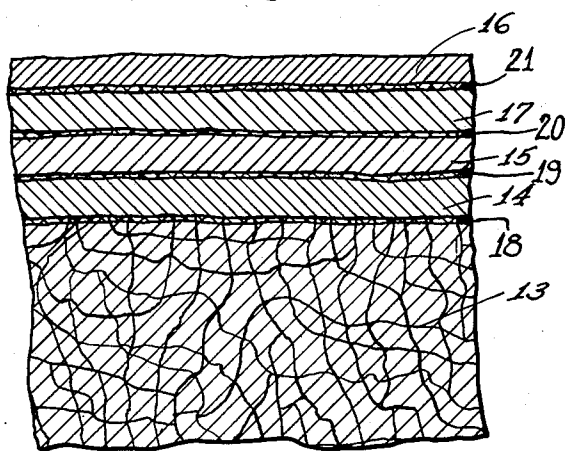


Fig. 3



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MULTIPLE COATED MOLYBDENUM
BASE ARTICLE

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1 Claim. (Cl. 29—198)

The present invention relates to an impact and corrosion resistant article particularly useful in environments of high temperatures and corrosive atmospheres. The present invention is also concerned with methods of manufacturing such impact and corrosion resistant articles.

The extensive development in the field of jet engines has necessitated the development of alloys for use in the manufacture of parts for such jet engines which can withstand the extremely high temperatures and the oxidizing atmospheres normally present in the operation of turbo-jet engines. For example, a turbine bucket attached to a turbine wheel will ordinarily be exposed to temperatures in excess of about 1450° F. and in order to function properly it must have a high degree of strength, toughness, creep-resistance, and resistance to the oxidizing gases present in the turbine engine.

In addition to their use in the manufacture of turbine buckets, articles produced in accordance with the instant invention may be employed under substantially any condition of elevated temperatures and deteriorating atmospheres. One such application occurs in nozzle diaphragm vanes in gas turbines which must withstand very severe conditions of temperature and thermal shock, but at a relatively low stress.

Refractory metals and refractory metal compounds, such as molybdenum, tungsten, tantalum and alloys of such metals, exhibit excellent properties of strength, toughness and creep-resistance at elevated temperatures. However, the oxidation resistance of such metals is quite poor. Although molybdenum has a melting point in excess of 4500° F. and good strength at elevated temperatures, it begins oxidation at temperatures as low as 900° F. The rate of formation of the molybdenum oxide increases with the temperature. Since the molybdenum oxide produced under these oxidizing conditions sublimes, complete disintegration of the molybdenum body will occur in a relatively short time under high temperature oxidizing conditions.

It has been proposed that the oxidation resistance of metals, such as molybdenum, may be materially increased while still preserving its high temperature strength properties by depositing certain corrosion and impact resistant metals or metalloids on the surface of the molybdenum. Under moderate or comparatively slow temperature changes a molybdenum body provided with a corrosion resistant layer can withstand thousands of hours of operation above temperatures of red heat without showing any evidence of oxidation of the molybdenum base.

A serious limitation encountered in the use of corrosion and impact resisting coatings on refractory metal articles has been the large disparity existing between the coefficients of thermal expansion of the refractory base metal and the coating materials. For example, molybdenum has one of the lowest coefficients of linear thermal expansion of all the materials presently known. The corrosive and impact resistant materials which display optimum properties for coating molybdenum, on the other hand, have coefficients of linear thermal expansion rough-

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ly two to four times greater than that of molybdenum. When a molybdenum article thus coated is subjected to changes in temperature or thermal shock this disparity between the thermal expansion of the coating and the molybdenum metal base often causes severe fracturing of the corrosion resistant coating. Rapid temperature changes enhance the fracture or rupture of the coating since the heating occurs through the coating which will expand before the body is heated. An increased expansion differential occurs. Such rapid temperature fluctuations and conditions of thermal shock are regularly encountered in starting, changing in altitude and stopping jet propelled aircraft. For example, it has been calculated that when a turbo-jet engine is started, the temperature of the turbine blades may increase at a rate as high as 130° F. per second.

By means of the instant invention the fracturing or rupturing of corrosion and impact resistant coatings on refractory metal bodies, due to variances in the thermal expansion characteristics of the base metal and the coatings, has been successfully minimized. This is achieved by providing a buffer or cushion between the refractory metal base and the ultimate outer corrosion and impact resistant coating. In accordance with the instant invention this "cushion" comprises at least one and preferably a plurality of layers of materials selected for their thermal expansion characteristics. The initial layer in immediate contact with the refractory metal article has a coefficient of linear thermal expansion slightly greater than that of the refractory metal base. Likewise, the coefficient of expansion of each successive layer is greater than the preceding underlying layer and greater than that of the refractory metal base. This sequence is carried out to and includes the ultimate or outer impact and corrosion resistant layer. In this manner rapid expansions and contraction of the article are of a relatively graded uniform rate from the refractory metal base to the outer corrosion resistant coating, and since the intermediate layer immediately underlying the outer coating has a coefficient of thermal expansion quite close to that of the outer coating rapid temperature changes will not cause fracturing of the outer coating.

Enhanced cushioning or control of relative expansion between the successive layers is obtained by blending or diffusing the adjacent coatings into each other. The resulting interface blend will have an expansion coefficient intermediate the coefficient of the adjacent layers. This diffusion or blending will occur automatically when the article is heated in use or can be developed by a heat treatment prior to use.

In accordance with the foregoing the primary object of the present invention is to minimize fracturing or rupturing of corrosion and impact resistant coatings for a refractory metal base by cushioning the coating on one or more layers of materials having coefficients of thermal expansion between the coating and the base metal.

Another object is to provide a heat resistant article including a refractory metal base coated with a plurality of layers including an outer corrosion resisting layer, wherein the coefficient of thermal expansion of each of the layers is progressively greater than the preceding underlying layer and greater than the coefficient of the refractory metal base.

A specific object is to provide a refractory metal base article having a plurality of successive coatings thereon which will not be fractured by the expansion and contraction of the underlying refractory base metal with the adjacent coatings diffused to provide interfaces with coefficients of expansion lying intermediate the expansion coefficients of the adjacent coatings.

A particular object is to provide a plurality of corrosion and impact resistant coatings for a molybdenum

base article wherein the coating on the molybdenum will not fracture under stresses produced in the expansion and contraction of the molybdenum base.

Yet another object is the provision of corrosion and impact resistant coatings for refractory metals, such as molybdenum, tungsten and the like, wherein the coatings overlaying the refractory metals display coefficients of linear thermal expansion progressively greater than the underlying layer and greater than the coefficients of thermal expansion of the refractory base metal.

Other objects, features and advantages of this invention will be readily apparent from the following discussion of a preferred embodiment thereof taken in conjunction with the annexed sheet of drawings in which:

Figure 1 is a view in elevation of a turbine blade provided with a corrosion and impact resistant coating according to the present invention;

Figure 2 is a fragmentary cross-sectional view, greatly enlarged, taken substantially along line II—II of Figure 1; and

Figure 3 is a view similar to Figure 2 illustrating corrosion and impact resistant coatings similar to those shown in Figure 2.

As noted previously, the present invention is concerned with the provision of corrosion and impact resistant coatings on heat resistant articles wherein such coatings will not fracture when the article is subjected to extreme temperature fluctuations. The instant invention may be applied to substantially any material which is to be coated with a substance having a coefficient of thermal expansion widely different than the material being coated. In practice this invention is particularly applicable to coating refractory metals and refractory compounds.

By "refractory metals" is meant metals particularly of the 4th, 5th and/or 6th group of the periodic system such as molybdenum, tungsten, tantalum and alloys of such metals.

In addition to these refractory metals the instant invention may also be applied to such refractory materials as ceramics, cermets and cemented carbides such as titanium carbide and tungsten carbide combined with a binder metal selected from the iron group such as nickel, cobalt or nickel-base alloys such as "Inconel."

Since, however, the instant invention is especially applicable in coating molybdenum with corrosion and impact resistant materials for use in turbine engines, the disclosure and discussion shall deal particularly with molybdenum and its alloys. It will be understood, however, that this invention is applicable to many materials and it is not the intention to limit the invention specifically to the coating of molybdenum.

In accordance with this invention a molybdenum article is coated with a plurality of layers of corrosion and impact resistant materials in such a manner that the outer coating, although having a coefficient of thermal expansion much greater than that of molybdenum, will not fracture or rupture when the article is subjected to extreme thermal shock. This is achieved by interposing or providing a plurality of intermediate corrosion and impact resistant layers between the molybdenum article and the outer coating. The initial layer in immediate contact with the molybdenum article is chosen to have a coefficient of thermal expansion slightly greater than that of molybdenum. In the same manner the layer immediately overlying the initial layer is chosen to have a coefficient of thermal expansion slightly greater than that of the initial coating in contact with the molybdenum. This progressive increase in expansion coefficient is repeated for successive layers with each layer having a coefficient of expansion greater than that of the preceding underlying layer up through and including the outermost layer. In this manner the intermediate layers will manifest a graded expansive response from the molybdenum base to the outer layer when the article is subjected

to thermal shock. This graded expansion minimizes fracturing or rupture of the outer layer.

The substances employed in forming this plurality of corrosion and impact resistant coatings on a molybdenum or molybdenum alloy base are numerous as indicated by the following table wherein a number of corrosion resistant materials are classified according to their coefficients of linear thermal expansion:

Material:	Coefficient of thermal expansion in./in./° C. $\times 10^{-6}$
Tungsten	4.3
Osmium	4.6
Molybdenum	4.9
Zirconium	5
Carboloy (Grade 44A-6% cobalt)	5.04
Carboloy (Grade 55A-13% cobalt)	6.08
Chromium	6.2
Tantalum	6.5
Carborundum SiC	6.58
Iridium	6.8
Columbium	7.1
Silicon	7.63
Vanadium	7.8
Graphite	7.86
Boron	8.3
Rhodium	8.3
Titanium	8.5
Platinum	8.9
Ruthenium	9.1
Hastelloy "B"	10.0
Hastelloy "A"	11.0
Thorium	11.1
Hastelloy "C"	11.3
Inconel	11.5
Hastelloy "D"	11.5
Iron	11.7
Iron	16.0
SAE 1020 steel	11.7
Palladium	11.8
"S" Monel	12.2
Cobalt	12.3
Beryllium	12.4
BMX-70BB	12.42
Ni ₃ Al	12.74
"Z" Nickel	13.0
Nichrome V	13.14
Nickel	13.3
Ni ₃ Al+15% Cr	13.91
"K" Monel	14.0
Gold	14.2
Stellite #1	14.4
Copper	16.5
Croloy 18-8	16.6
Stellite #6	16.9
Manganese	22

As may be seen from the above table any material lying below molybdenum and above the outer coating material may be employed as a thermal expansion cushioning layer between the molybdenum and outer coating. Preferably, however, a plurality of layers having progressively higher coefficients are employed.

In producing turbine blades and the like from molybdenum it is advantageous to employ at least one but preferably two or more intermediate layers between the molybdenum base and the outer coating.

As shown in the drawings reference 10 denotes generally a conventional turbine bucket consisting of a blade portion 11 and a fir-tree root portion 12 arranged for wedged engagement along the hub of turbine wheel.

As illustrated in the greatly enlarged view of Figure 2 the bucket consists of a body of molybdenum metal 13. The molybdenum body 13 is provided with an initial

layer 14 in immediate contact therewith. In the embodiment shown in the drawings, this layer preferably

A," "B," "C" or "D" and "BX-70BB." The compositions of these preferred alloys are as follows:

Percent compositions

	Mm	Si	Fe	Cr	B	Ni	Zr	Ca	C	Mo	W	Cb
Nichrome.....	0.01	4.54	5.02	14.82	4.53	70.00	0.01	0.01	0.68			
Inconel.....	0.01	0.80	1.05	18.17	4.86	74.4	0.01		0.24			
Inconel "X".....	0.70	0.40	5 to 9	14 to 16		70 min			0.03			0.70 to 1.20
Hastelloy "A".....	2.00	0.80	18 to 22			55.5 to 59.5			0.04 to 0.15	18 to 22		
Hastelloy "B".....	0.60	0.20	4 to 7			balance			0.12 max	26 to 30		
Hastelloy "C".....			4.5 to 7	15.5 to 17.5		balance			0.15 max	16 to 18	3.75 to 51.25 W.	

comprises zirconium which has a coefficient of lineal thermal expansion of about 5.0 as compared to 4.9 for molybdenum. Immediately overlying the zirconium layer 14 is another corrosion resistant layer 15. The layer 15 preferably comprises chromium having a coefficient of linear thermal expansion of about 6.2. The chromium layer 15 is overlaid with an outer coating 16 which preferably comprises a nickel-base alloy which displays maximum corrosion resistance in turbine engine gas streams.

The embodiment shown in Figure 3 is similar to Figure 2. In Figure 3 however a layer of titanium 17 overlies the chromium layer 15 between the outer layer 16 and the chromium layer 15. This arrangement is particularly useful where the outer coating 16 has a coefficient of linear thermal expansion substantially greater than that of the layer 15, in which case the layer 17 acts as a thermal expansion cushion between the layers 15 and 16. In addition, interfaces or diffusion zones 18, 19, 20 and 21 are formed between the successive layers or coatings in Figure 3. These interfaces are composed of constituents from both adjacent layers and will have thermal expansion coefficients intermediate those of the adjacent layers. Thus the layer 18 will have a coefficient of thermal expansion intermediate that of molybdenum and zirconium, while interface 19 will have a coefficient of expansion lying between that of zirconium and chromium. In the same manner, interface 20 has a coefficient of thermal expansion intermediate chromium and the nickel-base alloy outer coating.

These interfaces are developed by heat treatment at temperatures from about 1500° F. up to the liquidus temperature of the lower melting layer.

The material employed in forming the outer corrosion and impact resistant layer may comprise nickel, intermetallic compounds of nickel and aluminum such as Ni₃Al or nickel-base alloys. Nickel-base alloys are preferred due to their excellent corrosion resistance. Among the preferred nickel-base alloys which may be employed are "Nichrome," "Inconel" or "Inconel X," "Hastelloy

The alloy "BMX-70BB" comprises a mixture of 60% "Nichrome" and 40% "Inconel" by weight.

The thermal expansion corrosion resistant cushion layers provided between the molybdenum article and the outer corrosion resistant layers may be deposited upon the refractory metal base in any suitable manner. For example, electroplating may be employed and/or vapor deposition with or without a subsequent diffusion operation.

The outer layer is preferably applied by flame spraying or by spraying the metal powders from an aqueous suspension followed by fusion at elevated temperatures in an inert atmosphere. If nickel is employed as the outer corrosion and impact resistant coating it may be effectively deposited by electrodeposition.

It will be apparent to those skilled in the art that we have now provided a new and improved heat resistant article in the form of a refractory base having a corrosion and impact resistant coating thereon wherein the coating, which comprises a plurality of layers, will not fracture under stresses produced in the rapid expansion and contraction of the refractory base.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

We claim as our invention:

A jet engine part subject to conditions of oxidative corrosion in use comprising a base of molybdenum, a layer of zirconium overlying said molybdenum base, the interface between said molybdenum base and said zirconium layer containing a diffused mixture of molybdenum and zirconium having a coefficient of thermal expansion lying between that of molybdenum and zirconium, a layer of chromium over said zirconium layer, the interface between said chromium layer and said zirconium layer containing a diffused mixture of zirconium and chromium having a coefficient of thermal expansion lying between that of zirconium and chromium, and an outer layer of an impact resistant nickel base alloy forming the outer surface for said part.

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