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CORROSION AND IMPACT-RESISTANT ARTICLE

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Fig. 1

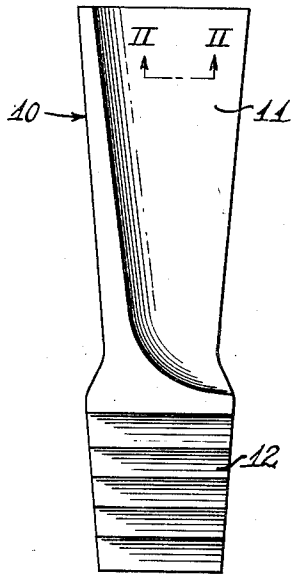


Fig. 2

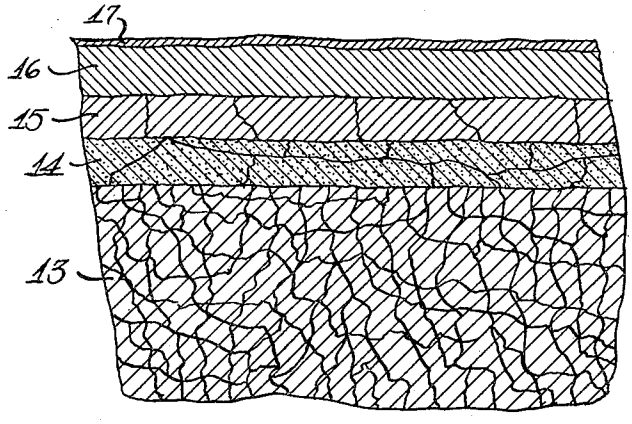
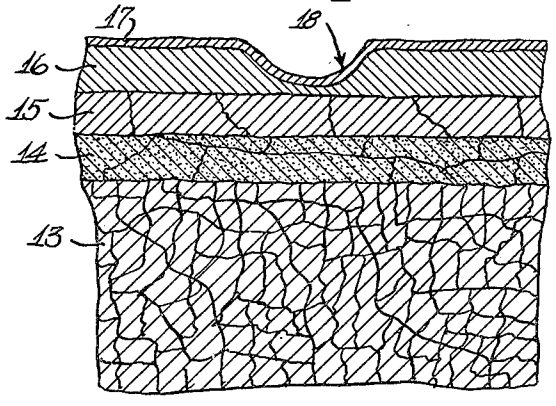


Fig. 3



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CORROSION AND IMPACT-RESISTANT ARTICLE

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4 Claims. (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 present invention may also be employed under conditions of higher temperature and lower stress than are encountered by turbine buckets. 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 such as molybdenum and tungsten exhibit excellent properties of strength, toughness and creep-resistance at elevated temperatures. However, the oxidation resistance of metals such as molybdenum 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 such high temperature oxidation conditions.

It will be understood that the remarks applicable to molybdenum are applicable also to molybdenum base alloys, particularly those containing 95% or more by weight molybdenum. The present invention is directed both to the use of substantially pure molybdenum bodies and the molybdenum base alloys mentioned.

It has recently been suggested that the oxidation resistance of a molybdenum article can be increased, while still preserving its high strength properties, by depositing certain metals, or metalloids on the surface of the molybdenum. Certain metals have the ability to form intermetallic compounds with the molybdenum surface and these intermetallic compounds have been found to be very corrosion-resistant. Typical of the coating materials are elements such as silicon, aluminum, and zirconium. The intermetallic compounds formed between these elements and molybdenum form an integral bond with the molybdenum surface. When the molybdenum body is provided with such intermetallic compound corrosion-resistant layers, the coated molybdenum body can withstand thousands of hours of operation above temperatures

of red heat without showing any evidence of oxidation of the molybdenum base.

While the above described oxidation resisting coatings very effectively protect the surface of the refractory metal from oxidation, they are subject to the disadvantage that the intermetallic compounds formed at the surface of the refractory body are quite brittle, and liable to failure due to impact. Such impact could result during the operation of gas turbine engines in aircraft due to the presence of foreign objects, even small particles, in the gas streams of the engine. These foreign objects may be received from the outside air, or may result from chipping of the combustion tubes, or from a number of other sources. These particles pass through the turbine at extremely high velocities, on the order of several hundred feet a second. When the objects strike the coated turbine blade, fracture of the coated surface often results, thereby exposing the refractory metal body to the corrosive atmosphere of the gas stream.

In the present invention, brittle, corrosion-resistant articles are provided with an impact resistant coating comprising a ductile nickel-chromium alloy, preferably containing boron, the coating being integrally bonded to the underlying brittle, corrosion-resistant surface, or alternatively, directly bonded to a molbdenum surface.

An object of the present invention is to provide a corrosion and impact-resistant article having the ability to withstand corrosive atmospheres normally present in gas turbine engines, and being resistant to fracture by high velocity particles in the gas stream.

Another object of the present invention is to provide an impact-resistant coating for refractory metal bodies which have a surface of brittle, corrosion-resistant material.

Still another object of the present invention is to provide a coated refractory metal suitable for use in manufacture of parts for turbo-jet engines, and the like.

Another object of the present invention is to provide a method for bonding an impact-resistant alloy layer onto the brittle surface of a corrosion-resistant article.

The present invention is concerned with providing brittle, corrosion-resistant surfaces such as molybdenum disilicide or molybdenum metal itself with an impact-resistant coating containing a nickel-chromium alloy. In a preferred embodiment of the invention, boron is included in the nickel-chromium alloy to lower the melting point and reduce the surface tension of the alloy thereby increasing its fluidity and free flowing characteristics. Such coatings have been found to be extremely resistant to impact and serve to protect the underlying corrosion resisting layer from fracture by high velocity particles.

The brittle, corrosion-resistant surfaces can be applied to the molybdenum or tungsten base in a variety of methods which involve no part of the instant invention. For example, the preferred method of coating molybdenum with silicon involves the deposition of silicon in vapor phase on a heated molybdenum body maintained at a temperature between about 1600° F. and 2300° F. in an atmosphere of hydrogen. The silicon may be introduced in the reaction chamber in the form of vaporized silicon tetrachloride, which decomposes under the condition in the reaction zone to yield free silicon. The liberated silicon readily combines with the surfaces of molybdenum to form intermetallic layers of molybdenum-silicon compounds. Coated molybdenum articles produced according to this process evidence a silicon concentration gradient at the surfaces thereof. For example, an intermetallic layer is ordinarily produced next to the molybdenum base metal consisting primarily of molybdenum-silicon compounds which have relatively low concentration of silicon, such as molybdenum monosilicide. The next layer overlying the molybdenum monosilicide layer contains molybdenum-silicon com-

pounds having higher silicon concentrations such as molybdenum disilicide. It is the molybdenum disilicide layer which is believed to contribute the most effective corrosion resistance to the article and it is this layer that needs to be protected against fracture by impact. However, the coating alloy of this invention has substantial corrosion resistance, and can be applied directly to a molybdenum article without the intermediate layer.

The nickel-chromium alloy which is used to provide the impact-resistant coating may contain varying amounts of nickel and chromium and preferably includes at least a small percentage of boron.

The following table illustrates the range of composition of the alloys which may be employed in the practice of the present invention and two specific alloy compositions:

Element	Range	Typical	
Mn	1.0 max.	0.01	0.01
Si	0.5 to 5	4.54	0.80
Fe	1.0 to 5.5	5.02	1.05
Cr	8 to 20	14.82	18.17
B	1.0 to 8.0	4.53	4.86
Ni	65 to 90	70.0	74.4
Zr	0.05 max.	0.01	0.01
Ca	0.20 max.	0.01	0.0
C	0.70 max.	0.68	0.24

The balance of the composition of the typical alloys listed consists of the usual impurities.

The amount of carbon in the alloy is an important consideration, as carbon tends to combine with chromium to form chromium carbide, thereby reducing the effective chromium content. The reduction in effective chromium content reduces the oxidation resistance of the alloy at high temperatures.

The silicon may be added as ferro-silicon, and serves to increase the high temperature resistance to oxidation.

Iron imparts fluidity to the alloy and renders it more workable. This metal may be added in the form of ferro-silicon, and it is also present in some of the other ingredients as an impurity.

The boron, as previously described, not only lowers the melting point of the alloy but increases the fluidity of the molten alloy by decreasing its surface tension.

Manganese occurs as an unavoidable impurity and lowers the high temperature resistance of the alloy. The first tenths of one percent are the most detrimental in this respect.

Calcium and zirconium are added to the alloy to act as deoxidizing agents. The more completely deoxidized the alloy is, the less susceptible it is to precipitation of oxides at the grain boundaries of the alloy. These two elements therefore serve to increase the high temperature resistance of the alloy.

Prior to coating the corrosion-resistant article with the nickel-chromium alloy it is very desirable to clean the surface of the molybdenum disilicide, or other corrosion-resistant coating to secure a better adhesion of the nickel-chromium alloy. This treatment can be carried out by first degreasing the article in a solvent such as trichloroethylene vapor. After degreasing, the surface of the coated molybdenum body is etched with a reagent capable of at least partially dissolving the silica, silicon and/or silicon rich phases present. One such reagent is an aqueous solution of hydrofluoric acid containing one part by volume of 40% to 50% hydrofluoric acid and two parts water. The article is etched for a period from 20 to 120 seconds, with 40 seconds being suitable for most purposes. The molybdenum disilicide surface is thereby rendered more receptive to the subsequently applied nickel-chromium alloy layer.

The process of applying the coating consists in liquifying the nickel-chromium alloy and spraying the liquified alloy onto the surface of the article. For most applications, the thickness of this coating is preferably on the order of 0.007 inch, but may extend within the range of about 0.002 inch to 0.020 inch, or even higher. Alternatively, the powdered alloy may be suspended in a liquid vehicle and sprayed on the surfaces to be coated.

After spraying, the coated article is then heated in a non-oxidizing atmosphere to braze the coating onto the corrosion-resistant surface. This brazing operation may be carried out in a dry hydrogen atmosphere, or under vacuum conditions, for a period up to 120 minutes at temperatures from about 1800° to 2300° F.

Other methods for applying the coating include dipping the article to be coated in a molten alloy bath, spraying the powdered alloy through a hot flame, or feeding the alloy as a rod into a flame and spraying the surface with the liquified metal.

The attached sheet of drawings illustrates more specifically the structure of a coated molybdenum body produced in accordance with the present invention.

In the drawings:

Figure 1 is a view in elevation of a turbine bucket provided with a coating according to the present invention;

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

Figure 3 is a view similar to Figure 2 and illustrates the effect produced when the coated article is struck with a high velocity particle.

As shown on 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 a turbine wheel.

As illustrated in the greatly enlarged view of Figure 2, the bucket **10** consists of a body of molybdenum metal **13** having a siliconized corrosion-resistant outer surface. The surface nearest the molybdenum body, designated at **14**, contains intermetallic compounds of molybdenum and silicon having a relatively low percentage of silicon, such as molybdenum monosilicide. The next adjoining layer **15** contains relatively brittle crystals of compounds containing higher percentages of silicon, such as molybdenum disilicide.

The outermost layer which provides the impact resistance to the molybdenum disilicide layer **15** consists of a nickel-chromium alloy containing boron, as previously described. This layer has been designated generally at numeral **16**. In operation, the nickel-chromium layer will be subjected to oxidation with the formation of a thin oxide film **17** which further aids in preventing diffusion of oxygen into the inner layers of the body.

Figure 3 illustrates the condition where the structure of Figure 2 is struck with a high velocity particle. The nickel-chromium layer **16** is sufficiently tough so that the impact does not break the continuous coating, but results merely in the formation of an indentation **18**, thereby preserving the corrosion-resistant properties of the underlying layers.

The impact resistance of articles produced in accordance with the present invention was tested by striking a molybdenum disilicide coated molybdenum body protected by a nickel-chromium alloy of the type herein disclosed with steel pellets at a velocity in excess of 330 ft. per second. Four such pellets were caused to strike a specimen 0.094 inch thick at points one quarter of an inch apart. The series of four pellets dented the coating, but did not fracture the same. After this ballistics test, the specimen was subjected to oxidation at a temperature of 1600° F. without evidence of failure.

From the foregoing it will be appreciated that we have herein provided a novel type of corrosion and impact resistant material particularly suited for use in the manufacture of parts for jet engines. The impact-resistant coatings have the ability to become securely bonded to molybdenum or brittle corrosion-resistant layers contain-

ing molybdenum and serve as a very effective shock absorbing layer for the underlying surfaces. The coatings can be applied to selected surface areas of a turbine bucket; or the entire bucket, including the airfoil and root portions, may be coated.

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:

1. An impact and corrosion resistant turbine bucket comprising a base of molybdenum metal and an impact resistant coating overlying and bonded to said molybdenum base, said coating comprising a nickel-chromium alloy consisting essentially of from about 65 to 90% nickel, from about 8 to 20% chromium, from about 1.0 to 8.0% boron with the balance consisting essentially of iron and silicon, said coating being capable of withstanding mechanical shock without fracturing.

2. An impact and corrosion resistant turbine bucket comprising a base of molybdenum metal and an impact resistant coating overlying and bonded to said molybdenum base, said coating comprising a nickel-chromium alloy consisting essentially of from about 65 to 90% nickel, from about 8 to 20% chromium from about 1.0 to 8.0% boron, from about 1.0 to 5.5% iron and from about 0.5 to 5.0% silicon, said coating being capable of withstanding mechanical shock without fracturing.

3. An impact and corrosion resistant turbine bucket comprising a base of molybdenum metal and an impact resistant coating overlying and bonded to said molybdenum base, said coating comprising a nickel-chromium alloy consisting essentially of from about 65 to 90% nickel, from about 8 to 20% chromium, from about 1.0 to 8.0% boron, from about 1.0 to 5.5% iron, from about 0.5 to 5.0% silicon and less than 0.7% carbon, said coating being capable of withstanding mechanical shock without fracturing.

4. An impact and corrosion-resistant turbine bucket comprising a base of molybdenum metal, a corrosion-resistant coating of molybdenum disilicide bonded to said molybdenum base, and an impact-resistant coating bonded to and overlying said molybdenum disilicide coating, said impact-resistant coating consisting essentially of a nickel-chromium alloy consisting essentially of 65% to 90% nickel, 8 to 20% chromium, and from 1 to 8% boron with the balance substantially iron and silicon and capable of withstanding mechanical shock without fracturing.

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