Sept. 25, 1956 R. A. KEMPE ET AL 2,763,919

COATED REFRACTORY BODY

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Fig. 1

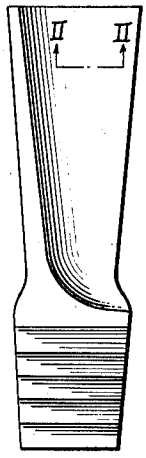


Fig. 2

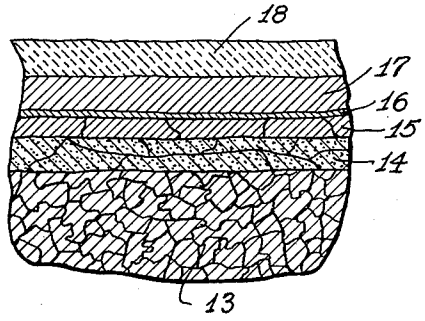


Fig. 3

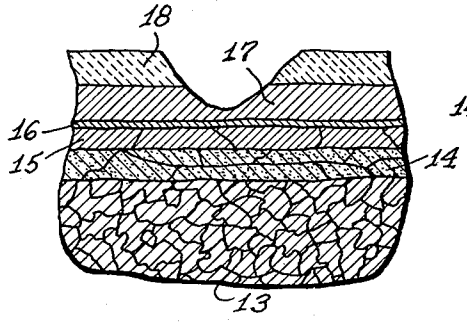
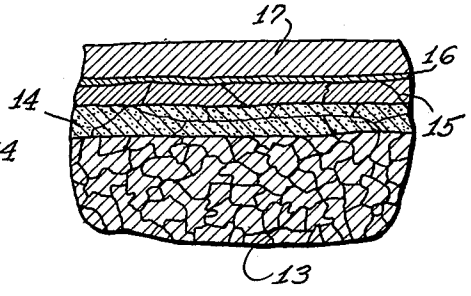


Fig. 4



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COATED REFRACTORY BODY

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1 Claim. (Cl. 29—195)

The present invention relates to a coated refractory metal article.

One important field in which the articles of the present invention find use is the manufacture of parts for turbo-jet engines and the like.

Turbo-jet engines are equipped with turbines operated by exhaust gases which drive an axial flow blower furnishing air to the burners. Such turbines operate at an extremely high temperature and one of the major difficulties encountered in the manufacture of turbo-jet turbines has been the provision of suitable material for turbine buckets which can withstand the effects of such high temperatures. A turbine bucket will normally be exposed to temperatures in excess of about 1600° F., and must have a high degree of strength, toughness, creep resistance, and resistance to the oxidizing gases present in the turbine engine.

Articles produced by 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 molybdenum is quite poor. Although the metal 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 oxide formation increasing with the temperature. The oxide which is produced under these conditions sublimes, thus causing complete disintegration of the molybdenum in a relatively short time.

In a newly developed process, it has been suggested that the oxidation resistance of a molydenum article can be increased, while still preserving its hot strength properties, by depositing certain metals, or metalloids on the surface of the molybdenum to cause the formation of intermetallic compounds. Typical of the coating materials are elements such as silicon, aluminum, and zirconium. The intermetallic compounds formed between the aforementioned metals, or metalloids, and molybdenum form an integral bond with the molybdenum surface and have been found to make the molybdenum substantially corrosion-resistant. For example, when a molybdenum turbine bucket is reacted with silicon to form an intermetallic compound layer containing molybdenum disilicide at the molybdenum surface, the coated molybdenum body can withstand thousands of hours of operation above temperatures of red heat without showing any evidence of oxidation of the base metal.

While the above described oxidation resisting coatings very efficiently protect the surface of the refractory metal from oxidation, they have the disadvantage that the intermetallic compounds formed at the surface of the refractory body are quite brittle, and very 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 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 foreign objects pass through the turbine at extremely high velocities, on the order of several hundred feet a second. As the objects strike the coated turbine blade, they have been found to cause fractures of the coated surface, thereby exposing the refractory metal body to the corrosive atmosphere of the turbine engine.

Another object of the present invention is to provide corrosion-resistant articles for use in parts for jet engines and the like provided with an impact-resistant surface.

Still another of the present invention is to provide gas turbine buckets having a high degree of corrosion resistance.

In general, the process of the present invention involves protecting the brittle corrosion-resistant surface of a coated refractory metal by providing a coating of a tough, ductile metal over the brittle corrosion-resistant surface, the ductile metal having the capacity to absorb impact due to high velocity particles to protect the brittle corrosion-resistant layer.

The brittle, corrosion-resistant surfaces can be applied to molybdenum or tungsten bodies through a variety of methods and such coating procedures 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 into the reaction chamber in the form of vaporized silicon tetrachloride, which decomposes under the condition in the reaction zone to yield free silicon. The latter readily combines with the surfaces of molybdenum to form intermetallic layers of molybdenum-silicon compounds.

A ductile tough metal, such as molybdenum, or chromium, or a metal of the iron group, such as iron or nickel or cobalt may then be deposited upon the corrosion-resistant surface. However, in order to secure a better adhesion between the ductile metal and the hard, brittle surface of the coated molybdenum article, it is preferable to prepare the surface of the molybdenum article for the deposition of the ductile metal. This type of treatment can be carried out in a variety of manners. For example, in one embodiment of the invention, the molybdenum disilicide is first degreased in a degreasing solvent, such as trichlorethylene vapor. After the degreasing operation, the surface of the metal is etched with a reagent capable of at least partially dissolving an extremely minute layer of silicon or silica which normally appears on the molybdenum disilicide surface. One such reagent is an aqueous solution of hydrofluoric acid containing one part hydrofluoric acid and two parts water. The article is etched for a period of from 20 to 120 seconds, with 40 seconds being suitable for most purposes. The molybdenum disilicide surface is thereby rendered more porous and receptive to the subsequently applied ductile metal coating.

In place of, or in addition to, the etching procedure described above, the surface of the molybdenum disilicide can be treated for the reception of the ductile metal coating by applying thereto various materials capable of forming an adherent surface with the ductile metal. This adherent layer can take a variety of forms, for example, it may consist of a thin electrodeposited flash of iron, nickel, or chromium, or it may suitably be composed of a ceramic material such as a vitrified mixture of alkaline earth aluminum silicates. Suitable ad-

herent layers have also been produced by spraying boric oxide compositions or metallic molybdenum onto the molybdenum disilicide layer.

After preparing the molybdenum disilicide surface for the reception of the ductile metal coating, the article is next given a coating of a ductile metal such as molybdenum, chromium, or a metal of the iron group, to a sufficient thickness to withstand adequately the conditions of impact present in the operation of the gas turbine engine.

A ductile layer can be deposited over the previously prepared surface in a variety of processes. Metals of the iron group and chromium can be electrodeposited through ordinary electroplating operations on the prepared surface. For example, a suitable ductile layer can be produced by electroplating soft chromium to a thickness of about 0.003 inch on the surface of the body. Chromium metal is a particularly desirable metal for use in the ductile layer since its coefficient of expansion is very close to that of molybdenum, and also, since the chromium deposit oxidizes under the conditions of operation of the turbine bucket to produce a dense oxide film, thereby functioning as its own corrosion protecting agent.

Molybdenum metal may also be employed as the ductile layer for the purpose of the invention. It is difficult to electroplate molybdenum to any substantial thickness, so that where molybdenum is used, it is usually necessary to spray the molybdenum coating over the object by ordinary metalizing procedures.

The thickness of the ductile metal coating is preferably on the order of 0.003 inch, but may extend within the range of about 0.001 inch to 0.030 inch or even higher.

In most instances, it is desirable to protect the ductile metal layer itself from oxidation and corrosion. While in the case where chromium is used as a ductile metal, this modification is not particularly necessary, it is necessary when using molybdenum as the ductile metal coating, due to the rapidity with which the molybdenum oxidizes.

A preferred corrosion resistant coating in accordance with the present invention is a vitrified mixture of alkaline earth aluminum silicates. Such a mixture can suitably contain about 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, and 1 to 10% boric oxide. Coatings produced from the above mentioned compositions have thermal shock resistance, and are impervious to oxygen and oxidizing gases. In addition, their coefficient of thermal expansion is very nearly that of the refractory base metal. Even more important, the ceramic compositions of the type indicated are nonvolatile at the operating temperature of the turbine engine and maintain a good bond to the underlying metal. It has been found that the volatility of the ceramic compositions is very substantially reduced by elimination therefrom of alkali metal compounds which tend to volatilize at the operating temperature. To reduce the firing temperature of the glass-like coating, minor amounts of compounds such as calcium fluoride, barium oxide and lithium oxide may be added.

To increase the viscosity of the glass, a small amount of zirconium oxide may also be added. Some zirconium goes into the solution in the glass and serves to increase the toughness and hardness thereof. Zirconium oxide also increases the refractoriness and lowers the coefficient of expansion of the glass, thus providing an improved fit between the coating and the base.

The procedure in applying the ceramic coating consists first of weighing and mixing the ingredients of the glass composition, and melting the batch at a temperature from about 2500 to 2700° F. Next, the glass composition is fritted by pouring the molten mass into a water bath. The glass is ground while wet in a ball mill or the like to a particle size of approximately 200 mesh, and thereafter dried. Next, suitable mill additions which may include refractory oxides, preferably containing zirconium oxide, together with binders and setting up agents are mixed with the fritted glass. Typical mill additions which may be included are the various clays, such as enamelers' clay, bentonite, montmorillonite, Florida kaolin and the like. In addition, metallic compounds, such as chromium oxide, zinc oxide, cobalt oxide, nickel oxide, strontium oxide, iron oxide, manganese dioxide, calcium chloride and barium oxide may be added.

The preferred setting up agent is methyl cellulose, since this agent has been found to increase the green film strength and reduce the tearing of the coat during firing.

The mixture of mill additions and fritted glass may be applied to the ductile metal layer by means of a spray gun to any desired thickness. After application of the coating, the article is transferred to a furnace where the coating is vitrified at temperatures which may suitably be in the range from 1700 to 1900° F. Ordinarily the baking may be continued until a vitrified coating of from 0.002 inch to 0.005 is obtained.

Articles coated with the type of ceramic composition described above exhibit a high degree of thermal shock resistance and may be re-heated to red heat and water quenched without destroying the coating.

The coatings are also extremely resistant to oxygen and prevent passage of oxidizing gas into the base metal. The coefficient of thermal expansion of the ceramic coating is somewhat less than that of the refractory metal base, so that a compression fit between the coating and the metal base is effected under operating conditions.

Several of the articles produced in accordance with the practice of the present invention have been illustrated in the drawings in which:

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 line II—II of Figure 1;

Figure 3 is a view similar to Figure 2 and illustrates the effect of shattering the exterior ceramic coating of the article by a high velocity particle; and

Figure 4 is a fragmentary cross-sectional view, highly magnified, of another structure which can be produced according to the present invention.

As shown on the drawings:

Figure 1 illustrates a conventional turbine bucket **10** consisting of a blade portion **11** and fir-tree root portion **12** for securing the bucket **10** in a turbine wheel.

As illustrated in Figure 2, the bucket **10** consists of a body of molybdenum metal **13** which is provided with a siliconized corrosion-resistant surface. The surface nearest the molybdenum body will contain intermetallic compounds of molybdenum and silicon having a low silicon content and usually consists of a layer **14** of crystals composed of molybdenum monosilicide.

The next crystal layer **15** contains intermetallic compounds of molybdenum and silicon having a relatively higher proportion of silicon, and usually includes a large percentage of the hard, brittle disilicide.

In accordance with the present invention, the layer **15** of molybdenum disilicide is provided with a thin adherent coating **16** of a metal such as molybdenum, chromium, or a metal of the iron group. As previously explained, the layer **15** of molybdenum disilicide may be etched with a reagent such as hydrofluoric acid to render it more receptive to the subsequent coating and the adherent layer **16** under those circumstances may be eliminated. Alternatively, both an etching process and a coating process may be employed.

The next layer **17** consists of a ductile, tough metal such as molybdenum, chromium, iron, or nickel capable of absorbing the shock occasioned by impact of the blade portion **11** with foreign particles. The exterior coating **18** preferably consists of a ceramic material containing

vitrified alkaline earth silicates of the type described previously.

The effect occurring when a high velocity particle strikes the composite body illustrated in Figure 2 is illustrated in Figure 3. If the velocity of the foreign particle is sufficiently high, it may penetrate the ceramic coating **18**, and impinge upon the ductile metal coating **17**. The ductile layer **17** is sufficiently tough and ductile so that extremely high velocity particles will be unable to penetrate this layer, the ductile layer **17** is thereby able to protect the relatively brittle molybdenum disilicide layer **15** against impact.

Figure 4 represents a somewhat modified structure of a turbine bucket in which the ceramic coating has been eliminated. The structure shown in Figure 4 includes a molybdenum body metal **13**, the layer **14** of crystalline molybdenum metal silicide, the layer **15** of molybdenum disilicide, a thin coating **16** of adherent material such as vitrified ceramics, boric oxide, molybdenum, or electrodeposited metals of the iron group, and the exterior layer **17** consists of soft electrodeposited chromium. Under operating conditions, the layer **17** will have a surface film of chromium oxide thereon protecting the remainder of the ductile chromium from oxidation.

From the foregoing, it will be evident that we have herein provided a novel method for increasing the impact resistance of brittle corrosion-resistant coatings. Articles provided with coatings of the present invention have been found able to withstand the conditions of high temperature and corrosion present in turbine engines for extended periods of time without failure.

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 adapted to withstand high stresses and impacts in high temperature corrosive atmospheres comprising, a strong, tough, creep-resisting refractory base metal article composed of metals selected from the group consisting of molybdenum and tungsten, a hard brittle oxidation-resisting coating selected from the group consisting of silicon, aluminum and zirconium and containing intermetallic compounds of said base metal and the coating bonded to said article, a ductile metal anchoring coating on said hard brittle coating selected from the group consisting of iron, nickel and, chromium, a ductile metal coating on said anchoring coating selected from the group consisting of molybdenum, chromium, iron, nickel and cobalt, and a vitrified ceramic oxygen-impervious coating covering said ductile coating.

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