

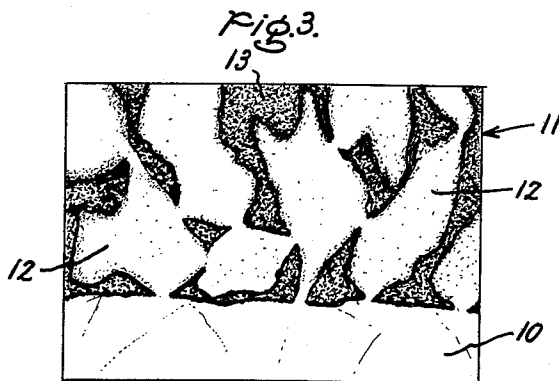
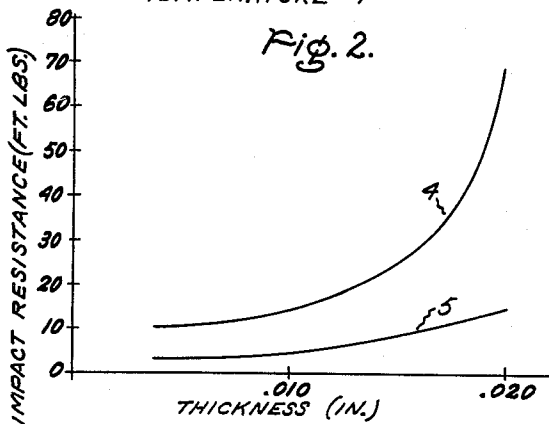
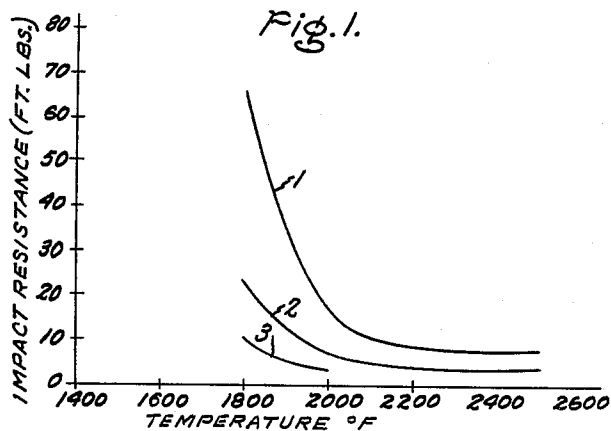
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SELF-REPAIRING COATINGS FOR METAL

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SELF-REPAIRING COATINGS FOR METAL

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This invention relates to the provision of protective coatings for structural components for use at elevated temperatures in reactive atmospheres, and more particularly to coatings containing a liquid phase rendering the coating self-repairing during use.

This application is a continuation-in-part of applicants' co-pending application, Serial No. 665,264, filed June 12, 1957, now abandoned and assigned to the same assignee as the present application.

Metals and metal alloys, retaining to a great degree their strength to elevated temperatures, have found greatly increased usage in recent years due to the development of equipment utilizing higher temperatures. For example, molybdenum and alloys in which molybdenum is the principal constituent, are known to have high strength at elevated temperatures and, except for the fact that these materials are subject to drastic corrosion or oxidation when exposed to oxidizing atmospheres at temperatures over about 1400° F., would be excellent as structural materials for the fabrication of components subjected to high temperature and high stress in gas turbine applications. Similarly, materials such as columbium, tantalum, zirconium, tungsten and chromium have also been proposed for use at high temperatures in oxidizing atmospheres but have generally required some type of protective coating to enable such use.

Many different coating materials have been applied to the various base metals in an attempt to prevent high temperature oxidation, but, while it has been found a relatively easy matter to provide stable, continuous coatings which exclude oxygen for long periods of time under static conditions, similar success has not been met in providing stable coatings where the bodies are flexed or otherwise subjected to oscillatory loads producing reversing stresses. Thus, these previously-known coatings have been effective for only brief periods of time. Furthermore, in applications such as gas turbines where the coated articles are subjected to the action of solid particles carried by the gas stream, the surfaces of the articles are impinged upon with sufficient force that the coating is either almost immediately ruptured, permitting access of the oxidizing atmosphere to the substrate and its consequent rapid corrosion and failure, or the coating is gradually eroded or braded by repeated impingements resulting in loss of coating and consequent destruction by oxidation of the article.

It is therefore a principal object of this invention to provide stable, adherent coatings for articles made of metals for use at elevated temperatures, which coatings resist oxidation and penetration of oxidizing atmospheres for long periods of time at elevated temperatures.

A further object of this invention is to provide articles constructed of metals for use at elevated temperatures having corrosion- and erosion-resistant coatings which are self-repairing during use.

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

In the drawings,

FIG. 1 is a graphical representation of the results of impact tests performed upon several molybdenum bodies coated in accordance with the present invention at various elevated temperatures;

FIG. 2 is a graphical representation of the relationship

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between the thickness of the applied coating and impact resistance at elevated temperatures; and

FIG. 3 is a schematic showing of a porous coating as applied to a metal body according to the present invention.

The present invention is predicated upon the discovery that under certain circumstances a corrosion and abrasion resistant, tightly adherent, porous covering layer or coating, having marked liquid phase retaining ability, can be provided on metal bodies. It is further based upon the discovery that there are special alloys which have the ability in the liquid phase of reacting with the substrate or matrix metal to form additional coating material thereby healing fractured or broken parts of the coating network to provide self-repair under high temperature operating conditions. It is a special feature of this invention that all essential parts of this network are contacted with the healing alloy and repairs thus are made automatically and immediately as the necessity arises, but without the loss of the healing or repairing liquid alloy due to centrifugal force or similar action incident to the use of the said refractory body.

Briefly stated, the present invention concerns the application of protective coatings to metals and alloys of metals such as molybdenum, chromium, columbium, tantalum, zirconium and tungsten, which protective coatings consist of an intermetallic compound of the base metal with a suitable reactive material and which contain a liquid phase containing a sufficient amount of the reactive material to heal or repair any cracks or other defects which occur in the coating during its normal usage.

In approaching the problem of selecting the proper materials to form coatings acceptable for use on the base materials mentioned in the preceding paragraph, several considerations must be kept in mind. The principal considerations which have to be considered in providing a coating for any selected basis metal are: (1) a corrosion resistant and impermeable intermetallic compound of the basis metal must be selected; (2) a method of applying a porous layer of the intermetallic compound on the surface of the basis metal must be obtained; and (3) a suitable liquid phase rendering the coating self-repairing must also be developed.

With particular regard to the alloy forming the liquid phase, several additional conditions must also be met. First of all, the material selected as the liquid phase must melt at a temperature below that at which it is desired to use the final article. Obviously, if the protective liquid material is in fact not liquid at the operating temperature, where protection of the substrate metal is desired, then the self-repairing properties will be greatly reduced. An additional factor is that the material making up part of the alloy phase of the molten material must be capable of dissolving enough of the material reactive with the basis metal to provide sufficient material to combine with the basis metal and form the self-repairing coating.

Another factor is that the alloy containing the reactive material must not dissolve the basis metal or, of course, destruction of the basis metal will result from the would-be protective coating. A factor which is allied with the destruction by the liquid phase of the basis metal is that of solubility of the coating material in the basis metal. If one or parts of the liquid phase are soluble in the basis metal, then no adequate, protective coating can be obtained.

Finally, it is apparent that if the coating is indeed protective, then it must be resistant to corrosion and impermeable to the passage of corroding gases there-through, as well as have sufficient resistance to erosion caused by impinging particles carried in the passing fluid streams.

Considering a specific problem which has been overcome by the present invention, previous attempts to provide buckets or blades for use in gas turbine engines with protective coatings have revealed three important sources of coating failure, namely, cracks which develop as the result of repeated thermal shocking of the coated bucket, overheating of the bucket, and impact damage caused by the impingement of solid particles entrained in the gas stream.

The most frequently occurring coating failure in previously known coated buckets has had its origin in thermal stresses resulting from rapid temperature changes and the relatively large difference in the thermal coefficient of expansion of the substrate metal and the coating. Under repeated rapid thermal cycling, i.e., alternately raising and lowering the temperature of the bucket producing thermal shocks, fatigue cracks develop in the coating, permitting oxidation of the substrate metal.

Where the previously known coatings have been secured to the substrate with a brazing alloy or the like having a melting point only a few hundred degrees above the normal operating temperature of the bucket, temporary overheating of the bucket has caused this relatively low melting point material to fail under stress, permitting the coating to become separated from the bucket and has resulted in subsequent bucket failure.

As is well known, in the actual operation of gas turbine engines, small particles of dust, sand, gravel, and even larger metallic objects, such as nuts and bolts, can be drawn into the air intake and entrained in the rapidly flowing gas stream, and propelled at high speeds through the engine. While it is possible to prevent intake of larger particles, or if actually ingested, to prevent them from reaching the turbine stage of the engine, it is not always practical and, in addition, no satisfactory solution is known for preventing the smaller particles from striking and abrading the rapidly moving, hot turbine buckets. With previously known coatings, some of these particles have had sufficiently high energy, relative to the bucket, to penetrate through the coating, permitting oxidation and resulting in failure of the bucket.

To prepare a composite body according to the present invention, the normal procedure is to select the desired material, which is generally one of the metals such as columbium, tantalum, molybdenum, zirconium, tungsten or chromium, or alloys of these metals in which the combined amounts of such metals is not less than about 70 weight percent, although the amount of any one of the metals constituting a part of an alloy can be substantially less than 50 weight percent. Additionally, metal other than those specifically mentioned may also be used. A quantity of powdered metal, usually the same as the basis metal although not necessarily, is then compacted into a porous structure and sintered on the substrate body so that pores of capillary size remain to retain a liquid phase alloy which is subsequently infused thereinto.

Once the porous outer layer is properly in position, the article is impregnated with a quantity of an alloy containing a sufficient amount of a material reactive with the sintered powder and with the substrate to react therewith and change the porous layer into a protective intermetallic compound. Reaction also takes place with any exposed basis metal with the formation of a protective intermetallic layer. Generally, some of the reactive materials which may be dissolved in the alloy are silicon, aluminum, boron, germanium, beryllium and carbon. The selection of the particular material used will depend upon the exact basis and porous metals chosen and will be determined in view of the considerations set forth earlier in the specification.

These intermetallics have excellent resistance to both corrosion and erosion which renders them capable of withstanding the conditions normally present in gas turbines, for example, and similar apparatus. After the reaction

of the alloy with the sintered powder material has taken place, there should be enough of the alloy remaining in the pores to provide excess reactive material to repair any breaks or cracks which may later occur in the coating as a result of thermal or mechanical stress cycling.

Considering a particular example of the invention as applied to a molybdenum base, the substrate should consist of at least 70 weight percent molybdenum. It has been found that a suitable alloy for infusing the pores of the sintered molybdenum layer on the outer surface of the substrate consists of gold containing from about 1.0 to 30 weight percent silicon. The thickness and degree of porosity of the porous molybdenum coating in which the gold-silicon alloy is to be infiltrated depends upon the operating conditions to which it is to be subjected. In general, however, thicknesses of from about 0.005 to 0.050 inch and having a porosity of from 50 to 75 volume percent molybdenum and 50 to 25 volume percent porosity, respectively, are desirable for most applications. It will be appreciated, therefore, that these coatings, involving the porous molybdenum or molybdenum-rich alloy sintered layer and the gold alloy infiltrated therein, are composed in gross of from about 20 weight percent silicon, 50 percent gold, and the remainder substantially all molybdenum when a 1.0 percent silicon-gold alloy is infiltrated into a porous molybdenum coating having 50 percent porosity by volume; about 30 weight percent silicon, 25 weight percent gold, and the remainder substantially all molybdenum when the same alloy is infiltrated into a 25 percent by volume porosity molybdenum coating; about 35 weight percent silicon, 20 percent gold, and the remainder substantially all molybdenum when a 30 percent silicon-gold alloy is infiltrated into a 50 percent by volume porosity molybdenum coating; and about 40 weight percent silicon, 8 percent gold, and the remainder substantially all molybdenum when a 30 percent silicon-gold alloy is infiltrated into a 25 percent by volume porosity molybdenum coating.

In the practice of the invention, a molybdenum or molybdenum-rich alloy article is provided with a porous coating of molybdenum or molybdenum-rich powder sintered in place on its surface. The coated article is then immersed in a molten bath of an alloy consisting essentially of at least 1.0 weight percent silicon and the remainder substantially all gold. The gold-silicon alloy must contain at least about 1.0 weight percent silicon in order that molybdenum disilicide may be formed as the product of the reaction which occurs between the molybdenum comprising the sintered porous coating and the alloy. If a smaller amount of silicon is present in the molten alloy, other molybdenum silicides are formed which are not oxidation resistant at temperatures of about 2200° F. and higher. Gold alloys containing amounts of silicon greater than 1.0 percent are desirable and such alloys containing as much as about 30 weight percent silicon or more may be used, depending upon the operating temperature to be employed.

As is well known, the binary alloys of gold and silicon form a simple eutectic system. The gold-silicon eutectic melts at about 698° F. and the liquidus, or temperature at which these alloys become completely molten, decreases from the melting point of pure gold, 1945° F., as a smooth curve to 698° F. at the eutectic composition, 94 percent gold and 6 percent silicon. As the silicon content is increased, the liquidus increases as a curve having a progressively decreasing slope from 698° F. to become substantially constant at about 2552° F. at an alloy containing about 80 percent silicon, and at 100 percent silicon, of course, is the melting point of silicon, i.e., about 2590° F. As will be appreciated, all the alloys comprising this system are completely molten at temperatures at and above the liquidus temperature. Alloys containing less than 6 percent silicon are composed of a liquid phase and an alpha phase solid solution between 698° F. and the liquidus temperature, and alloys containing more

than 6 percent silicon are composed of a liquid phase and silicon in the solid state between 698° F. and the liquidus temperature. At temperatures below the eutectic temperature, i.e., 698° F., all gold-silicon binary alloys are completely solid and composed of an alpha solid solution and silicon.

As already mentioned, when the coated molybdenum article is immersed in the completely molten gold-silicon alloy, the silicon in the alloy reacts with the molybdenum in the porous coating to form a porous coating of molybdenum disilicide, the molten gold-silicon alloy filling and being retained within the pores and interstices and covering the outer surface of the porous coating. This molten gold-silicon alloy wets the surfaces and pores of the coating and serves as a reservoir of liquid containing silicon which is available to react with molybdenum surfaces which may be subsequently exposed by the rupture of the molybdenum disilicide coating to form a new layer of molybdenum disilicide at the point of rupture. Molybdenum disilicide is quite resistant to oxidation at elevated temperatures and, further, is quite hard, although alone is somewhat brittle. The gold-silicon alloy above its melting point is held in the porous molybdenum disilicide coating by capillary attraction and at the elevated temperatures contemplated is stable and, since it is liquid, is not liable to rupture by thermal stresses. In fact, if such thermal stresses tend to form cracks in the molybdenum disilicide, the molten gold alloy appears to immediately fill them and the silicon is available to repair the defect by forming a new protective layer of the disilicide.

Since the operating temperature range of such coated molybdenum bodies is contemplated to lie between about 1480° F., the temperature at which unprotected molybdenum and molybdenum-rich alloys begin to oxidize in a catastrophic manner, and temperatures as high as about 2500° F., and since the gold-silicon alloy employed should have a major portion in the liquid phase at the particular operating temperature, it will be apparent that the alloys of our invention should contain from at least 1.0 to about 30 percent silicon and preferably from 1.0 to about 20 percent silicon, the remainder substantially all gold. These alloys are useful in this temperature range since the liquidus for these alloys is about 1830° F. for 1.0 percent silicon, about 1650° F. for 2.0 percent silicon, about 1115° F. for 5.0 percent silicon, about 698° F. for 6.0 percent silicon, about 1115° F. for 7.5 percent silicon, about 1470° F. for 10 percent silicon, about 1870° F. for 15 percent silicon, about 2070° F. for 20 percent silicon, and about 2300° F. for 30 percent silicon. If higher operating temperatures are contemplated, then, of course, the silicon content may be increased commensurately.

The following specific examples have been selected to illustrate how such an alloy containing even a relatively small amount of silicon present in gold may be successfully employed with the sintered porous molybdenum coating to protect molybdenum articles at high temperatures as shown by the various test results set forth.

A number of molybdenum articles were produced with a porous coating by dipping the articles in a slurry of molybdenum powder with an average particle size of 2 to 4 microns suspended in water. This slurry may consist of from about 50 to 120 grams of this powder suspended in about 15 cc. of water. The articles were dried and the thickness of the powder layer deposited thereon was built up by successive dipping and drying steps until the desired thicknesses were obtained. For example, using such a suspension, 3 to 5 dipping and intervening drying steps were needed to form a coating about 0.020 inch in thickness. The coated articles were then fired at about 2550° F. in a protective atmosphere and permitted to cool in the atmosphere to cause the molybdenum powder to sinter into a porous layer firmly attached to the basis metal. It was found that the resulting porous layer con-

sisted of about 60 volume percent molybdenum and 40 volume percent porosity. It will, of course, be immediately apparent to those skilled in the art that variations in powder particle size, temperature of sintering and other variables may be employed to control the porosity, strength and firmness of attachment of the porous layer to the substrate and that other means may be employed to prepare the porous layer. Furthermore, while the particular articles disclosed herein were composed of substantially pure molybdenum coated with substantially pure molybdenum powder, it will be obvious that a coating prepared from powdered molybdenum-rich alloy may be applied to either a substantially pure molybdenum substrate or to a molybdenum-rich alloy substrate and powdered substantially pure molybdenum may be applied to a molybdenum-rich alloy substrate in the same manner with equal facility.

The porous surface layers of these articles were then infiltrated with a gold base alloy containing about 1.5 weight percent silicon. This alloy begins to melt at about 700° F. and is completely molten at 1650° F. The gold-silicon alloy was melted and the articles dipped into the melt. It was found that all the pores of the coating were rapidly filled and that the molybdenum in the porous coating reacted with the alloy to form molybdenum disilicide. Because an essentially infinite silicon source (the melt) was used, the gold-silicon alloy in the pores was approximately 1.5 percent silicon after reaction and impregnation were completed. These coated articles were then subjected to a number of tests, examples of which are hereinafter set forth.

A number of molybdenum panels $\frac{5}{8}$ inch square and 0.100 inch thick were provided with porous coatings of sintered molybdenum powder about 0.005 inch, 0.010 inch, 0.015 inch and 0.020 inch in thickness and impregnated with the 1.5 percent silicon-gold alloy as previously set forth.

One such specimen having a sintered porous coating 0.010 inch thick was, after impregnation, subjected to a temperature of 2500° F. in a flowing air atmosphere for 1000 hours without failure of the coating. Periodically during this heating, the specimen was removed from the furnace and cooled to room temperature in order to weigh and inspect the coating, after which the specimen was reheated by placing it directly in the hot zone of the furnace. This thermal cycling was performed 20 times during the test.

This specimen was then heated at one end with a gas-oxygen torch to 2500° F. The heated end of the specimen was held at 2500° F. for five seconds and then quenched in a stream of water to room temperature. This heating and quenching cycle was repeated for 55 cycles before failure occurred in the coating. During this thermal cycle, the heating rate was about 120° F. per second and the cooling rate about 140° F. per second. Another substantially identical but freshly prepared coated specimen withstood 88 cycles under the same test conditions.

Referring to FIG. 3 of the drawings, numeral 10 represents a molybdenum body, or specimen, to which a coating 11, like that just described has been sintered. The coating 11 is integrally attached to the base 10 and is made up of the molybdenum disilicide porous matrix 12 which holds the gold-silicon alloy 13 by capillary attraction when the article is being used. Of course, the same structural arrangement is present when metals other than molybdenum are used.

The resistance of the coatings to impact was determined in the following manner. Coated specimens were heated to various elevated temperatures in air by a gas-oxygen torch and a projectile of known weight impelled against the heated surfaces thereof from a .22 caliber pistol. This pistol was powered by compressed gas so that the velocity and hence the energy of the projectile was closely controllable and readily determined. The projectile was

a .22 caliber lead slug which was provided with a hardened steel tip ground to a radius of $\frac{1}{32}$ inch at the front end. Since the pistol barrel was rifled, the projectile always struck the heated specimen with the steel tip and with the axis of the projectile perpendicular to the specimen's surface.

Specimens having coatings of three different thicknesses were tested in this manner: 0.005 inch, 0.015 inch and 0.020 inch, and at three different temperatures, 1800° F., 2000° F., and 2500° F. The highest projectile energy which did not cause penetration through the coating has been plotted in FIG. 1 with impact resistance in foot pounds as the axis of ordinates and the temperature in degrees F. as the axis of abscissas. Curve 1 represents the highest projectile energies which did not cause the penetration of the specimens having the 0.020 inch thick coating at the various elevated temperatures, while curves 2 and 3 are similar plots for the specimens provided with 0.015 inch and 0.005 inch thick coatings, respectively.

In FIG. 2, this data has been plotted with impact resistance in foot pounds as the axis of ordinates and the coating thickness in inches for two temperatures, i.e., curve 4 for tests at 1800° F. and curve 5 for tests at 2000° F.

It will be seen from the foregoing that the coatings are oxidation resistant in oxidizing atmospheres, are thermally stable, and resist the diffusion of oxygen therethrough at temperatures at least as high as 2500° F. Further, that these coatings have a quite high resistance to impact at temperatures as high as 2500° F. and are not susceptible to failure from repeated thermal shocks.

Considering the application of the present invention with regard to another of the metals listed, specifically, zirconium, a zirconium body was dipped into a suspension of zirconium powder, amyl acetate and cellulose nitrate. One hundred grams of zirconium, 50 cc. of amyl acetate and 10 cc. of cellulose nitrate were used. It was found that the zirconium samples dipped into this slurry would acquire a layer of zirconium about 1 mil thick. The layer was dried and the sample redipped to build up the coating to an approximate thickness of about 0.015 inch. The coating thus applied to the body and the body were sintered in vacuum by heating the sample slowly to a sintering temperature of 1000° C. and holding this temperature for about 2 hours. Good adherence and no cracking of the porous structure thus obtained were observed. In this case, the alloy selected for infiltration of the pores of the outer coating was a silver-silicon bath consisting of 6.0 percent silicon and the remainder substantially all silver. The eutectic in this system is at 1472° F. so that reaction was effected at about 1600° F. It was found that the zirconium did not dissolve in the bath after 30 minutes but did react to form a surface layer consisting of zirconium disilicide.

It will be understood that the binary system of silver and silicon also possesses eutectic compositions similar to the gold-silicon alloy used on the molybdenum base bodies and that the temperature at which the zirconium body is to be used will play a major part in determining the specific amount of silicon which should be present in the bath. If the contemplated temperature of operation is high enough, then increased percentages of silicon can be used, whereas if lower temperatures are contemplated, then the silicon content can be lowered slightly, although to become molten, it will be necessary for the eutectic temperature to be reached.

The silver-silicon alloy used on the zirconium bodies was also used in the same compositional percentages on columbium, tungsten and chromium and was found to form a suitable reaction product, and formed a protective coating infiltrated with the alloy to provide the self-repairing properties. It should be mentioned in connection with the chromium that the chromium might often

be used as an additional protective coating on the outside of a different substrate material such as molybdenum and that the abrasion and corrosion resistant porous coating will be applied over the chromium coating. In this case, a chromium powder can be used rather than a molybdenum powder since the chromium is the material which is exposed to the corroding atmosphere.

A binary alloy of silver containing dissolved aluminum is effective on substrate bodies of columbium or containing major proportions of columbium, since the aluminum will react with the columbium to form a protective intermetallic compound.

Obviously, alloys may be used for infiltrating the porous outer coating other than those which have been specifically mentioned. For example, ternary alloys will work as effectively as the binary alloys, providing that sufficient solubility of silicon is possible and provided that the particular alloy chosen does not adversely react with the substrate material. Alloys which were prepared and found acceptable for use on zirconium bodies consisted of the following ingredients. The first was 55 weight percent silver, 30 weight percent bismuth and 6.0 weight percent silicon. Another which was found suitable was 12.2 weight percent germanium, 81.9 weight percent antimony and 5.9 weight percent silicon, while a further composition consisted of 6.8 weight percent copper, 89.6 weight percent bismuth and 3.6 weight percent silicon. It is thus apparent that any number of alloys can be used, provided they meet the conditions set forth earlier in the specification.

While for the purpose of illustrating our invention, the foregoing specification has set forth several specific examples, we do not intend that our invention be limited in any manner except as recited in the appended claims.

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

1. A composite article comprising a solid substrate body, and a corrosion resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of an intermetallic compound of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article and which contains an amount of a material reactive with said substrate metal sufficient to form a corrosion resistant intermetallic compound of a composition corresponding to that of said porous matrix.

2. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal reactive with silicon to form a silicide, and a corrosion resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article and which contains an amount of silicon sufficient to react with said substrate metal and form a corrosion resistant compound.

3. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, tantalum, columbium, tungsten, chromium and alloys thereof, and an oxidation resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article and which contains an amount of silicon sufficient to react with said substrate metals and form a corrosion resistant compound.

4. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent

of a metal selected from the group consisting of molybdenum, zirconium, columbium, tantalum, tungsten and chromium, and alloys thereof, and an oxidation resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network consisting of silver containing a sufficient amount of silicon to react with said substrate metal and form a corrosion resistant compound, said alloy being liquid at the temperature at which said article is used.

5. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, columbium, tantalum, tungsten and chromium, and alloys thereof, and an oxidation resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article, said alloy consisting of 55 weight percent silver, 39 weight percent bismuth and 6.0 weight percent silicon.

6. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, columbium, tantalum, tungsten and chromium, and alloys thereof, and an oxidation resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article, said alloy consisting of 12.2 weight percent germanium, 81.9 weight percent antimony, and 5.9 weight percent silicon.

7. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, columbium, tantalum, tungsten and chromium, and alloys thereof, and an oxidation resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of a silicide of said substrate metal present as a porous matrix defining a capillary network, and an alloy located in said capillary network which is liquid at the temperature of use of said composite article, said alloy consisting of 6.8 weight percent copper, 89.6 weight percent bismuth and 3.6 weight percent silicon.

8. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent molybdenum, and a corrosion resistant coating secured to and overlying at least a portion of the surface of said substrate body, and consisting essentially of a porous molybdenum disilicide as a matrix, and a gold-silicon alloy held within the pores of said matrix, said layer having the gross composition, by weight, of from about 20 to about 40 percent silicon, 8.0 to about 50 percent gold and the remainder being substantially all molybdenum.

9. A composite article as recited in claim 8 in which said porous body of molybdenum disilicide was formed by reacting a porous layer consisting of at least 70 weight percent molybdenum and having from 25 to 50 percent by volume porosity with sufficient silicon to convert substantially all the molybdenum in said layer to molybdenum disilicide.

10. An article as recited in claim 8 in which said layer has the gross composition, by weight, of from about 20 to 30 percent silicon, 25 to 50 percent gold and the remainder substantially all molybdenum.

11. An article as recited in claim 8 in which said layer has the gross composition, by weight, of from about 35

to 40 percent silicon, 8.0 to 20 percent gold and the remainder substantially all molybdenum.

12. A method for providing the surface of an article composed of at least 70 weight percent of molybdenum with an oxidation, erosion and abrasion resistant coating comprising the steps of sintering to at least a portion of the surface of said article an adherent porous coating of metal consisting of at least 70 weight percent molybdenum, said coating having from about 25 to 75 percent by volume porosity, and impregnating said porous coating with an alloy consisting essentially of from about 1.0 to 30 weight percent silicon and the remainder substantially all gold.

13. In combination with a solid metal body for use at elevated temperatures and comprising at least 70 weight percent molybdenum, a self-repairing coating protecting said body against abrasion and oxidation, said coating consisting essentially of a matrix of molybdenum disilicide having pores dispersed throughout, and an alloy consisting of from about 1.0 to 30 weight percent silicon, the remainder substantially all gold, retained at said elevated temperatures in a liquid state in the pores of said body by capillary attraction to provide silicon for reaction with said body repairing cracks or similar defects occurring in said coating.

14. A method for providing the surface of a metal body composed of at least 70 weight percent molybdenum with an abrasion and oxidation resistant coating comprising the steps, applying a coating of molybdenum powder to the surface of the metal body, sintering the molybdenum powder into an adherent porous coating on the body, and immersing the body in an alloy consisting essentially of 1.0 to 30 weight percent silicon, the remainder substantially all gold to impregnate the sintered coating and form a porous molybdenum disilicide matrix containing molten gold-silicon alloy.

15. In combination with a solid metal body for use at elevated temperatures and comprising at least 70 weight percent zirconium, a self-repairing coating protecting said body against abrasion and oxidation, said coating consisting essentially of a matrix of zirconium disilicide having pores dispersed throughout, and an alloy consisting of not less than about 3.0 weight percent silicon, the remainder substantially all silver, retained at said elevated temperatures in a liquid state in the pores of said body by capillary attraction to provide silicon for reaction with said body repairing cracks or similar defects occurring in said coating.

16. A composite article comprising a solid substrate body consisting essentially of at least 10 weight percent of a metal selected from the group consisting of molybdenum, zirconium, tantalum, columbium, tungsten, chromium and alloys thereof and an oxidation-resistant coating secured to and overlying at least a portion of the surface of said substrate body, said coating consisting of an intermetallic compound of said substrate which is present as a porous matrix defining a capillary network and a metal located in said capillary network which is liquid at the temperature of use of said composite article and which contains material reactive with said substrate metal to combine therewith and form said intermetallic compound.

17. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, tantalum, columbium, tungsten, chromium and alloys thereof, a porous matrix composed of an intermetallic compound of said substrate metal defining a capillary network secured to and overlying at least a portion of said substrate body, a metal located in said capillary network which is liquid at the temperature of use of said composite article, and a material selected from the group consisting of silicon, aluminum, boron, germanium, beryllium, and carbon which is soluble in said capillary-held liquid metal and reactive with said substrate metal, said selected material being dissolved in said

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liquid metal to combine with said substrate metal and form said intermetallic compound.

18. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, tantalum, columbium, tungsten, chromium and alloys thereof, a porous matrix composed of an intermetallic compound of said substrate metal defining a capillary network secured to and overlying at least a portion of said substrate body, a metal selected from the group consisting of gold, silver, bismuth, antimony, copper and alloys thereof which is liquid at the temperature of use of said composite article located in said capillary network, and a material which is soluble in said capillary-held liquid metal and reactive with said substrate metal, said material being dissolved in said liquid metal to combine with said substrate metal and form said intermetallic compound.

19. A composite article comprising a solid substrate body consisting essentially of at least 70 weight percent of a metal selected from the group consisting of molybdenum, zirconium, tantalum, columbium, tungsten, chromium and alloys thereof, a porous matrix composed of an intermetallic compound of said substrate metal defining a capillary network secured to and overlying at least

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a portion of said substrate body, a metal selected from the group consisting of gold, silver, bismuth, antimony, copper and alloys thereof which is liquid at the temperature of use of said composite article located in said capillary network, and a material selected from the group consisting of silicon, aluminum, boron, germanium, beryllium and carbon which is soluble in said capillary-held liquid metal and reactive with said substrate metal, said selected material being dissolved in said liquid metal combined with said substrate metal to form said intermetallic compound.

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