Aug. 27, 1963 A. D. JOSEPH 3,102,044

APPLYING PROTECTIVE COATING FROM POWDERED MATERIAL
UTILIZING HIGH TEMPERATURE AND LOW PRESSURE

Filed Sept. 12, 1960 2 Sheets-Sheet 1

FIG. I

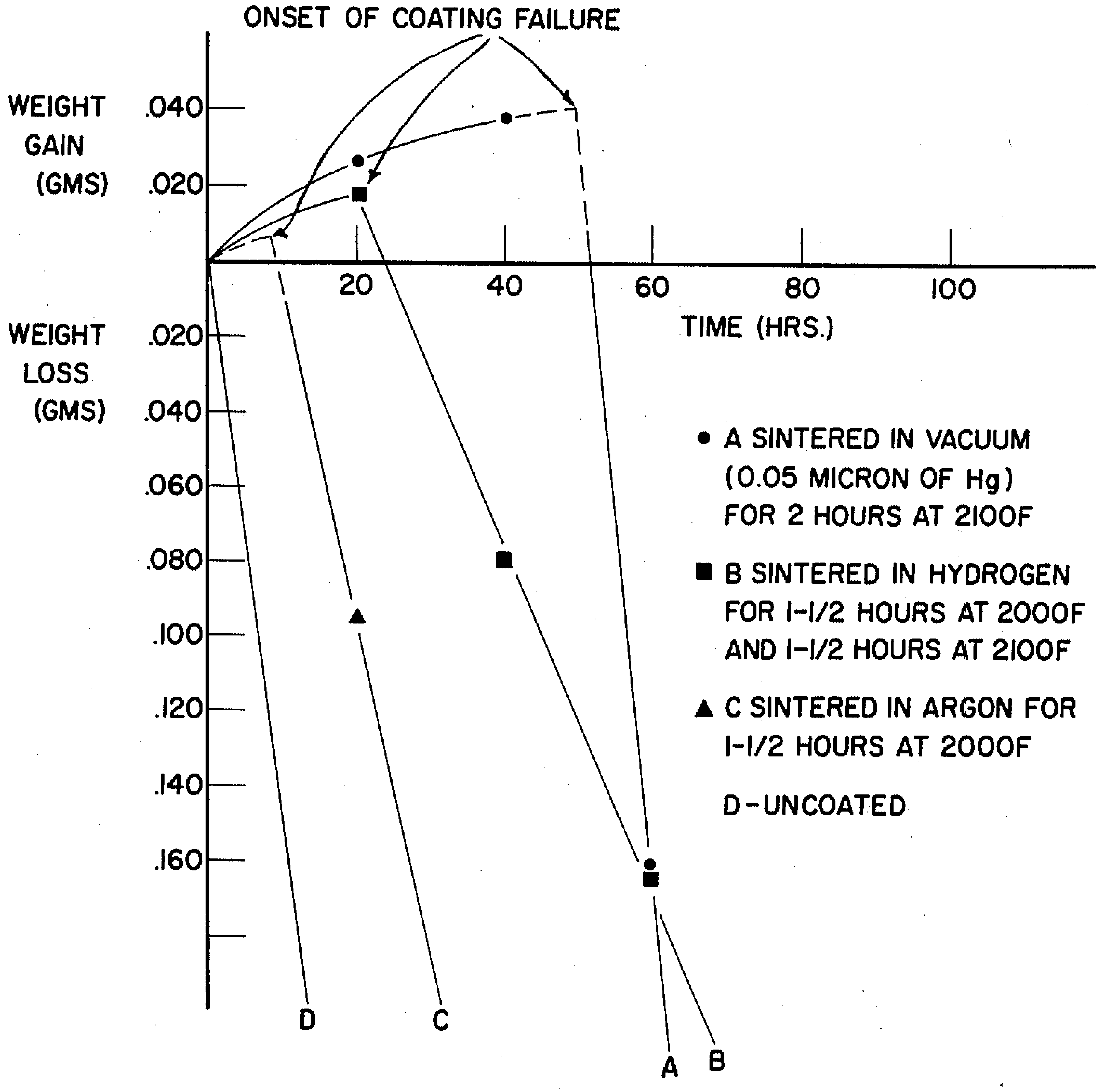
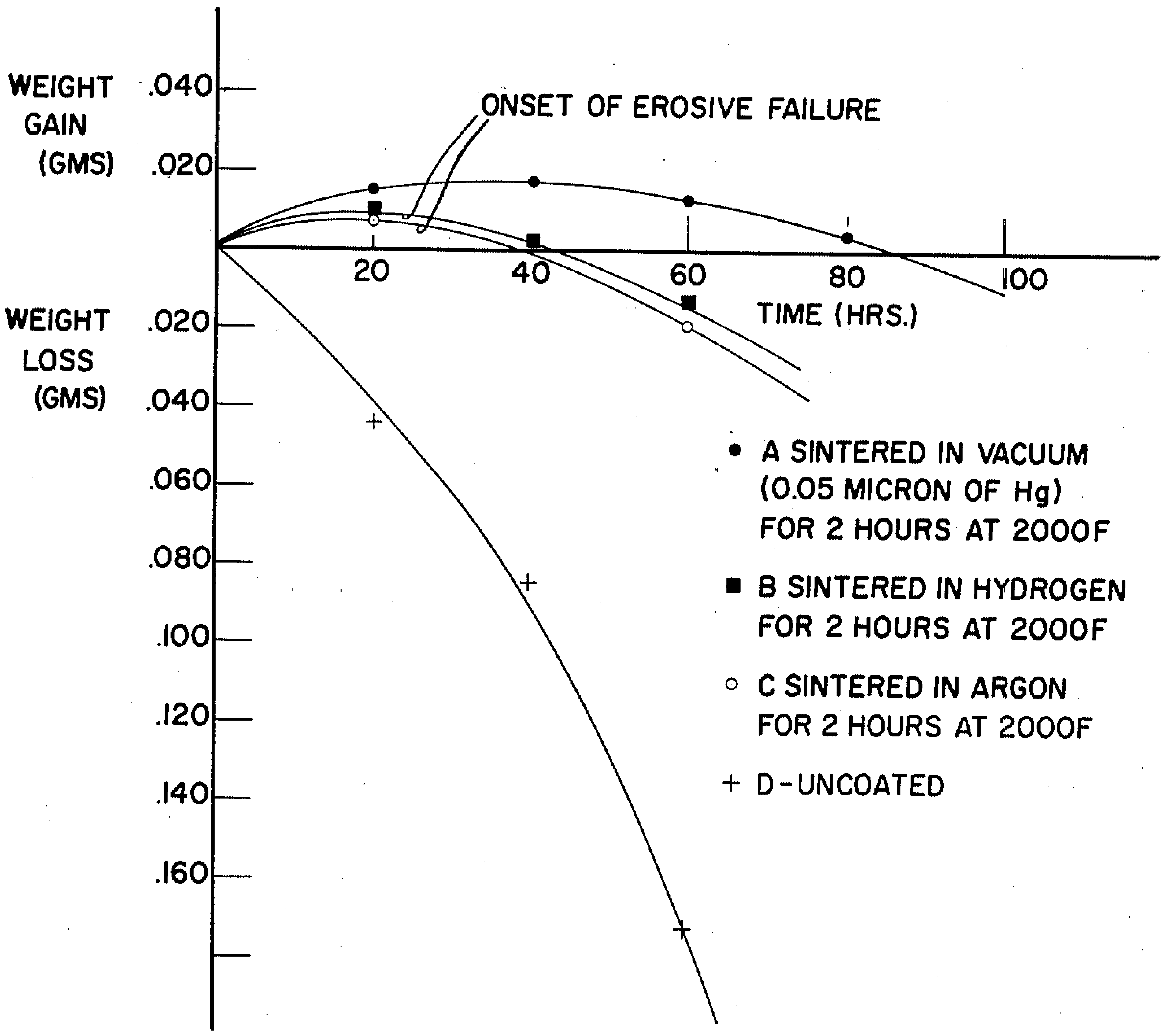


FIG. 2


WEIGHT GAIN (GMS)
.040
.020
ONSET OF EROSIVE FAILURE
20
40
60
80
100
TIME (HRS.)
WEIGHT LOSS (GMS)
.020
.040
.060
.080
.100
.120
.140
.160
● A SINTERED IN VACUUM (0.05 MICRON OF Hg) FOR 2 HOURS AT 2000F
■ B SINTERED IN HYDROGEN FOR 2 HOURS AT 2000F
○ C SINTERED IN ARGON FOR 2 HOURS AT 2000F
+ D-UNCOATED

United States Patent Office

3,102,044
Patented Aug. 27, 1963

3,102,044

APPLYING PROTECTIVE COATING FROM POWDERED MATERIAL UTILIZING HIGH TEMPERATURE AND LOW PRESSURE

A. David Joseph, South Windsor, Conn., assignor to United Aircraft Corporation, East Hartford, Conn., a corporation of Delaware

Filed Sept. 12, 1960, Ser. No. 55,358
17 Claims. (Cl. 117—22)

This invention relates to the treatment of metals and alloys to render them resistant to oxidation and thermal shock.

More particularly, this invention relates to a process for forming a coating or hard surface portion on metals and alloys, or articles made from metals or alloys, which coating or hard surface portion is highly resistant to oxidation and thermal shock; and to metals or alloys or articles thereof having such coatings or hard surface portions.

According to the present invention, hard, non-brittle, high wear resistant layers or coatings are formed on metals and alloys or articles made therefrom by applying a composition comprising powdered metal, metal oxides, or mixtures of the foregoing to the surfaces thereof, and heat treating the resulting materials at high temperatures under extremely low absolute pressures.

In recent times, industry has developed alloys of special character which are capable of retaining their high mechanical strength at high operating temperature. These so-called high temperature alloys are particularly applicable in parts for jet engines and gas turbines, for which application the demands made on the structural parts with respect to their strength at elevated operating temperatures are very exacting.

Typical high temperature alloys which may be mentioned include the nickel, cobalt, chromium, columbium, molybdenum, and tungsten base alloys, as well as alloys containing mixtures of two or more of the foregoing materials. Also may be mentioned the iron base alloys, for example tool steel. Additionally, if desired, the improved process described herein may be used to protect such high temperature metals as nickel, cobalt, chromium, columbium, molybdenum, and tungsten against decomposition or oxidation at high temperature.

It should be understood, however, that the present invention is not restricted to protecting any particular metal or alloy from oxidation and thermal shock. Rather, the process described herein is applicable to a wide variety of metals and alloys whenever it would be advantageous to protect such metals and alloys from oxidation and thermal shock.

The coating compositions of the present invention comprise finely divided powder or dust of metals, metal oxides, or mixtures of the foregoing. Alloys of metals, metal oxides or mixtures of the foregoing in a finely divided state may be also used. Among the coating materials suitable for use may be mentioned finely divided powders or dust of aluminum, magnesium, chromium, columbium, cobalt, tantalum, tungsten, silicon, titanium, and other refractory metals, including mechanical mixtures of two or more of the foregoing metals as well as alloys of two or more of the foregoing metals. Also suitable are powders or dust of the oxides of the foregoing metals, or mixtures or alloys thereof, alone or in combination with the foregoing metals or metallic alloys.

As an example of metallic powder compositions especially suitable for coating columbium base alloys may be mentioned a mechanical mixture of finely divided titanium and aluminum powder, or a finely divided alloy of titanium and aluminum, both or either containing a major portion by weight of titanium. To such compositions may be added, if desired, up to 30 percent by weight of chromium, columbium, cobalt, tantalum, aluminum oxide, or mixtures of the foregoing. The titanium content of such mixtures may be as high as 64 percent or more by weight, and the aluminum content as high as 36 percent or more by weight.

As an example of a metallic powder composition especially suitable for coating nickel, cobalt and chromium base alloys may be mentioned a mechanical mixture of finely divided aluminum and silicon or a finely divided alloy of aluminum and silicon, both or either containing a major portion of aluminum. To such a composition may be added, if desired, up to 30 percent by weight of chromium, columbium, cobalt, titanium, tantalum, or aluminum oxide, or mixtures of the foregoing. The aluminum content of such a composition may be as high as 90 percent or more by weight and the silicon content as high as 10 percent or more by weight.

The metallic powders or dusts usually having a size range of less than 325 mesh (43 microns) although coarser particles, ranging in size from about 100 mesh (147 microns) to 325 mesh (43 microns) may also be used. Especially good results are achieved when the size range of the metallic particles is less than 400 mesh (38 microns), or between about 0 to 38 microns, and preferably between about 0 to 10 microns. In general, it may be said that the finer the particles, the better the coatings produced. The mesh sizes reported are Tyler standard.

The metallic dusts or powders described hereinabove may be applied to the specimen or stock to be treated in any suitable manner. Thus, fine film of the metallic dust or powder may be blasted or dusted onto the specimen; or a liquid dispersion of the metallic dust or powder may be applied to the specimen or stock, after which the solvent may be evaporated to leave a coating of the metallic coating composition on the specimen. Other methods of applying the finely divided metallic coating compositions will readily suggest themselves to persons skilled in the art.

Prior to coating, the surfaces of the base metal or specimen should be thoroughly cleaned of dust or dirt, as by water rinsing, liquid blasting, washing in suitable organic and inorganic solvents, and any other method of cleaning which is standard in the art. Care should be taken in cleaning the base metal or stock to insure against injury thereto.

According to a preferred embodiment of the present invention, the metallic coating compositions described hereinabove are dispersed in a suitable liquid dispersant, and the resulting dispersion is applied to the specimen by spraying, brushing, dip-coating, or any other conventional method.

The ratio of metallic powder to liquid dispersant in such a dispersion will depend upon the type of metallic powder used, the particular dispersant employed, thickness of the coating desired, method by which the coating is applied, and so forth. In general, the ratio of metallic powder to liquid dispersant varies from about 25 to 50 percent, by weight, or higher.

The liquid dispersant may be any suitable, readily volatilizable organic solvent, or mixture of solvents. Among the solvents that may be mentioned are alcohols, such as methyl, ethyl, propyl and butyl alcohol, esters such as methyl, ethyl, propyl, butyl and amyl acetate, and ketones, such as acetone.

The organic solvents mentioned are merely illustrative and not limiting in any respect. It should be understood that almost any volatile liquid that will act as a suitable dispersant for the metallic powders or dust can be utilized, and use of any such liquids is contemplated. The main requirement of the volatile liquid substance or dispersant is that it be reasonably safe to use, inexpensive, and sufficiently liquid at ordinary temperature to act as a dispersant for the metallic dust so that the dispersion can be sprayed or suitably coated on the specimen, and at the same time be sufficiently volatile to evaporate when exposed to atmospheric or other conditions as will be hereinafter described.

If desired, a binder or sticking agent may be added to the liquid dispersant to hold the powder or dust composition to the surface of the specimen after evaporaion of the solvent. Use of the binder enables the powders or dusts to adhere to the specimen for prolonged periods of time, thereby precluding the necessity of heat treating immediately after coating or of taking special precautions in handling the treated specimen. The binder should be such as to be substantially completely decomposed during sintering, or at a temperature below actual sintering temperature. Suitable binding or sticking agents that may be mentioned include nitrocellulose, naphtalene and stearates. Other sticking or binding agents will be readily apparent to those skilled in the art.

Suitable wetting agents may also be added to the dispersant if required.

The dispersion of the metallic powders or dust described hereinabove in either a liquid or lacquer dispersant, i.e. a dispersant containing a binder or sticking agent, is deposited on the surface of the specimen to be coated in the manner already described. After application, the solvent is allowed to evaporate, thereby leaving a layer or coating of powder or dust on the specimen.

If a sticking agent is added to the dispersant, upon evaporation of the solvent, the sticking agent will remain dispersed throughout the dust or powder in the coating, and will serve to hold the powder or dust to the specimen.

Evaporation of the volatile solvent, or volatile portion of the lacquer, containing a sticking agent, may be conveniently brought about by allowing the coated specimen to be stored in an atmospheric environment at ordinary room temperature. If desired, suction or vacuum and/or elevated temperatures, may be used to accelerate evaporation of the volatile solvent. In any event, evaporation of the solvent leaves a fine layer of the metallic dust or powder on the surface or surfaces of the specimen, or on the walls or sides thereof, and also on the walls or sides defining interstices, slots, holes, and so forth which may be present in the specimen.

When a binder or sticking agent is added to the liquid dispersant, the coating layer, upon evaporation of the solvent, comprises a uniform intermixture of the coating dust or powder interspersed throughout the non-volatile, binder or sticking agent. The dried coating adhering to the specimen comprises metallic particles and binder, the metallic dust or powder being suspended in or interspersed throughout the binder.

The thickness of the coating may vary from specimen to specimen. In general, a sprayed thickness of 0.003 to 0.015 inch in thickness is contemplated. Such coatings lead to a coating after sintering of from about 0.0001 inch to 0.005 inch in thickness. Preferably, the thickness of the coating after sintering is about 0.001 to 0.005 inch.

When evaporation of the solvent has been completed, the resulting specimens are heat treated in a suitable furnace or oven to permanently fix the metallic dust or powder to the specimen. The temperature of the furnace or oven is maintained at a sintering temperature. By sintering temperature is meant a temperature which will permanently bond the metallic dust or powder in the coating layer to the specimen by fusion. The sintering temperature is at about or just below the melting point of the dust particles, and, of course, is less than the melting point of the metallic material that forms the specimen.

Sintering temperatures of about 1800° F. to 3500° F., are contemplated. The sintering temperature of course, depends upon the base metals being treated, and the nature of the coating materials. For coating tungsten base alloys, for example, sintering temperatures up to 3500° F. may be used, depending, of course, on the nature of the coating materials. For chromium and nickel base alloys, sintering temperatures between about 1800° F. and 2300° F. are especially suitable. In general, however, the sintering temperature should be below about 3500° F. and at least about 1800° F.

The sintering period may vary from about ½ to 10 hours. Especially good results are achieved when the sintering is carried out for about 1 to 2 hours, and this period may be considered optimum.

Although it is known in the prior art to sinter coatings of finely divided metallic dusts on to metallic specimens, such sintering is ordinarily carried out at atmospheric pressure or at pressures approaching atmospheric pressure. Also, it is known to conduct such sintering operations at atmospheric or close to atmospheric pressures in a reducing medium, such as hydrogen, or in an inert gas medium, such as krypton, argon, neon, or other inert gases.

It has been discovered that the coatings produced by such prior art sintering operations, although satisfactory for relatively short periods, are not able to withstand prolonged exposure to high temperature in oxidizing mediums. Moreover, such coatings contain considerable voids, thereby increasing the susceptibility of the coated specimen to erosive failure upon exposure to oxidation and thermal shock.

According to the present invention, it has been discovered that superior coatings are produced by sintering at greatly reduced pressures, or stated differently, by sintering under conditions of high vacuum. The sintering operations of the present invention are carried out under absolute pressures of less than 1 micron and preferably less than 0.1 micron of mercury. Especially good results are achieved when sintering is carried out under absolute pressures of 0.05 to 0.005 micron of mercury.

The specimens coated according to the present invention are able to withstand oxidation and thermal shock for considerably longer periods of time than has heretofore been possible.

Further, the coatings of the present invention are essentially void-free, and are substantially uniform in thickness over the entire coated portion of the stock. This considerably reduces the susceptibility of the specimen or stock to erosive failure at high temperature.

If desired, more than a single coating or diffusion layer may be formed. For example, the process may be carried out by first applying a powdered metal coating and sintering under the conditions described hereinabove, and thereafter applying another layer of powdered metal and subjecting the previously treated article to a further sintering treatment. The second layer of powder may be the same as the first or it may be a different metal, mixture of metals, or alloy of metals.

The invention will be clear from the following examples, which, though illustrative, are not intended to limit the invention in any way.

Example I

A coating powder containing 90 weight percent aluminum powder having a particle size of —400 mesh and 10 percent silicon powder having a particle size of —325 mesh was prepared mechanically by mixing the described aluminum and silicon powders and blending in a ball mill.

A liquid dispersant containing the following proportions of ingredients was prepared:

Acetone	ml	100
Amyl acetate	ml	650
Nitrocellulose	gm	15

Enough of the powdered mixture was added to the dispersant to give a resulting dispersion containing 1 gram of metallic powder (0.9 gram of aluminum powder and 0.10 gram of silicon powder) per milliter of dispersant. The resulting dispersion was sprayed onto a jet engine turbine vane made of a high temperature cobalt base alloy.

The solvent was evaporated by allowing the specimen to stand at a room temperature.

Following evaporation of the solvent, the specimen with the coating adhered thereto was placed in a National Research Corporation vacuum furnace. The temperature of the furnace was raised to 2000° F., and a vacuum of 0.05 micron of mercury was drawn on the chamber enclosing the specimen.

Sintering was carried out for 2 hours at 2000° F., and under an absolute pressure of .05 micron of mercury. After sintering the vacuum was maintained and the specimen was cooled to 500° F. The specimen, hereinafter referred to as specimen A, was then removed from the furnace and allowed to cool to room temperature.

Two control specimens, B and C, respectively, coated in the same manner, were sintered at about the same temperature, but under one atmosphere of hydrogen and one atmosphere of argon, respectively.

The treated specimens were erosion tested by heating at 2000° F. The results of the tests are given in FIGURE 1, which shows a graph of weight loss or gain as the ordinate and time as the abscissa. A fourth specimen, D, which was not coated, was included in the tests for comparison purposes.

As is apparent from FIGURE 1, the period of time to onset of coating failure for specimen A was more than twice as long as that for specimen B and nearly 5 times as long as that for specimen C.

Example II

Example I was repeated with the exception that a turbine blade made of a nickel-base alloy was substituted for the cobalt-base alloy turbine blade of Example I.

FIGURE 2 shows the results of erosion tests performed on the treated specimens at about 2000° F. Referring to FIGURE 2, curve A′ shows the results of the erosive test for the specimen produced in Example D. Curves B′ and C′ were coated in the same manner as specimen A′, but were sintered under 1 atmosphere absolute pressure of hydrogen and argon, respectively. Curve D′ refers to a fourth specimen which was not coated, and which is included merely for comparison purposes. Here again, the period of time to onset of erosive failure was nearly twice as great for the specimen sintered under the vacuum conditions of the present invention, as for the specimens sintered in hydrogen and argon atmospheres, respectively.

Example III

Example I was repeated, with the exception that the metallic powder added to the dispersant was a mechanical mixture of the following metals:

	Weight percent
Aluminum	80
Aluminum oxide	10
Silicon	10

Results similar to those of Example I were obtained.

Example IV

Using the procedure of Example I, a turbine blade of columbium base alloy was coated with the dispersant of Example I containing 1 gram per milliter of a finely divided metallic powder comprising 64 weight percent titanium and 36 weight percent aluimnum. Results similar to those of Example I were obtained.

The invention in its broader aspects is not limited to the specific mechanisms described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. In a method of protecting metal and alloy pieces against decomposition by contacting the pieces with finely divided particles of a member selected from the group consisting of refractory metals, alloys, oxides, and mixtures thereof, and sintering by heating, at a temperature of 1800° to 3500° F., the improvement which comprises conducting the sintering operation at an absolute pressure of less than 1 micron of mercury.

2. The improvement of claim 1 wherein the average size of the finely divided particles is less than 147 microns.

3. The improvement of claim 1 wherein the average size of the finely divided particles is less than 38 microns.

4. In a method of protecting against decomposition at high temperatures, pieces of a base material which is a member selected from the group consisting of nickel, cobalt, chromium, columbium, molybdenum, tungsten and iron metals and metal base alloys thereof, the improvement which comprises contacting the piece with a composition comprising finely divided particles of a member selected from the group consisting of aluminum, magnesium, chromium, columbium, cobalt, titanium, tantalum, tungsten, silicon, alloys thereof, oxides thereof, and mixtures of the foregoing, and sintering the particles to the piece by heating to a temperature of between about 1800° and 3500° F. at an absolute pressure of less than 1 micron of mercury.

5. The method of claim 4 wherein a thin, uniform coating of the composition is adhered to the piece prior to sintering.

6. A method of protecting pieces of columbium base alloy from decomposition at high temperatures which comprises contacting the pieces with a composition comprising finely divided particles of titanium and aluminum, and sintering the particles to the piece by heating to a temperature of between about 1800° and 3500° F. at an absolute pressure of less than about 1 micron of mercury for a period of at least about 0.5 hour.

7. The method of claim 6 wherein the composition comprises finely divided particles of an alloy of titanium and aluminum.

8. The method of claim 6 wherein a thin uniform coating of the composition is adhered to the piece prior to sintering.

9. The method of claim 6 wherein the composition comprises, based upon the weight of said particles, about 64 weight percent titanium and 36 weight percent aluminum, and wherein the sintering is accomplished by heating to a temperature of about 2000° F. at an absolute pressure of about 0.05 micron of mercury for about 2 hours.

10. In a method of protecting pieces of columbium base alloy from decomposition at high temperatures, the improvement which comprises contacting the pieces with a composition comprising finely divided particles of titanium, aluminum and a member selected from the group consisting of chromium, columbium, cobalt, tantalum, oxides thereof, alloys thereof, aluminum oxide and mixtures of the foregoing, and sintering the particles to the piece by heating to a temperature of between about 1800° and 3500° F. at an absolute pressure of less than about 1 micron of mercury for a period of at least about 0.5 hour.

11. The improvement of claim 10 wherein the composition comprises, based upon the weight of said particles present, up to 64 percent titanium, up to 36 percent aluminum, and up to 30 percent of said member.

12. A method of protecting against decomposition at high temperatures, pieces of a base material which is a member selected from the group consisting of nickel, cobalt and chromium base alloys, which comprises contacting the pieces with a composition comprising finely divided particles of aluminum and silicon, and sintering the particles to the base material by heating to a temper-

ature of 1800° to 3500° F. at an absolute pressure of less than 1 micron of mercury for a period of at least 0.5 hour.

13. The method of claim 12 wherein the composition comprises, based upon the weight of said particles, about 90 percent aluminum and about 10 percent silicon, and wherein the sintering operation is carried out at a temperature of about 2000° F., at an absolute pressure of less than 0.05 micron of mercury for about 2 hours.

14. The method of claim 12 wherein a thin uniform coating of the composition is adhered to the base material prior to sintering.

15. The method of claim 12 wherein the composition comprises finely divided particles of an alloy of aluminum and silicon.

16. In a method of protecting against decomposition at high temperatures, pieces of a base material which is a member selected from the group consisting of nickel, cobalt, and chromium base alloys, the improvement which comprises contacting the pieces with a composition comprising finely divided particles of aluminum, silicon and a member selected from the group consisting of chromium, columbium, cobalt, titanium, tantalum, oxides thereof, alloys thereof, aluminum oxide, and mixtures of the foregoing, and sintering the particles to the base material by heating to a temperature of 1800° to 3500° F. at an absolute pressure of less than 1 micron of mercury for a period of at least 0.5 hour.

17. The improvement of claim 16 wherein the composition comprises, based upon the weight of said particles, up to 90 percent aluminum, up to 10 percent silicon, and up to 30 percent of said member.

References Cited in the file of this patent

UNITED STATES PATENTS

1,365,499	Kelley	Jan. 11, 1921
1,899,569	Howe	Feb. 28, 1933
2,858,600	Vigor	Nov. 4, 1958

OTHER REFERENCES

Davy: Industrial High Vacuum, pp. 214–215, Pitman & Sons, London, 1951.