# United States Patent

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## [54] DUCTILE, HIGH-TEMPERATURE OXIDATION-RESISTANT COMPOSITES AND PROCESSES FOR PRODUCING SAME

**3 Claims, No Drawings**

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[51] **Int. Cl.** .......................................................... **B32b 15/00**
[50] **Field of Search** .......................................... 29/195, 194, 197, 191; 117/71; 75/171, 176

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**ABSTRACT:** A ductile, high-temperature, oxidation-resistant metal composite is disclosed that comprises a superalloy substrate and a coating composition having the following percentages by weight of ingredients:

| | |
|---|---|
| chromium | 5% to 50% |
| aluminum | 5% to 10% |
| silicon | 0.5% to 3% |
| cobalt | 0 to 5% |
| nickel | balance |

A process for producing the composites is also disclosed wherein the coating composition containing the foregoing ingredients as powdered metals, a fugitive organic binder and a volatile solvent for the binder is applied to a clean substrate and thereafter the coated material is dried and heated under nonoxidizing conditions for a time sufficient to create a diffusion zone between said coating and said substrate.

# DUCTILE, HIGH-TEMPERATURE OXIDATION-RESISTANT COMPOSITES AND PROCESSES FOR PRODUCING SAME

## BACKGROUND OF THE INVENTION

This invention relates to metal composites containing the “superalloys.” More particularly it relates to composites that contain coating compositions that enable such alloys to resist oxidation at elevated temperatures.

Alloys have been developed for uses wherein the alloys are subjected to relatively severe conditions such as high temperature oxidation and high stresses. These alloys, commonly referred to as superalloys, for the most part withstand these severe environmental conditions, however certain parts of fabricated items are subjected to conditions that exceed the limits of the alloys. For example, the TD Nickel alloys (containing about 98 percent nickel and containing about 2 percent thorium oxide of submicron size dispersed through the nickel base) and the nickel and cobalt based alloys are generally suitable for most uses up to temperatures of about 2,000° F. Above about 2,000° F. the oxidation rate becomes excessive. In order to protect these alloys against oxidation at these elevated temperatures, coatings are needed. Several coating systems are known that will protect the alloy substrates against the attach, however, none are known that offer oxidation resistance and are also ductile, particularly when applied as relatively thin layers, e.g. 5 mils. In some applications such as in jet engine turbines, the performance of the engine is limited by the maximum operating temperatures that can be used. The vanes of the engine operate at higher temperatures than do the blades in the engine. While the beforementioned alloys are promising materials for jet engine parts, it would be an advantage to have a material having a substrate of one of the superalloys and coated with a composition so that the material would be ductile and withstand the oxidation at the elevated temperatures e.g. above about 2,000° F. It is believed to be an advancement in the art to provide a ductile material that has the capability of withstanding oxidation at elevated temperatures, thus enabling the composite to be used in environments that heretofore were considered to be prohibitive for most materials.

## SUMMARY OF THE INVENTION

In accordance with one aspect of the invention, there is provided a ductile, high temperature, oxidation-resistant metal composite comprising: (a) a superalloy substrate as its principal component and (b) a coating bonded to the substrate and consisting essentially of nickel, chromium, aluminum and silicon in the following percentages by weight of the total coating composition:

chromium— 5% to 50%

aluminum— 5% to 10%

silicon—0.5% to 3%

cobalt— 0 to 5%

nickel—balance

In accordance with an additional aspect of this invention, there is provided a process for producting the ductile, high temperature, oxidation-resistant metal composites, the process comprising: (a) applying to a clean surface of a superalloy substrate a coating composition comprising a powdered metal material, a fugitive organic binder and a volatile solvent for said binder; the metal material consisting essentially of the following weight percentages of ingredients:

chromium— 5% to 50%
aluminum— 5% to 10%
silicon—0.5% to 3%
cobalt— 0 to 5%
nickel—balance

In accordance with an additional aspect of this invention, there is provided a process for producing the ductile, high temperature, oxidation-resistant metal composites, the process comprising: (a) applying to a clean surface of a superalloy substrate a coating composition comprising a powdered metal material, a fugitive organic binder and a volatile solvent for said binder; the metal material consisting essentially of the following weight percentages of ingredients:

chromium— 5% to 50%
aluminum— 5% to 10%
silicon—0.5% to 3%
nickel—balance

(b) drying the applied coating and (c) heating the coated substrate under nonoxidizing conditions at a temperature and for a sufficient time to create a diffusion zone between said coating and said substrate.

In accordance with another aspect of this invention there is provided a process for producing the high temperature, oxidation-resistant composites; the process comprises (a) applying to a clean surface of a superalloy substrate a first coating composition comprising a powdered metal material, a fugitive organic binder and a volatile solvent for said binder; the metal material consisting essentially of the following weight percentages of ingredients:

| | |
|---|---|
| chromium | 5% to 50% |
| silicon | 1% to 3% |
| nickel | balance |

(b) drying the applied coating; (c) heating the substrate containing the first coating under nonoxidizing conditions at a temperature and for a sufficient time to create a diffusion zone between the substrate and the first coating; (d) applying to the first coating a second coating composition comprising a powdered metal material, a fugitive organic binder and a volatile solvent for the binder; the metal material consisting essentially of the following weight percentages of ingredients:

| | |
|---|---|
| aluminum | 80% to 100% |
| cobalt | 0% to 20% |

(e) drying the second coating, and (f) heating the coated substrate containing the first and second coatings under nonoxidizing conditions at a temperature and for a sufficient time to create a diffusion zone between the first and second coatings.

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above description of some of the aspects of the invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The superalloys are well known. Typical alloys of this classification are given in Metals Handbook 8th Edition 1961, Vol. 1, published by American Society for Metals. As previously mentioned, these alloys are particularly useful in jet engines, especially as turbine blades, however, the vanes (the other primary components) operate at higher temperatures than do the blades. The nickel and cobalt based alloys are particularly well protected against oxidation at higher temperatures by the coating compositions of the present invention. Of the foregoing alloys, the thorium oxide dispersion nickel alloys and thorium oxide dispersed nickel-chromium alloys are preferred for many jet engine usages and can be effectively protected by the practice of this invention.

The articles produced by the practice of this invention comprise, in addition to the superalloy substrate, a layer of a quarternary composition consisting essentially of nickel, chromium, aluminum and silicon in the amounts specified herein. A diffusion zone is produced by the heating at elevated temperatures between the coating and the substrate. In this zone some of the metal materials from the coating diffuse into the metal matrix that is adjacent to the coating. This diffusion zone insures good bonding of the coating and improves the resistance to the oxidation attack that is believed to occur at grain boundaries. It is to be noted that there is no sharp line of delineation between the coating and the substrate in the as-coated condition. Electronprobe analysis at various depths from the surface of the coated article show the diffusion of the various metals into the substrate.

As will be described in more detail hereinafter, the metal composite of this invention can be prepared by either of two processes. In one method the coating can be applied by slurry techniques hereinafter described, wherein the slurry contains all of the desired metals in the desired amounts. Although the foregoing "one-step" coating method yields a composite superior to an uncoated superalloy, a second method is a "two-step" method wherein a first layer of a coating composition containing nickel, chromium and silicon is applied and after drying and heat treating, a second layer, consisting of aluminum or aluminum-cobalt is applied via essentially the same slurry technique as is used in applying the first layer. Although the composites are described as being produced by providing "layers" of various composition, the metal composite does not have completely discrete layers of compositions as a result of the diffusion of metals into the adjacent material during the heating steps described herein. Additionally, the composites do not necessarily have a uniform analysis since the various metals can diffuse into the substrate at a different rate. The overall composition is a previously given.

In the "one-step" coating process the Ni, Cr, A1, and Si, if not initially in the form of finely divided powders, are pulverized to form such powders. The particle sizes or ranges of particle sizes suitable are those metal powders that are commonly employed in powder-metallurgy techniques, and usually have particles small enough that all of the particles will pass through a 325-mesh screen (U.S. Standard Sieve Series).

Instead of the metallic ingredients being in elementary form, any two or more or all of them can be preformed as an alloy material wherein the proportions of the components thereof are such as would be employed if they were present as a physical admixture.

The metal powders are thoroughly mixed together in a suitable blender or mixing device (e.g. a "V" blender) until a substantially homogeneous composition has been obtained. A similar procedure is followed if a mixture of different alloys or of elemental metal (or metalloid) and of alloyed material is employed.

The powdered metal is converted into a liquid coating composition, adapted for application (e.g., by dipping, brushing spraying or the like) to the superalloy substrate, by suspending it in a suitable vehicle, e.g., a solvent solution of temporary or fugitive binder which can be a natural or synthetic binder.

Examples of fugitive binders that can be employed are solvent solutions or dispersions of the various available synthetic polymers, such as polyacrylamide, polyvinyl acetate and the homopolymers and copolymers of the lower alkyl (e.g., $C_1$ through $C_5$) acrylates and methacrylates with each other and with other compounds containing a monoethylenically unsaturated grouping. It is preferred to employ an ordinary nitrocellulose (pyroxylin) lacquer wherein the solvent is, for example, amyl acetate.

The concentration of the powdered metal in the vehicle and the amount of solvent in the same are varied as desired, depending upon such factors such as the particular method of applying the coating (brushing, spraying, or dipping), the desired thickness of the individual coating, the number of coatings to be applied, the viscosity of the vehicle, the desired covering power of the coating composition, and other influencing factors. Typically, the metal powder is present in the coating composition in an amount corresponding to about 1,500 g. to about 3,000 g. per 1,000 g. of the vehicle.

The powders are mixed with the vehicle by mechanical stirring. Any suitable mixer can be used, however, mixers of the type generally employed in mixing paints are preferred for this purpose. Mixing is continued at any suitable temperature for a time sufficient to provide a substantially homogeneous composition.

The coating is applied to the cleaned surface of the superalloy substrate. The surface of the part can be cleaned by dry abrasive blasting such as with iron or aluminum oxide grit, or by chemical cleaning such as acid pickling for 1 minute in a solution of one part concentrated HF, one part concentrated $HNO_3$ and one part water. There is no preferred cleaning method insofar as wettability or protectiveness of the coating is concerned. Hence the selected cleaning method depends primarily upon such other factors as, for instance, convenience, availability of suitable equipment, and accessibility of the surface to be coated. If all surfaces are readily accessible, spraying is the preferred method of application. The applied coating on the superalloy part is then air dried. The air-dried coating will vary in weight with the amount of the initially applied wet coating, but usually will be within the range of from about 50 to about 150 mg./cm$^2$. Heavier coatings can be obtained, if desired, either by applying one or more fresh layers over the air-dried coating followed by air drying after each successive application of the liquid coating material.

After air drying, the coated part is heated under relatively high-temperature conditions. This can be done, for instance, by placing the coated article on heat-resistant pads, e.g., quartz or alumina pads or boats, or suspending it by tantalum wires in a cold-wall furnace. Firing is done at a temperature which is near, at or slightly above the melting point of the "as-applied" metallic coating, but which is preferably about 5°–10 ° F. above the melting point. In such a furnace, the coated part is supported or suspended inside the heating element wherein it is heated by radiation, and is therefore quickly heated to a uniform temperature.

The time and temperature of firing the coated part in all cases are sufficient to effect a diffusion of the metals in the coating into the substrate. Generally, this diffusion treatment is effected by heating under nonoxidizing conditions at a fusion temperature ranging from about 2,300° F. to about 2,450° F. for a period of from about 10 minutes to about 1 hour. Thus, this heat treatment can be carried out in an atmosphere of an inert gas, e.g., helium, argon, krypton, zenon or other members of Inert Gas Group of the Periodic Table of the Elements. Advantageously the nonoxidizing conditions for the heat treatment are obtained by heating the coated part under a high vacuum, e.g., at less than 0.001 or 10 $^{'7E'3}$ torr, and preferably at less than 0.0001 or 10$^{'7E'4}$ torr. The temperature and time of treatment depend upon such influencing factors as, for example, the particular coating composition and substrate employed. Heating for about 15 to about 20 minutes at 2,325°–2,450° F. at a pressure aluminum, less than 0.001 torr can be used with satisfactory results in many instances. If desired, heating can be carried out initially under partial vacuum and completed in an atmosphere of an inert gas.

Any furnace capable of attaining the required temperature and pressure values in firing the coated structure without oxidation thereof, e.g., by firing it under high vacuum or in an atmosphere of an inert gas, can be employed.

The thickness of the fused coating can range from about 3 mils to about 8 mils, but is preferably within the range of from 4 to 5 mils.

The metal coatings with which this invention is concerned can be applied selectively to portions of parts or assemblies. Also, modifications of the primary compositions (or even basically different compositions if believed to be necessary) can be applied to specific areas of the same part or assembly wherein experience indicates that different compositions would be more suited to the particular environmental conditions.

The fused-slurry coating technique used in practicing this invention is simpler and less expensive than pack-cementation processes employed in the prior art in applying metallic coatings to metallic substrates. The fused-slurry coating method requires only one-thousandth (or less) coating material as that required (but not all consumed) when the aforementioned prior art processes are used. Furthermore, less line (usually, at most only about 1 hour) is required by the method of this invention whereas all pack-cementation processes require one or more heat treatments that require from about 4 to about 16 hours for each single treatment, not including the long heat-up and cool-down cycles.

The coatings with which this invention is concerned are substantially uniform in composition. This is due mainly to the technique of applying them to the superalloy substrate. In this respect they differ markedly from coatings applied to a pack-cementation process wherein the coated part is embedded in an insulating powder pack inside a retort and is heated by conduction. By this technique the parts nearest the walls of the retort are heated up much more rapidly than those at the center; hence, the resulting coatings are not uniform either in composition or in thickness.

Another advantage of the coatings involved in the instant invention, and that accrues both from the composition of the coating and from the preferred technique by which it is applied, is the ease with which patch or repair work can be done in fixing a damaged surface. In making a repair it is only necessary to clean the area where the defect exists or the damage has been done, apply the same composition used in forming the original coating, and heattreat the repaired area or the entire part under vacuum or in an inert atmosphere as heretofore has been described.

In the "two-step" process for producing the composites of this invention, essentially the same method of applying the metal powder slurries is used. The major difference in the "two-step" process is that aluminum or aluminum and cobalt are not incorporated as ingredients of the coating composition used to obtain the first coating and are subsequently added via a slurry technique followed by the drying and diffusion steps. In this manner sufficient aluminum can be added to effect improved oxidation resistance without obtaining low-melting phases. The first coating apparently acts as a better base for the application of aluminum than the superalloys and thus reduces the formation of low melting phases while the amounts of aluminum are being diffused. As measured by electroprobe analysis, some aluminum is detected at about 28 mils from the surface when a 5 mils total coating thickness is used. Significant amounts of aluminum (above 1 percent) are detected at about 10 mils from the surface of the coating. In many instances, particularly when the environment of the element is subjected to elevated temperatures, such as above about 2,200° F., composites produced by the "two-step" process are preferred over those produced by the "one-step" process. Also, for particular substrates, an aluminum and cobalt mixture such as a Al–20 Co mixture has been found to provide a preferred second layer.

In each process care must be taken during the heating step to achieve the desired amount of diffusion of the various elements into the matrix of the other compositions without forming local low-melting phases. Formation of the local low-melting phases causes spalling of the coatings. The firing temperatures and sequence is even more critical when the "two-step" method is used since the final coating application consists essentially of aluminum, therefore, as the aluminum diffuses into the matrices of the first coating and the substrate to form the metal composite, local areas of the coating, due to the high-aluminum content of the second coating, can form a composition that has a melting point below the firing temperature or the temperature of the environment in which the composite is to be used. For these reasons when a substrate of a superalloy of the TD-Ni type (2 percent thorium oxide dispersed in the nickel) is used, the following "two-step" process is especially preferred.

A slurry of Ni–30Cr–1Si at an application of about 80 mg./cm.$^2$ is applied to the substrate to yield about a 4 mils thick coating. After the coating is dried and fired in a vacuum at about 2,430° F. for about 15 to 20 minutes, a second coating of Al–20 Co is applied at an application of about 5–25 mg./cm.$^2$ to yield a total coating thickness of about 5–8 mils, with from about 8 to about 12 mg./cm.$^2$ being preferred to yield a total thickness of about 5 mils. After the coating is dried it is fired in a hydrogen atmosphere according to the following heat treating cycle: heat to about 2,050° F. in about 1 hour, hold at about 2,050° F. for about 2 hours, raise to 2,100° F. and hold at that temperature for about 2 hours, hold at each of 2,150° F. and 2,200° F. for about ½-hour intervals, then 2,300° F. for about one half hour, an overall heat treatment cycle of about 7½ hours is achieved.

It is also preferred when the substrate is a superalloy of the TD–NiCr alloy-type that the above procedure be followed with the exception that the first coating is preferred to be a nickel-chromium-silicon mixture of the approximate composition Ni–20Cr–3-Si. Although higher levels of Cr can be used in the first coating and the benefits of this invention can be achieved, there are no additional benefits to be gained since the Td–NiCr substrates generally contain a maximum of about 20 percent Cr.

It is also contemplated within the broad scope of this invention that it can be desirable to introduce a single or a plurality of "diffusion barriers" into the metallic composite between the superalloy substrates and the metallic coating described hereinbefore to reduce the amount of diffusion. The substrate can also be provided with a plurality of alternate layers of (1) a diffusion barrier and (2) the coating of this invention, the first layer of the diffusion barrier being superimposed directly on the substrate. Examples of suitable diffusion barriers are tungsten, rhenium, tantalum and molybdenum. The layer of diffusion barrier can be of any desired thickness, e.g., from 0.5 to 1 mil in thickness.

To more fully illustrate some of the aspects of this invention, the following nonlimiting examples are presented. All parts, percentages and proportions are by weight unless otherwise indicated.

## EXAMPLES 1–9 —ONE-STEP PROCESS

Nickel, chromium, aluminum, silicon, and in some instances additionally columbium, are weighted out in the proportions given in table I, charged into a conventional V-blender; and blended for 2 hours.

The blended powder mixture is then added to a lacquer of high purity, low-residue nitrocellulose in a solution of amyl acetate solvent in the approximate proportion of 1 to 1 by volume, and is thoroughly mixed for about 10 minutes. The nitrocellulose lacquer employed can be one such as type L–18 manufactured by Raffi and Swanson, Wilmington, Mass. To minimize gravity separation, there can also be incorporated into the slurry a small amount of a dilutant as, for example, toluene. The amount of toluene or its equivalent can be from about 10 to 20 percent by weight of the nitrocellulose lacquer component of the slurry.

The resulting slurry or coating composition is poured into the jar or reservoir of a conventional paint-spray gun. Such a receptacle is preferably provided with means for continuous, mechanical stirring of the slurry in order to prevent settling of the metallic powders.

In this example the cleaned TD nickel parts (by dry abrasive blasting) are coated with the individual coating compositions identified in table I.

The parts are sprayed with the slurry using normal paint-spraying technique. After spraying, the parts are allowed to air dry for 1 hour. The air-dried weight of the coating is in the range of about 50 to about 100 mg./cm.$^2$.

The air-dried parts are then placed across small ceramic (alundum) combustion boats which, in turn, are placed in a vacuum furnace. The furnace is sealed and pumped to a vacuum of less than $10^{\text{'}7E\text{'}4}$ torr at which point heating is begun. The heat is initially applied slowly until at a low temperature (less than 500° F.) it is apparent (evidenced by the sudden increase in pressure within the furnace) that the amyl acetate solvent is volatilizing from the lacquer component of the coating composition. At this point heating is temporarily interrupted until it is observed that the pressure in the furnace is again at a level of $10^{\text{'}7E\text{'}4}$ torr or lower. Thereafter, heating is continued to the particular furnace temperature specified in the individual example of table 1, and all of which temperatures are within the range of from 2,325° F. to 2,425° F. The parts are held at the recorded temperature for either 15 or 20 minutes, i.e., as is specified in the individual example of table I.

At the end of the firing period the furnace heat is turned off. When the furnace has cooled to a temperature sufficiently low to prevent damage to the internal parts of the furnace, air is admitted thereto, and the furnace is opened and the parts are removed.

The furnace employed in firing the coated specimen parts of these examples is a cold-wall, metallic-resistance element furnace, the heat-up time being about 10 minutes and the cool-down time about 30 minutes in carrying out the described firing step. In larger vacuum furnaces of similar or different design and/or with larger work loads, longer heat-up and cool-down times are necessary. However, these factors are not critical in the chemistry involved in the firing step nor in the performance characteristics of the finished, coated part.

The data in table I are believed to be self-explanatory. It will be noted from examples 4 and 8 that alloys 5 and 7 can be readily fused onto the nickel-base substrates at a temperature as low as 2,325° F. Alloy 6 (Used in examples 5, 6 and 7) may have an even lower fusion point. In general, the coatings are tightly adherent and fairly dense. The common "bent" means that the coated coupon can be bent sharply without destroying or injuring the coating, and that the metallic coating is, therefore, ductile.

TABLE I

| Example | Coating composition | Coating temperature, ° F, | Time, min, | Coating remarks |
|---|---|---|---|---|
| 1 | Ni-30Cr-8Al-1.0Si | 2,400 | 20 | Fused-bent O,K. |
| 2 | | 2,380 | 15 | Do. |
| 3 | | 2,350 | 15 | Fused-ran down. |
| 4 | | 2,325 | 15 | Fused-some porosity. |
| 5 | Ni-30Cr-8Al-3Cb-1,0Si | 2,400 | 20 | Fused-bent O,K. |
| 6 | | 2,380 | 15 | Do. |
| 7 | | 2,350 | 15 | Fused-ran down. |
| 8 | Ni-30Cr-8Al-0.75Si | 2,325 | 15 | Fused-rough. |
| 9 | Ni-20Cr-5Al-0.25Si | 2,425 | 15 | Porous-NG bend. |

The results of oxidation tests on some of the samples of the composites produced in this example are given in table II. In this test the composites are subjected to 16–24 hour cycles at about 2,300° F. followed by 5 minutes at about ambient (room) temperature. In carrying out the tests the samples are placed in a quartz boat which is manually inserted in a furnace that is maintained at the test temperature. After each oxidation exposure period the boat is withdrawn from the furnace and the samples are air-cooled for about 5 minutes.

TABLE II

[Results of Oxidation Tests at 2,300° F. on slurry-coated TD nickel (substrate-13 mils thick)]

| Coating composition | Test time (hrs.) | Weight gain (mg./cm.$^2$) | Remarks |
|---|---|---|---|
| Ni-30Cr-8Al-1.0Si | 17 | 2.6 | |
| | 119+ | 3.4 | |
| | 187+ | 2.8 | |
| Ni-30Cr-8Al-3Cb-1.0Si | 17 | 1.8 | |
| Ni-30Cr-8Al-0.75Si | 95 | 3.0 | Bent-O. K. |
| | 163 | 4.0 | |

EXAMPLE 10 —Two-Step Process

A uniform mixture of metal powder is prepared by blending 97 parts of (nickel—20 parts chromium) and three parts of silicon for a period of about 2 hours. The uniform powder metal mixture is formulated into a slurry as in examples 1–9. The slurry is applied to a 60 mils thick TD-NiCr substrate in the manner illustrated in examples 1–9. The slurry is applied at a level to yield a uniform coating of about 80 mg./cm.$^2$ after the coated substrate is heated in a vacuum of about 10$^{'7E'3}$ to 10$^{'7E'4}$ torr and at a temperature of about 2,360° F. for a period of about 15 minutes.

A mixture of aluminum and cobalt powders is prepared by blending about 80 parts of aluminum and 20 parts of cobalt for a sufficient time to obtain a uniform mixture. A slurry similar to that used for the first coating is prepared and applied in essentially the same manner except that sufficient slurry is used to yield an application of about 10 mg./cm.$^2$ after the coated article is heated according to the following schedule:

heating to 2,050° F. for 1 hour
hold at 2,050° F. for 2 hours
raise to 2,100° F. and hold for 2 hours
raise to 2,150° F. and hold for ½ hour
raise to 2,200° F. and hold for ½ hour
raise to 2,250° F. and hold for ½ hour
raise to 2,300° F. and hold for 1 hour

The heating cycle is carried out in a hydrogen atmosphere in a furnace using radiation type heating.

Analysis of a sample by electronprobe indicates the composition of 5 mils of coating to be as follows:

Cr — 15-20%

Al— 4—5%

Si— 2—3%

Co—0.3–0.4%

Ni—balance

Samples of the composite when subjected to 2,300° F. oxidation tests indicate that the samples are satisfactory after about 400 hours. Uncoated TD–NiCr fails within 250 hours under similar conditions. The criterion used for failure is a weight change of 11 mg./cm.$^2$.

EXAMPLE 11

A similar process is used except that 60 mils thick TD-Ni is used as the substrate and the second coating is Al-20Co. An application level of about 10 mg./cm.$^2$ of the Al-20Co coating after heating is obtained. The analysis of 5 mils of coating is as follows:

Cr—5—10%

Al—5—9%

Si—2—2.5%

Co—0.3—0.5%

Ni—balance

Samples indicate that satisfactory performance is achieved at 2,300° F. under oxidizing conditions for over 100 hours. Uncoated TD–Ni fails after less than 5 hours at about 2,300° F.

EXAMPLE 12

Where the substrate is TD–Ni. as in table 3, sample 13, and the first coat is Ni-30Cr-1Si and the second coat is 10 mg./cm.$^2$ of Al-20Co, the actual analysis of the 5 mils of coating is as follows:

Cr—12—26%

Al— 5—15%

Si— 1—2%

Co—0.1—0.4%

Ni—balance

Additional examples using the processes and heat treatments from examples 10 and 11 are listed in table 3. Good protection can be obtained on TD–Ni substrates by increasing the amount of Al–20Co applied in the second step. However, optimum life in 2,300° F. oxidation tests appears to be at a ratio of about 10–12 to 1 in first to second coating weight.

TABLE III

[Results of oxidation tests on two-step coated TD-Ni and TD-(Ni-20Cr) samples, Second step heat treatment was as per schedule in Example 10, Substrates were 60 mils thick]

| | First step | | | Second step | | 2,300° F. oxide life (hrs,) |
|---|---|---|---|---|---|---|
| Substrate | Coating | Weight (mg./cm.²) | Temperature ° F. | Coating | Weight (mg./cm².) | |
| TD-Ni | Ni-20Cr-3Si | 79 | 2,370 | Al-20Co | 16 | 160 |
| TD-Ni | Ni-30Cr-1Si | 72 | 2,430 | Same | 5.6 | 122 |
| TD-Ni | Same | 72 | 2,430 | do | 8.7 | 168 |
| TD-Ni | do | 79 | 2,430 | do | 9.3 | 260 |
| TD-Ni | Ni-20Cr-3Si | 80 | 2,370 | do | 10.0 | 240 |

All samples bent satisfactorily after oxidation exposure.

We claim:

1. A ductile, high temperature, oxidation-resistant metal composite comprising a superalloy substrate as its principal component and a coating composition bonded to said substrate, said coating consisting essentially of nickel, chromium, aluminum and silicon in the following percentages by weight of said coating composition:

chromium— 16% to 50%

aluminum— 5% to 10%

silicon—0.5% to 3%

cobalt— 0% to 5%

nickel—balance

2. A composite according to claim 1 wherein said superalloy substrate is thorium oxide dispersion-nickel superalloy.

3. A composite according to claim 1 wherein said superalloy substrate is thorium oxide dispersion nickel-chromium superalloy.

* * * * *

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# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,620,693 Dated November 16, 1971

Inventor(s) GEORGE T. PEPINO, JR. AND LAWRENCE SAMA

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Title, please delete--AND PROCESSES FOR PRODUCING SAME--.

In the ABSTRACT insert the following paragraph directly after "substrate." --The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72Stat.435; U.S.C. 2457). Rights to practice the invention for any use primarily related to aeronautical and space applications are available through the National Aeronautics and Space Administration.--

Column 1, line 26 "attach" should read--attack--.
Column 1, lines 63 through 75 should be deleted.
Column 4, line 43 "10 '7E'3" should read--$10^{-3}$--.
Column 4, line 44 "10 '7E'4" should read--$10^{-4}$--.
Column 4, line 48 delete "aluminum," and insert--of--.
Column 4, line 74 "line" should read--time--.
Column 5, line 8 "to" should read--by--.
Column 6, line 66 "10 '7E'4"should read--$10^{-4}$--.
Column 6, line 73 "10 '7E'4" should read--$10^{-4}$--.

Column 7, TABLE I, Examples 5, 6 and 7 "Ni-30Cr-8Al-3Cb-1,0Si" should read--Ni-30Cr-8Al-3Cb-1.0Si--.

Column 7, lines 70 and 71 "10 '7E'3" should read--$10^{-3}$ and "10 '7E'4" should read--$10^{-4}$--.

Signed and sealed this 6th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents