

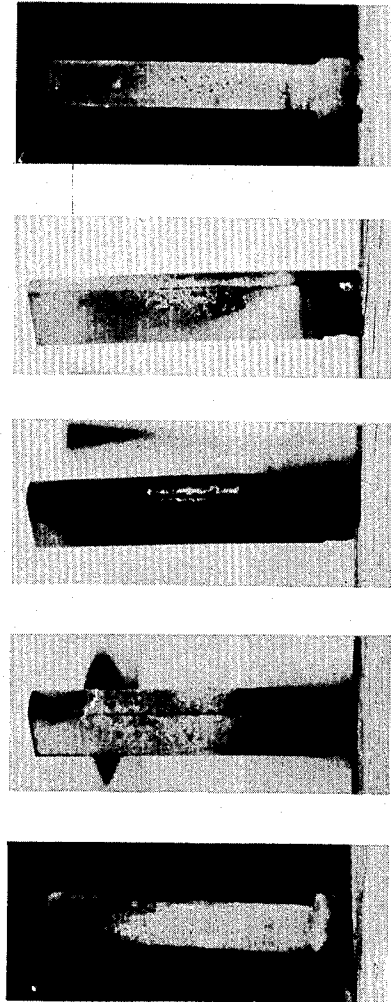
Nov. 11, 1969

F. P. TALBOOM, JR., ET AL
COATED NICKEL-BASE AND COBALT-BASE ALLOYS HAVING
OXIDATION AND EROSION RESISTANCE AT
HIGH TEMPERATURES

3,477,831

Filed Jan. 27, 1966

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SPECIMEN 1
EXAMPLE 1
COATING

SPECIMEN 2
EXAMPLE 2
COATING

SPECIMEN 3
CONVENTIONAL
Al - BASE
COATING

SPECIMEN 4
Al-10Si
COATING

SPECIMEN 5
EXAMPLE 1
COATING

EROSION TEST BARS AFTER OXIDATION-EROSION TEST OF 100
HOURS AT 2100°F.

FIG. 1

INVENTORS
FRANK P. TALBOOM, JR.
JOHN A. PETRUSHA

BY *Finnegan & Henderson*

ATTORNEYS

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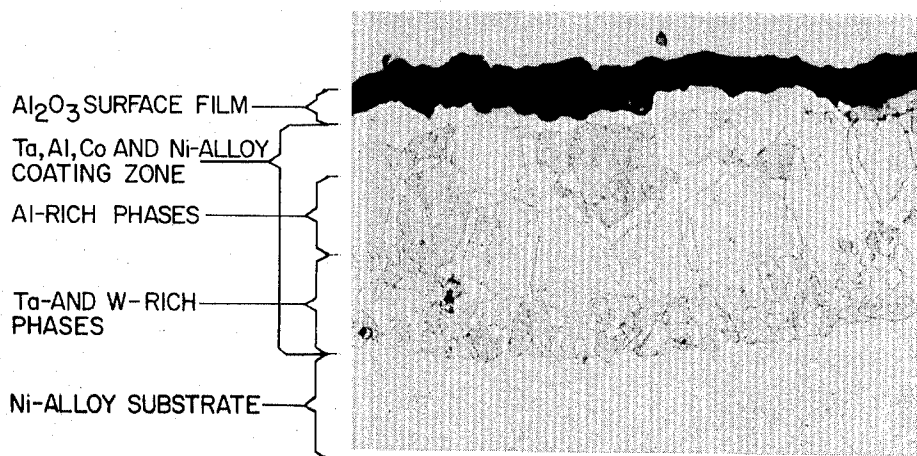


FIG. 2

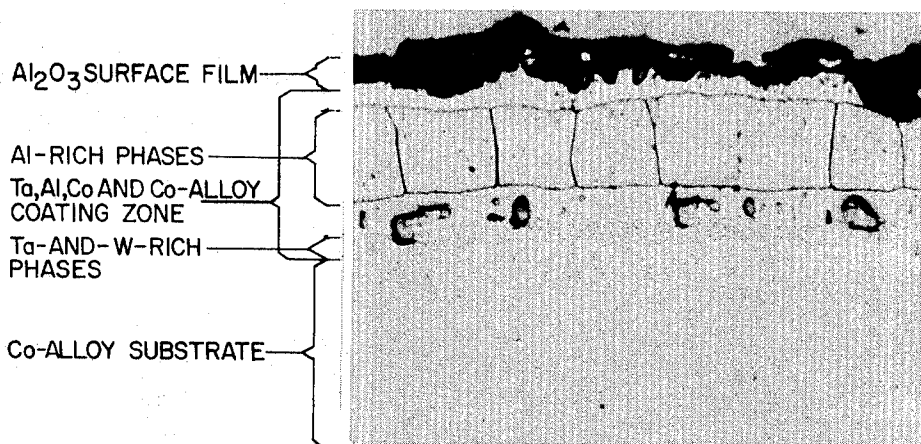


FIG. 3

INVENTORS
FRANK P. TALBOOM, JR.
JOHN A. PETRUSHA

BY *Finnegan & Henderson*
ATTORNEYS

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2

3,477,831

COATED NICKEL-BASE AND COBALT-BASE ALLOYS HAVING OXIDATION AND EROSION RESISTANCE AT HIGH TEMPERATURES

Frank P. Talboom, Jr., Glastonbury, and John A. Petrusha, Marlborough, Conn., assignors to United Aircraft Corporation, East Hartford, Conn., a corporation of Delaware

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9 Claims

ABSTRACT OF THE DISCLOSURE

An oxidation and erosion resistant coating for high temperature nickel-base and cobalt-base alloys is provided by depositing tantalum on the substrate to form a surface zone, superimposing an aluminum-containing composition on the tantalum-containing layer, said aluminum composition preferably consisting essentially of aluminum and cobalt, and diffusing the aluminum-containing composition into the tantalum coated substrate to form a coating zone comprising a Ta-modified Co-Al-substrate metal coating zone. This coating zone forms an outer Al_2O_3 film on exposure to oxidizing atmospheres.

This invention relates to novel coatings for nickel (Ni)- and cobalt (Co)-base alloys that will protect such alloys from oxidation at high temperatures, and to a method for creating such coatings.

More particularly, this invention relates to a tantalum (Ta)- modified aluminum (Al)-base coating for both Ni-base alloys having Ni as their principal component and Co-base alloys having Co as their principal component. The coatings of this invention are created by first forming a thin, uniform Ta containing layer on the surface of the substrate by a vapor deposition, pack cementation, or other suitable processes. These processes produce deposition of Ta on the substrate surface, forming a thin Ta-rich surface zone metallurgically bonded to the base metal of the substrate. An intimate mixture of Al-base powders, preferably a mixture of Co and Al powders, is then deposited on the surface of the substrate by dipping, painting or spraying it on in the form of a slurry or dispersion in an organic solvent. The powder covered substrate is then heat treated in a reducing, inert or vacuum atmosphere furnace to cause interdiffusion of the Al and preferably Co powder mixture into the substrate surface, resulting in the production of a final coating zone consisting essentially of Al, Ta, Co, and the base metal of the substrate.

The coatings of this invention provide excellent long-term protection to Ni- and Co-base substrates at metal temperatures up to 2000° F., medium-term protection at metal temperatures up to 2100° F., and short-term protection at metal temperatures up to 2200° F. or more under conditions of high velocity gas erosion such as typically are encountered in a gas turbine engine.

It is noteworthy that the coatings of this invention provide highly superior protection for both Ni-base alloys and Co-base alloys.

Although Ni-base alloys typical of those in current use do not begin to melt until the temperature of about 2380° F. is reached, such alloys in gas turbines, if unprotected, fail rapidly at turbine inlet temperatures of 1800° F. or above. The mechanism of failure is by preferential inter-granular oxidation attack at grain boundaries or by general or gross oxidation. Penetration at grain boundaries leads to notches in the loci of penetration, and stresses created at these notches in turn can lead eventually to mechanical failure of the part. An important func-

tion of the coatings of this invention is to prevent such inter-granular oxidation attack on Ni-base alloys.

Co-base alloys generally present more serious oxidation problems than Ni-base alloys. The Co-base alloys are generally subject to higher temperatures in use than their Ni-base alloy counterparts. Co-base alloys thus are subject to more rapid general oxidation attack.

Virtually since the introduction of jet aircraft engines during World War II pressures have existed for their constant upgrading. The importance for upgrading has been in large part created by the fact that slight increases in turbine inlet temperatures can provide significant increases in thrust. In turn, slight increases in thrust yield important increases in engine efficiency and economy, but as turbine inlet temperatures are increased performance requirements for engine parts become much more demanding. Current engines using parts with available coatings are rated at turbine temperatures of about 1900° F. More advanced engines being made today operate at turbine inlet temperatures of about 2000° F. for constant operation. Work is being done on engines designed to run at turbine inlet temperatures of about 2100° F.

Metal temperatures of turbine blades are nominally 250 to 300° F. below turbine inlet temperatures in a given engine, but hot spots can be caused in blades and they may go through heat zones that causes them to reach turbine inlet temperatures. Momentary engine "overshoots," or sudden but brief increases in turbine inlet temperatures caused, for example, by large thrust demanded on take-off or by a spurt of fuel admitted to the combustion chamber at anytime during operation, can result in increases in turbine inlet temperatures of as much as 300° F. above constant operation temperatures. Such "overshoots" can cause corresponding temporary increases in turbine blade metal temperatures of about 300° F. above normal. The clear need thus exists for higher temperature coatings that will give good protection to Ni-base and Co-base alloys at metal temperatures up to at least 2100° F.

Further, the coatings of this invention are designed for use on both turbine blades and turbine vanes. The turbine vanes can reach temperatures as high as 200° F. above turbine inlet temperature. Thus, it will be seen that oxidation protective coatings at extremely high temperatures are greatly needed in the industry.

The highest turbine inlet temperatures that uncoated blades can stand without rapid failure due to high velocity gas erosion is about 1800° F. Better existing coatings, such as Al-10 Si, will protect blades at turbine inlet temperatures up to about 1900° F. By contrast, however, the coatings of this invention give superior protection to Ni-base alloy blades against high velocity gas erosion for times up to 5,000 hours or more at turbine inlet temperatures of at least 2100° F. The coatings of this invention will also give short time protection to Ni-base alloys at turbine inlet temperatures up to at least 2400° F., thus affording reliable protection against momentary engine overshoots.

Existing coatings such as the Al-10 Si coating discussed above are completely unsatisfactory on Co-base alloys, and do not provide adequate protection even up to turbine inlet temperatures of about 2000° F., at which temperature severe spalling problems may occur. However, the coatings of this invention afford long time protection to such Co-base alloys at much higher turbine inlet temperatures of up to around 2200° F.

Expressed in terms of metal temperatures, the coatings of this invention provide protection for Ni-base alloys and Co-base alloys at temperatures up to about 2200° F. for times of about 50 hours with ability to protect at even higher temperatures for shorter periods of time. They achieve a coating life of over 400 hours

at metal temperatures of about 2000° F. on Ni-base alloy and a coating life of over 300 hours at metal temperatures of about 2000° F. on Co-base alloys. The coatings of this invention have a life of many thousands of hours on both Ni-base and Co-base alloys at metal temperatures of about 1800° F.

Stated more generally, it has been found that the coatings of this invention provide oxidation resistance to Ni-base alloys and Co-base alloys at temperatures about 100° F. in excess of the temperatures to which such protection is afforded by any previously known coatings for such alloys, and provide protective coatings lives twice as long as those provided by any such known coatings at any given temperature.

As engine temperatures go up, problems multiply. This invention meets the need for a superior coating that will fulfill the requirements imposed by higher engine operating temperatures. The final product of this invention achieves both a high surface melting point and outstanding oxidation resistance. In protecting turbine blades and vanes at higher operating temperatures, melting temperatures of coatings are of considerable importance. Basically, coatings must be oxidation resistant. However, once oxidation resistance is achieved, the relatively low melting points of some prior aluminide type coatings can become a severely limiting factor preventing further increase in turbine inlet temperatures. There has thus been a long-felt need for coatings having both superior oxidation resistance and high melting points that would be able to withstand the exigencies of higher engine operating temperatures without failure.

Existing coatings furnish adequate oxidation resistance at turbine inlet temperatures up to 1900° F., but when the turbine inlet temperature is moved up to 2100° F., these coatings become subject to melting by exposure to hot spots or momentary engine overshoots. Characteristically, coatings on Ni-base and Co-base substrates tend to soften at temperatures below their melting points. The closer the melting point is approached, the softer the coating becomes. As exposure temperatures of coatings are increased, erosion is accelerated by softening of the coating. Coatings thus can be caused to fail by gross erosion when exposed to high velocity turbine gas at temperatures appreciably below their melting points, a characteristic that again emphasizes the importance of a high melting point for a satisfactory coating.

A concomitant problem has been to achieve a coating that in spite of its having a high melting point can nevertheless be applied at a temperature that is compatible with the heat treating temperature of the Ni-base and Co-base substrates. In most Ni-base alloys and Co-base alloys for turbine blades and vanes a good temperature for initiation of heat treating is about 1975° F. Ideally, then a coating for such blades should be capable of being applied at this temperature. It is a beneficial result of this invention that the coatings taught can be applied at the relatively low heat treating temperatures characteristic of Ni-base and Co-base substrates but still yield coatings having much higher melting points than their application temperatures.

The improved oxidation protective coatings of this invention have desirably high melting points in excess of the maximum temperature limits to which existing Ni-base and Co-base alloys can be exposed without encountering melting or unacceptable softening of the substrate itself.

Generally, as engine operating temperatures are increased, oxidation resistance is lower; erosion is increased; and more frequent inspection and replacement of engine parts is required. Although they extend the life of engine hardware, current production coatings do not provide the protection and longevity required for extended use of engines in the 1800–2000° F. turbine inlet temperature range. Such coatings are inadequate for these high engine operating temperatures because as the turbine inlet

temperature is raised these coatings display the following inadequacies:

(1) Excessive interdiffusion between coating and substrate takes place with consequent dilution of coating composition and lowering of its protection potential.

(2) Melting points of existing coatings are close to metal temperatures experienced in higher temperature engines.

(3) At such temperatures existing coatings offer insufficient oxidation resistance.

(4) When their melting points are closely approached, such coatings suffer from excessive gas erosion by the turbine gas stream.

(5) Some existing coatings, when applied to Co-base alloys, become highly susceptible to spalling as engine temperatures are increased.

(6) As higher engine temperatures are used more rapid interdiffusion between the coating and the substrate occurs, diffusing components such as Al from the coating into the substrate, leaving no Al at the surface for the formation of Al-oxide or other protective oxide films on the outer surface of the substrate, which oxide films provide the primary oxidation resistance of the coatings.

(7) As exposure to high temperature oxidation continues, the adherence between the Al-oxide (Al_2O_3) pellicular film on the outer surface of the coated substrate and the remaining portion of the coating deteriorates. Since the primary oxidation resistance of the coating is afforded by this outer Al_2O_3 film, the loss of adherence between this film and the coated substrate greatly reduces the effectiveness of the protection afforded by the coating, and renders the coated article subject to extensive oxidation attack.

In view of the foregoing, it is a primary object of this invention to provide as a new and improved article of manufacture a Ni-base or Co-base alloy substrate having an oxidation protective coating metallurgically bonded thereto comprising a Ta-rich coating zone located between the substrate and an aluminum oxide (Al_2O_3) outer coating film located at the surface of the coated composite, which article achieves greatly improved adherence between the outer Al_2O_3 oxidation protective coating surface film and the remainder of the coated Ni-base or Co-base composite article, and to provide a process for producing such an article.

Another object of this invention is to provide for Ni-base and Co-base alloys a new and improved Ta-modified Co-Al coating composition that has a melting point in excess of the upper limit of temperatures to which existing Ni-base and Co-base alloys can be exposed without melting or unacceptable softening of the substrate.

It is another object of this invention to provide a superior coating for Ni-base and Co-base alloys that can be applied by heat treatment at relatively low temperatures, but when once applied will have a melting point well above such temperatures.

A further object of this invention is to provide a new and improved coating composition for Ni-base and Co-base alloys that has a high melting point and also possesses room temperature ductility. The latter characteristic of such coatings makes them capable of deforming with indentations or defects imposed on the coated parts, thus making the coatings resistant to failure from ballistic impact at low temperatures.

Another object of this invention is to provide a new and improved coating for Ni-base and Co-base turbine blades and vanes that will enable them to be operated at temperatures where they can perform more efficiently and still be protected from failure through inter-granular oxidation attack.

Yet another object of this invention is to provide a process for applying a Ta-modified Co-Al coating composition to Ni-base and Co-base alloys, which process achieves oxidation protective coatings on such alloys having more uniform Ta content than has been heretofore

possible, and results in greatly improved adherence of the Al_2O_3 coating surface film to the remainder of the coated composite.

A still further object of this invention is to provide an improved process for applying Ta-modified Co-Al coatings on Ni-base and Co-base alloys which results in the production of improved oxidation protective coatings on such alloys having vastly superior adherence between the Al_2O_3 outer coating surface film and the remainder of the coated composite; which adherence provides superior high temperature oxidation resistance to the alloys coated by this process.

Additional objects and advantages will be set forth in part in the description that follows, and in part will be obvious from the description, or may be learned by practice of the invention, the objects and advantages being realized and attained by means of the compositions, methods and processes, particularly pointed out in the appended claims.

To achieve the foregoing objects and in accordance with its purposes, this invention in a preferred embodiment provides an article of manufacture having good stress rupture strength at high temperatures, high-temperature oxidation resistance, and resistance to cyclic thermal fatigue failure which comprises a substrate consisting of essentially a Ni-base alloy or a Co-base alloy, the article having a defect, oxidation, interdiffusion, thermal shock, melting, and erosion resistant surface zone metallurgically bonded to the surface zone and consisting essentially of a Co-Al composition having atomic ratio of Co to Al from 2:5 to 1:1, which Co-Al composition is modified by from 0.1 to 1.0% by weight of the surface zone of Ta, the surface zone being further characterized by ductility at room temperature, and a melting point higher than that of the substrate.

It should be understood that the coating zone of this invention consists essentially of an interdiffusion product of the base material of the substrate, Ta, which is applied in the first process coating step, and Co and Al which are applied in the second process coating step. Therefore, the composition of the coating zone will consist essentially of Co, Al, and Ta, as described in the above embodiment, only when the substrate being coated is substantially pure Co. If the substrate is substantially Ni, then the coating zone consists essentially of a Co-Ni-Al composition having an atomic ratio of Co-Ni to Al or from 2:5 to 1:1, which Co-Ni-Al composition is modified by from 0.1 to 1.0% by weight of the surface zone of Ta.

In like manner, where the substrate is a Co alloy or a Ni alloy, the surface zone will consist essentially of the particular alloy of the substrate together with the Co of the second coating composition in an atomic ratio to Al of 2:5 to 1:1, with the overall Co-Ni alloy-Al or Co-Co alloy-Al composition being modified by from 0.1 to 1.0% by weight of the surface zone of Ta.

In a more general form this invention provides an oxidation-resistant article having a Ni-base or Co-base substrate and an oxidation and erosion resistant coating zone metallurgically bonded to the substrate which comprises a Ta-rich subzone adjacent to the substrate, and an aluminum-base outer coating zone having an oxidation resistant Al_2O_3 surface coating film adherently bonded to the remainder of the coated composite article. The overall coating contains Al, the Ni- or Co-alloy of the substrate and Ta. The Ta is present in the overall coating in amounts from 0.1 to 1.0% by weight. The Ta is deposited on the substrate in accordance with the Ta-deposition first step of the process of this invention. The Al_2O_3 surface film, located at the outer surface of the coated article, provides primary oxidation and erosion resistance. However, for this resistance to be effective at the temperatures and for the time periods contemplated by this invention it is necessary that this Al_2O_3 surface film have good adherence to the remainder of the coated composite. Such adherence has been found to be achieved by inter-

posing a Ta-rich coating subzone between the substrate and the Al-base surface coating zone which provides the Al for the formation of the Al_2O_3 surface film. Thus the Ta-rich subzone promotes the superior adherence of the Al_2O_3 surface film which is the key to the improved oxidation and erosion resistance provided by the coatings of this invention.

Any Al-base coating composition can be used to supply the Al for formation of the Al_2O_3 surface film, including pure Al and various Al-based compositions. Al-Co compositions have produced particularly beneficial results and are the preferred second coating compositions of this invention.

As used in this specification and in the appended claims, the terms "Ni-base alloy" and "Co-base alloy" will be understood to include both pure Ni and Co substrates and those alloys in which Ni and Co, respectively, is the principal component and is present in an amount of not less than 40% by weight of the alloy.

The invention further comprehends a two-step process for producing a coated metal article having good stress-rupture strength at high temperatures, high-temperature oxidation resistance, and resistance to cyclic thermal fatigue failure, the article comprising a metal substrate consisting essentially of a Ni-base alloy or a Co-base alloy, and the method comprising the first step of forming a thin Ta-containing layer at the surface of the article being coated by vapor deposition, pack cementation, or equivalent processes, this Ta-containing zone consisting essentially of uniformly distributed Ta and the base metal of the substrate; and the second step of contacting the Ta coated substrate with a mechanical mixture of finely divided powders consisting essentially of 5 to 40% by weight of Co, and the balance Al, placing the substrate while in contact with the metal powders in an inert, reducing or vacuum atmosphere, and heating the substrate while in contact with the metal powders to a heat treatment diffusion temperature of from 1600 to 2100° F. for a time period sufficient to create a coating zone on the substrate, adherently and metallurgically bonded thereto, which coating zone has a Ta-modified Co-Al-substrate base metal composition.

The first step of the process of this invention is the Ta-deposition step, resulting in the formation of the Ta-rich coating zone on the substrate surface. This step is carried out by a process which will promote and effect diffusion between the Ta and the substrate, resulting in metallurgical bonding of the Ta-coating zone to the substrate, by the formation of an intermetallic composition between the Ta and the alloy of the substrate. Thus the coating zone produced in this first stage of the coating process of this invention consists essentially of Ta and the base metal of the substrate, i.e., the Co- or Ni-alloy. The first stage of this process is therefore carried out by vapor deposition using tantalum halides, by a pack cementation process or by other suitable procedures.

In the vapor deposition process the Ni- or Co-alloy substrate is heated to a temperature sufficient for the desired interdiffusion of the Ta into the substrate to occur, generally about 1400 to 2200° F., and at such temperature, is exposed to the Ta halide vapors in the presence of a reducing atmosphere. This results in the formation of a hydrogen halide gas which is vented from the reaction zone, and the deposition of Ta on the substrate and its interdiffusion into the substrate to form a Ta-Ni-(or Co-) alloy coating zone of the desired thickness, metallurgically bonded to the substrate.

The so-called "pack cementation" process is a form of vapor deposition, in which the object to be coated, i.e., the Ni- or Co-alloy is surrounded by a particulate pack mixture containing, for example, the metal to be reacted with or deposited on the object to be coated (e.g., Ta), an activator or energizer (usually a halide salt, such as, NaCl, KF, NH_4I , NH_4Cl , and the like), and an inert filler material (e.g., Al_2O_3 , SiO_2 , BeO, MgO, and the like).

This mixture, held in a suitable container (steel box, graphite boat, or refractory oxide crucible, for example), is then heated to a desired coating temperature, in a prescribed atmosphere, and held for a length of time sufficient to achieve the desired coating. In the instant process the pack-cementation process is carried out at a temperature of from 1600 to 2200° F., and preferably at 2000° F. for a time period of two to 16 hours, and preferably about 4 hours, under a high vacuum, preferably on the order of about 1 micron or less. When conducted properly, the pack-cementation process will result in a controlled-thickness Ta-containing coating on the Co- or Ni-base alloy substrates coated in accordance with this invention. The coating zones on these substrates consist essentially of Ta and the metal or metal alloy of the substrate, and will be metallurgically bonded to the substrate by the Ta-alloy intermetallic reaction products formed during the Ta-deposition step. The coating zone is characterized by a uniform distribution of Ta.

The Ta-containing first coating zone produced in the first step of this invention generally has a thickness of from about 0.2 mil to about 1.5 mil. The thickness of this coating zone is preferably between about 0.4 and about 0.5 mil, and a thickness of about 0.5 mil is considered optimum.

The use of vapor deposition, pack-cementation or other equivalent processes which promote diffusion between the Ta and the substrate in the first stage of the instant process is important to the effective production of the coatings of this invention. It may also be possible to use such processes as electroplating or plasma-spraying to apply the Ta in the first stage of this process, provided the Ta can be subsequently properly diffused into the surface of the substrate by heat treatment. However, such processes have not produced coatings equivalent to the vapor deposition and pack-cementation steps described above, and hence the latter procedures are preferred.

Following the formation of the Ta-substrate alloy coating zone, the Ta coated Co- or Ni-alloy substrates are preferably subjected to a further diffusion step. Optimum results are generally obtained by subjecting the Ta-coated substrate resulting from the vapor deposition or pack-cementation step described above to further diffusion heat treatment at a temperature of about 1600 to 2200° F. for an additional 2 to 16 hour period in a vacuum atmosphere of preferably less than 1 micron. This optional step results in more complete diffusion of surface Ta into the coating zone at the surface of the substrate, resulting in a more Ta-rich surface zone. This additional step may also be beneficial in removing any hydrogen dissolved in the Ta.

This optional additional heat treatment diffusion step, like the initial pack cementation or vapor deposition step, need not be carried out under a vacuum, but may be carried out under an argon or other inert atmosphere or under hydrogen. In neither of the latter instances the heat treatment diffusion step will be effected at atmospheric pressure.

After the Ta coating step of the process has been completed, the surfaces of the tantalum coated article can be cleaned by vapor blast to prepare the article for application of the Co-Al second coating composition. Exemplary of such cleaning is a vapor honing for one minute with —325 mesh Al_2O_3 at 40 p.s.i. Use of this vapor blast rather than a more conventional dry grit blasting with a heavier Al_2O_3 grit minimizes the chance of stripping the Ta-coating zone from the substrate surface during cleaning. It is preferable to omit this surface cleaning step if possible, i.e., if a surface receptive to the subsequent Co and Al coating step can be presented without the need of surface cleaning.

Of course, subject to limitation of such possible stripping, and the preferred omission of any cleaning step, the Ta coated substrate surface can be cleaned by any conventional technique for removal of dust or dirt par-

ticles, such as by water rinsing, liquid blasting, washing in suitable organic and inorganic solvents, and any other method of cleaning that is standard in the art. As pointed out above, care should be taken in cleaning the Ta-coated substrate to insure that it is not injured. It will be appreciated that any of the above standard cleaning processes can also be used to clean the Co- and Ni-alloy substrates prior to the initial Ta coating stage of the process.

The Co and Al powders preferably used as the second coating composition, in the second step of the process of producing the coatings of this invention, usually have 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 may also be used. Especially good results are obtained when the size range of the Co and Al powders 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 can be said that the finer the particles, the better the coatings produced. The mesh sizes referred to above are Tyler Standard.

The metallic dust or powders of Co and Al described above can be applied to the Ta coated Ni-base or Co-base alloy part, metal core, or substrate, to be treated in any suitable manner. A fine film of the Co and Al powders can thus be blasted or dusted onto the specimen; or a dispersion of the powders in a solvent liquid can be applied to the substrate, after which the solvent can be evaporated leaving a coating of the powder mixture on the substrate. Other methods of applying the Co and Al powder mixture will readily suggest themselves to persons skilled in the art.

In accordance with the preferred embodiment of this invention, a Co and Al powder mixture is dispersed in a suitable liquid dispersant, and the resulting dispersion is applied to the substrate by spraying, brushing, dip-coating, or any other conventional method.

The ratio of Co and Al powder mixture to liquid dispersant may vary from about 1 to 5% by weight or higher. The liquid dispersant can be very suitable, readily volatilizable organic solvent, or mixture of solvents. Among the solvents that can be used are alcohols, such as, methyl, ethyl, propyl, and butyl alcohol, esters such as methyl, ethyl, propyl, butyl, and amyl acetate, and ketones, such as, for example, acetone.

The organic solvents mentioned are illustrative and not limiting. It should be understood that almost any volatile liquid that will act as a suitable dispersant for the Co and Al powder mixture can be utilized, and any such liquid 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 temperatures to act as a dispersant for the metallic powders 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 described below.

If desired, a binder or sticking agent can be added to the liquid dispersant to hold the powder mixture to the surface of the substrate after evaporation of the solvent. Use of a binder enables the powders to adhere to the substrates for prolonged periods of time, thereby precluding the necessity of heat treating immediately after application or of taking special precautions in handling the treated substrate. The binder should be one that will be substantially completely decomposed during diffusion heat treatment or at a temperature below actual diffusion heat treatment temperature. Suitable binding and sticking agents that can be used include nitrocellulose, naphthalene, and stearates. Other sticking or binding agents will be readily apparent to those skilled in the art.

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

The dispersion of Co and Al powder described above in either a liquid or lacquer dispersant, i.e., a dispersant con-

taining 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 of Co and Al powder mixture on the substrate. As pointed out above, the second coating composition, in accordance with the broadest teachings of this invention, can be pure Al or any Al-base composition suitable for formation of the Al_2O_3 surface oxidation protective film. However, the invention is here described in terms of the use of the preferred Co-Al second coating composition.

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 substrate.

Evaporation of the volatile solvent or volatile portion of the lacquer containing a sticking agent can be conveniently brought about by allowing the coated substrate to be stored in an atmospheric environment at ordinary temperatures. If desired, suction or vacuum and elevated temperatures can also be used to accelerate evaporation of the volatile solvent. Evaporation of the solvent leaves a fine layer of Co and Al powder mixture on the surface of the substrate including any walls or sides defining interstices, slots, holes, and so forth, that may be present in the substrate.

No separate step is necessary for evaporation of the solvent from the powder dispersion after its application to the previously Ta coated substrate. After the dispersion is applied to the substrate, it can be immediately heat treated, and the solvent will be flashed off or evaporated during this heat treatment.

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

Preferably the mixture of cobalt and aluminum powders is formed into a slurry with the dispersant or binder or sticking agent. The substrate can then be dipped into the slurry or the slurry can be sprayed or brushed on to the substrate. The substrate in turn can be masked in selective areas to prevent adherence of the slurry or dispersion to such masked areas and to prevent the formation of any coating on such areas during subsequent heat treatment. These same areas can also be masked during the previous Ta-deposition step or the Ta applied in that step can be removed from the surfaces to be masked during the Co and Al coating application by grinding, or other machining techniques.

The amount of Co and Al powders applied to the Ta-coated substrate can vary from substrate to substrate. But in general, an amount between about 10 milligrams per square centimeter of substrate area and about 30 milligrams per square centimeter of substrate area is contemplated. Such amounts result in production of a coating of the desired thickness after heat treatment of the Co and Al second coating composition.

Preferably after allowing the solvent to be completely evaporated from the substrate, the resulting specimens are heat treated in a suitable furnace or oven to cause diffusion of the Co and Al into the previously Ta modified substrate surface zone, thereby producing the improved coatings of this invention. Heat treatment temperatures of from 1600 to 2100° F. are used in this heat treatment step, and temperatures of 1950 to 2000° F. are preferred.

The heat treatment period can vary from about 1 hour to 20 hours or more. Particularly good results are achieved when the heat treatment is carried out for about 4 hours.

In accordance with the present invention, superior coatings are produced by heat treatment of the Co and Al second coating composition in a hydrogen atmosphere furnace. The diffusion is carried out under atmospheric pressure, or preferably at a pressure slightly greater than atmospheric. The hydrogen atmosphere is particularly critical and should have a maximum dew point of -40° F. or less, preferably -60° F. It is important that the hydrogen be as completely free of oxygen as possible.

Although a high purity hydrogen atmosphere furnace is preferred for the final heat treatment step used in producing the coatings of this invention, it is also possible to use a high purity argon or other inert atmosphere or a vacuum atmosphere heat treatment step.

The second coating composition of this invention in its preferred form contains 5 to 40% by weight of Co and 60 to 95% by weight of Al. An optimum composition contains 80% by weight of Al and 20% by weight of Co.

The final coating produced by the two step process of this invention, described above, consists essentially of Co, Al, Ta, and the base metal or metal alloy of the substrate. This coating zone has a thickness of from 2 to 6.5 mils. A coating thickness of about 5.5 mils is optimum.

Of the essence of the present invention is a dramatic and unexpected increase in the effectiveness of Al-base coatings on Ni- and Co-base alloy substrates achieved by first forming on the substrate a thin, uniform Ta-containing coating zone, and subsequently applying and interdiffusing into the Ta-containing coating zone an Al-base coating composition, preferably consisting essentially of Co and Al.

The resulting coating consists essentially of Co, Al, Ta, and the base metal or alloy of the substrate. The coating thus preferably contains Co from the second coating composition, and a Co-alloy or Ni-alloy from the substrate, in aggregate, in an atomic ratio to Al of from 2:5 to 1:1, and the Co-alloy-Al composition is modified by 0.1% to 1.0% by weight of the coating zone of Ta.

The coatings produced in accordance with this invention have a more uniform distribution of Ta throughout the coating zone, and hence a higher useful Ta content than can be achieved by any previously known process. Comparable coatings can not be obtained merely by applying a mixture of Ta, Co, and Al powders on the substrate and subsequently heat treating. Such coatings were produced on Mar-M200 Ni-base alloys using a coating composition having a Co:Ta:Al ratio of 1:3:8, by weight. The as-coated articles were found to contain no Ta at or near the coating-substrate interface.

The Ta modifier uniformly present in the coatings of this invention produces unexpected beneficial results, including increasing the diffusional stability of the coating, and most importantly in unexpectedly improving the adhesion between the Al_2O_3 surface oxide layer formed on the coating during oxidative exposure and the remainder of the coated composite, thereby greatly improving the oxidation resistance of articles produced in accordance with this invention. These coatings provide oxidation protection at temperatures 100° F. in excess of any temperatures to which equivalent protection is provided by existing coatings for Ni- and Co-base alloys, and provide endurance life and oxidation exposure of twice as long as that provided by previously available coatings for such alloys.

In addition, the coatings of this invention are not susceptible to the acute spalling problems which have heretofore been encountered in attempts to provide oxidation protective coatings for Co-base alloys.

It is important that the cobalt and aluminum powders used in forming the coatings of this invention be of the highest purity obtainable. Co and Al powders should be of 99% or greater purity. Inclusion of even small amounts of silicon (Si) may prove undesirable. Even though gross

oxidation resistance may not be affected, Si may cause unacceptable reduction in the melting point of the coating through introduction of low melting phases between Al and Si as well as between Ni or Co and Si. Si may also adversely affect the ductility of the coatings produced.

Titanium (Ti) is also preferably avoided, since it confers no benefit to the coating and may lower its heat resistance. Ti may also tend to degrade the beneficial diffusion arresting effects that Ta has on Al. If metal powders of the highest purity obtainable consistent with economic factors are used, the danger of undesirable side effects from additional elements introduced as impurities is greatly reduced.

For a clearer understanding of the invention, specific examples of it are set forth below.

EXAMPLE 1

A Ni-base alloy called Mar-M200 and having the following nominal composition by weight:

Ni-12.5W-10Co-9Cr-5Al-2Ti-1Cb-0.15C-0.05Zr-0.015B is subjected to a pack cementation process as follows. An alloy specimen is surrounded by a particular pack mixture containing Ta, NH_4Cl and Al_2O_3 , which mixture is held in a graphite boat. The pack, containing the alloy specimen is then heated to a temperature of 2000° F. at a vacuum of about 1 micron and held at that temperature for about 4 hours.

During this treatment the Ta reacts with the Ni-alloy substrate to form a surface zone about 0.5 mil thick containing intermetallic reaction products of Ta and the alloy of the substrate.

The alloy specimen was prepared for the pack cementation process by grit blasting its surface with No. 60 Al_2O_3 grit at 40 p.s.i. for 2 to 5 minutes, followed by degreasing with trichlorethylene at 180° F. for 5 to 10 minutes.

After the pack cementation process resulting in the formation of the 0.5 mil thick Ta containing surface zone on the alloy substrate was completed, the Ta-coated alloy specimen was subjected to a further heat diffusion step by heating it at a temperature of 2000° F. for 4 hours in a vacuum furnace at a pressure of less than 1 micron.

The surface of the Ta-coated alloy specimen was then cleaned by vapor honing for 1 minute with —325 mesh Al_2O_3 at 40 p.s.i. The specimen was then ready for application of a Co-Al second coating composition.

A mixture of high purity metallic powders of the following composition was prepared:

50 grams of analytical grade Co powder (—325 mesh or finer)

200 grams flake Al powder (7 microns)

The following liquid dispersant was also prepared:

680 milliliters nitrocellulose lacquer, Pratt and Lambert No. 2012 (primarily amyl acetate and nitrocellulose binder).

A ball mill container was filled with a minimum of 5 pounds of 1 inch diameter porcelain milling balls or enough balls to fill the container $\frac{1}{3}$ full. A measured quantity of Co and Al powder mixture was then placed in a container and a measured amount of liquid dispersant was added until the balls, powder and liquid in the container filled it from $\frac{1}{2}$ to $\frac{3}{4}$ full. The contents of the ball mill were then milled to a slurry for from 8 to 16 hours at about 14 r.p.m.

For good results the viscosity of the slurry was kept at between about 600 and 1000 cps. at 65 to 85° F. as measured with a Brookfield Viscometer using the No. 1 spindle at 10 r.p.m. or equivalent. If necessary, the viscosity was reduced by adding additional dispersant and mixing thoroughly once more, either by ball milling or rotating the container without milling media for approximately 1 hour. If the viscosity was too low it was increased by adding additional Co and Al powder mixture and milling as described or by blending with a slurry of a higher viscosity and milling, as described, for 1 hour.

The resulting dispersion was then sprayed onto the previously Ta-coated Ni-alloy specimen.

The solvent was evaporated by allowing the specimen to stand at room temperature. Following evaporation of the solvent, the specimen, with it adhered applied powders, was placed in a hydrogen atmosphere cyclic furnace at 2000° F. High purity hydrogen having a dew point of about —60° F. was introduced into the furnace to a pressure slightly exceeding atmospheric.

Diffusion heat treatment was carried out on the coated Ni-alloy specimen for 4 hours at 2000° F. and under a pressure of hydrogen slightly greater than atmospheric.

After the diffusion heat treatment was completed, the hydrogen atmosphere was maintained and the coated specimen was cooled to 500° F. It was then removed from the furnace and allowed to cool to room temperature.

The resultant alloy article had an interdiffused coating zone about 5.5 mils thick adherently bonded to the alloy substrate consisting essentially of Co, Al, Ta and the Ni-alloy of the substrate.

The coating of this example was subjected to a dynamic oxidation testing environment, i.e., to flowing air at 2100° F., for 100 hours. During this time no coating failure was observed. To graphically illustrate the superiority of the coatings of the present invention over well known existing coatings, erosion bar specimens made up according to Example I were simultaneously oxidation-erosion tested with certain commercially available coatings on similar alloy substrates. The coating compositions, substrate compositions and heat treatment time of these various test samples are set forth in Table I below:

TABLE I

Specimen No.	Coating composition	Substrate composition	Heat treatment
1-----	Example I-----	Ni-12.5 W-10 Co-9 Cr-5 Al-2 Ti-1 Cb-0.15 C-0.05 Zr-0.015 B-1 Si ²	2,000° F., 4 hours (hydrogen).
2-----	Example II-----	Co-20 Cr-15 W-10 Ni-1.5 Mn-0.1 C-0.3 Fe-0.25 Zr ³	1,800° F., 4 hours (hydrogen).
3-----	Chromalloy UC ³	Co-21.5 Cr-10 W-9 Ta-1.5 Ni-1 Fe-0.86 C-0.25 Zr ⁴	Pack-cementation.
4-----	PWA-47 ⁵ -----	Ni-18.5 Co-15 Cr-5 Mo-4.3 Al-0.4 Fe-3.3 Ti-0.1 Cu-0.07 C-0.03 B ⁶	1,975° F., 4 hours (hydrogen).
5-----	Example I-----	do. ⁶ -----	2,000° F., 4 hours (hydrogen).

¹ Mar-M200, cast Ni-base alloy, Martin Metals Co.

² L-605, wrought Co-base alloy.

³ Al-base coating, deposited by pack cementation.

⁴ Mar-M302, cast Co-base alloy, Martin Metals Co.

⁵ Al-1081 (by weight) coating, deposited by slurry spraying with diffusion heat treatment.

⁶ Udmet 700, wrought Ni-base alloy.

Both of the conventionally coated alloy specimens failed due to generalized oxidation prior to reaching 100 hours of oxidation testing. This is clearly illustrated by visual examination illustrated by FIGURE 1 which shows general erosion of all the coated specimens of Table I except for the three bars coated in accordance with the teachings of this invention and designated "Example I" and "Example II" in FIGURE 1. The "Example I" and "Example II" bars were still in excellent condition after 100 hours of dynamic oxidation testing.

FIGURE 2 is a photomicrograph of a trailing surface of the Ta and Co-Al coated Mar-M200 Ni-base alloy erosion bar produced in accordance with Example I, and enlarged 500 times to show the composition of the coating after oxidation-erosion testing in flowing air for 100 hours at 2100° F. This photomicrograph (FIG. 2) shows the Al_2O_3 surface film at the exterior surface of the coated article and underneath this a coating zone consisting essentially of Ta, Al, Co and the Ni-alloy of the substrate. At the substrate-coating interface the metallurgical bonding between the substrate and the coating zone is clearly shown. Ta-rich, Al-

rich, and W-rich phases in the coating are also shown in FIG. 2.

It was noted in carrying out the above comparative oxidation-erosion tests that the thickness of the coatings of this invention was greater than the deposited thickness of any of the commercial coatings. Therefore, in order to determine whether this increased coating thickness was responsible for the improved oxidation resistance of these coatings a Ni-base alloy specimen having the composition Ni - 12.5W - 10Co-9Cr-5Al-2Ti-1Cb-0.15C-0.05Zr-0.015B and a Co-base alloy specimen having the composition Co - 20Cr - 15W-10Ni-1.5Mn-0.1C- $<3\text{Fe}$ - $<1\text{Si}$ were each coated with a single layer of a CoAl coating applied in the same manner used to apply the second coating composition of Example 1. The coating in each instance was applied to a thickness of 5.5 mils, and the samples were then oxidation erosion tested at 2100° F. Both of these specimens failed in less than 100 hours, the Ni-alloy specimen failing by localized oxidation and the Co-alloy specimen failing by coating spalling. These tests showed that the greater coating thickness of the coatings of this invention was not primarily responsible for the superior oxidation and erosion protection which they afford.

A Ni-base alloy specimen prepared in accordance with the procedure of Example 1 was thermal fatigue tested by exposure to a combustion flame of JP-5 fuel (a high flash point kerosene-type jet fuel) and air providing an atmosphere closely approximating that encountered in a gas turbine engine. The sample was initially exposed for 30 minutes at 2000° F. to the combustion flame, and was subsequently exposed for 100 cycles of 1 minute at the 2000° F. temperature followed by 30 seconds at a cold 200° F. temperature. The cooling was provided by a cold air blast in the absence of the flame. Upon completion of the 100 cycles the part was inspected and the entire process repeated until coating failure or until 1400 cycles were completed. The total 1400 cycles consisted of:

600 cycles at 2000° F., followed by
400 cycles at 2100° F., followed by
400 cycles at 2200° F.

At the completion of the test the samples were examined by optical microscopy.

The Ni-base alloy specimen coated in accordance with Example 1 completed 1500 cycles of testing in this manner (700 cycles at 2000° F.). The base metal alloy cracked at 1000 cycles, but no coating spalling had occurred at the completion of 1500 cycles.

EXAMPLE 2

In this example a Co-base alloy specimen was coated by substantially the same procedure followed in Example 1. This Co-alloy specimen had the following nominal composition:

Co-20Cr-15W-10Ni-1.5Mn-0.1C- $<3\text{Fe}$ - $<1\text{Si}$.

This Co-alloy specimen was first Ta-coated by the pack cementation process of Example 1. It was then subjected to further heat treatment diffusion of the Ta for 4 hours at 2000° F. in the manner described in Example 1.

A Co and Al powder dispersion in nitrocellulose lacquer, prepared in the manner described in Example 1 was then applied to the surface of the Ta coated Co-alloy specimen in an amount of 25 milligrams per square centimeter. This application, as in Example 1, was by spraying.

The coated Co-alloy specimen was then inserted in a hydrogen atmosphere furnace and heat treated by the procedure described in Example 1, except that the heat treatment temperature used in this example was 1800° F. and the heat treatment was carried out for 4 hours.

The coated alloy of this example was also subjected to dynamic oxidation testing in flowing air at 2100° F. for

100 hours, and survived this test with no failure. The superiority of the coatings of the present invention on Co-base alloys is graphically illustrated by FIGURE 1 which shows the specimen produced in Example 2 after this 100 hours of oxidation-erosion testing. This sample was still in excellent condition after the testing.

FIG. 3 is a photomicrograph of a trailing surface of the Ta and Co-Al coated L-605 Co-base alloy erosion bar produced in accordance with Example 2, enlarged 500 times to show the composition of the coating after oxidation erosion testing in flowing air for 100 hours at 2100° F. This photomicrograph (FIG. 3) shows the Al_2O_3 surface film at the exterior surface of the coated article and underneath this a coating zone consisting essentially of Ta, Al, Co and the Co-alloy of the substrate. FIG. 3 shows the metallurgical bonding at the substrate-coating interface and Ta- and Al-rich phases in the coating.

A Co-alloy specimen produced in accordance with this example was subjected to thermal fatigue testing by exposure to a combustion flame of JP-5 fuel and air in the manner described in Example 1. The specimen coated in accordance with this invention completed 1400 cycles of testing, and although the base cracked at 500 cycles, no coating spalling had occurred at the end of the 1400 cycle test.

The exact mechanism of modification or change wrought by the application of a thin Ta first coating, in the first coating step of the process of this invention, on the final coatings produced in accordance with this invention is not fully understood.

After exposure of the specimens of Example 1 and Example 2 to dynamic oxidation environments at 2100° F. for 100 hours, the coating zones of these specimens were analyzed and found to contain less than about 0.5% Ta. It is believed that the Ta which remains in the surface zone after such oxidative exposure has a more uniform distribution than that which is achieved by applying Ta by procedures other than the present process. This uniform Ta content greatly promotes the adherence of the outer oxide pellicular film of Al_2O_3 to the remainder of the coated composite, and it is this outer Al_2O_3 film which provides the primary oxidation resistance of the coating.

Analysis of the coatings of this invention after oxidation testing also revealed that an extremely high concentration of tungsten from the alloy substrate had formed at the coating substrate interface of the Ni- and Co-base alloys coated in accordance with this invention (as shown in FIGS. 2 and 3), and that a change in chemistry had occurred in a light-etching micro constituent at the outer edge of the coatings produced in accordance with this invention on the Ni-base alloy specimens. Some or all of these unexpected occurrences may contribute to the improved oxidation resistance afforded by the coatings of this invention. Without being bound to any particular theory, applicants believe that the primary basis for the improved coating performance results from improved adherence of the outer Al_2O_3 coating film to the remainder of the coated composite, and that this improved adherence results from the process of this invention in first depositing a uniform Ta coating layer on the Ni- or Co-base alloy substrate prior to application and interdiffusion of the Co and Al second coating composition of this invention.

EXAMPLES 3-6

Results similar to those obtained in Example 1 are obtained by applying a Ta coating and subsequently a Co and Al coating composition, in the precise manner described in Example 1, onto Ni-base alloys having the compositions set forth below. This procedure results in the formation of a coating similar to that formed in Example 1, which consists essentially of Co, Al, Ta and the particular Ni-base alloy selected:

Ni-19.5Cr-13.5Co-0.7C-3Ti-1.4Al-4Mo-0.005B-0.08Zr

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Ni-8Cr-10Co-1Ti-6Al-6Mo-0.11C-4.3Ta-0.15B

Ni-2.2ThO₂

Ni-18.5Co-15Cr-5Mo-4.3Al-<

4Fe-3.3Ti-0.1Cu-0.07C-0.03B

EXAMPLES 7-8

Results similar to those of Example 2 are obtained by applying first Ta, and then Co and Al coating compositions, by the procedures set forth in Example 2 to the following Co-base alloys, resulting in the production of a coating zone on these alloys consisting essentially of Co, Al, Ta, and the selected base alloy of the substrate:

Co-21.5Cr-10W-9Ta-1.5Ni-1Fe-0.86C-0.25Zr

Co-21Cr-0.45C-1.75Fe-11W-2(Cb+Ta)

We claim:

1. An article of manufacture having good oxidation and erosion resistance at high temperatures which comprises: a substrate selected from the group consisting of Ni-base alloys and Co-base alloys; and an oxidation and erosion resistant surface coating zone comprising Ta, Al and the selected alloy of the substrate adherently bonded to the substrate, said surface zone having an exterior surface film of Al₂O₃ and a Ta-rich subzone adjacent to the substrate.

2. The article of claim 1 in which the surface zone contains from 0.1 to 1.0% by weight of Ta.

3. An article of manufacture having good stress-rupture strength at high temperatures, high-temperature oxidation resistance and resistance to cyclic thermal fatigue failure, which comprises: a substrate consisting essentially of an alloy selected from the group consisting of Ni-base alloys and Co-base alloys, and an oxidation and erosion resistant surface coating zone adherently bonded to the substrate, the surface zone having an exterior surface film of Al₂O₃ and a Ta-rich subzone adjacent to the substrate, said surface zone consisting essentially of Co, Al, Ta and the selected alloy of the substrate.

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4. The article of claim 3 in which the selected alloy of the substrate is a Ni-base alloy having Ni as its principal component.

5. The article of claim 3 in which the selected alloy of the substrate is a Co-base alloy having Co as its principal component.

6. The article of claim 3 in which the surface coating zone consists essentially of: Co and the selected alloy of the substrate, in aggregate, in an atomic ratio to Al between 2:5 and 1:1; and 0.1%–1.0% by weight of the surface zone of Ta.

7. The article of claim 6 in which the coating zone has a thickness of 2 to 6.5 mils.

8. The article of claim 6 in which the selected alloy of the substrate is a Ni-base alloy having Ni as its principal component.

9. The article of claim 6 in which the selected alloy of the substrate is a Co-base alloy having Co as its principal component.

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ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, JR., Assistant Examiner

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