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(54) Title: CORROSION, EROSION AND WEAR RESISTANT ALLOY STRUCTURES AND METHOD THEREOF

(57) Abstract

High performance alloy structures are improved in corrosion and erosion and wear resistance characteristics by the incorporation of an interdispersed phase and a ternary or quaternary alloy of platinum, rhodium or palladium, the alloy base metal and an alloying element such as aluminum in the structure surface with the use of relatively less of the precious metals for a given depth of case by virtue of the conjoint incorporation of the interdispersed phase.
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CORROSION, EROSION AND WEAR RESISTANT
ALLOY STRUCTURES AND METHOD THEREFOR

Background Of The Invention

This invention has to do with corrosion, erosion
and wear resistant alloy structures, and methods
therefor. More particularly, the invention relates to
more economical diffusion coating of alloys having as
base metals iron, cobalt and nickel, while obtaining
benefits of increased resistance to corrosion
characteristic of rhodium or platinum ternary alloys,
e.g. with aluminum and the alloy base metal.

The invention is further concerned with
improvements in specific properties of such ternary alloy
systems by the incorporation of discrete particulate
matter, such as alumina, or a hard carbide such as
tungsten carbide for their specific erosion or wear
characteristic.Remarkably, the use of the discrete
particulate matter enables reductions in the quantity of
rhodium or platinum precious metal needed to form a
diffusion coated case of adequate depth on the alloy
structure being treated, so that the addition of the
erosion and wear properties resulting from incorporation
of the mentioned discrete particulate matter, has the
further and unexpected benefit of lowering the precious
metal requirement and thus the material costs of the
product, enabling a widely improved product at lower
cost.

In the production of diffusion alloy coatings
such as are employed on high performance metal parts,
including turbine vanes and blades, pump parts, and other
parts subject to unusual demands for erosion, corrosion and wear resistance it is desirable to produce such coatings on a wide variety of structures, by which term herein is meant a shaped article in an intermediate or final configuration for its intended use, to do so rapidly and repeatably so as to obtain superior performance. The incorporation of various discrete interdispersed phase-forming materials into diffusion coatings enables obtention of individually tailored properties responsive to the selective inclusion, in a controlled interdispersion, of refractory oxide, nitride or hard carbide material and/or elemental metal additives, which are kept and remain interdispersed, i.e. remain as discrete particulate material in the interdiffusion layer, with a high degree of control as to location, concentration, and, thereby, as to properties of the final product.

Prior Art

It is known to form intermetallic compounds and alloys on high performance parts such as turbine blades and blades by subjecting the surface of the part to a diffusion of one or more constituents of a diffusion pack to form an interdiffusion layer, sometimes referred to as a diffusion coating. Typically, the pack comprises the one or several metals to be diffused, frequently aluminum, aluminum oxide, a halogen and possibly other materials depending on the particular objective of the diffusion. The pack is heated for long periods at very high temperatures, and an intermetallic compound is formed typically both outwardly and inwardly of the part
original surface. This kind of coating can lend extreme corrosion resistance properties to structurally superior, more easily formed, less costly metals, is renewable, and provides a product of improved properties.

A related approach to improving specifically the corrosion resistance of high performance alloy structures is disclosed in U.S.P. 3,961,910, issued June 8, 1976 to Baladjanian and Clark. There, use of rhodium preplated and diffused into the alloy structure, followed by aluminum diffusion from an aluminizing pack resulted in the formation of a ternary alloy of aluminum, rhodium and the base metal, e.g. nickel, which ternary alloy was found to be especially effective against corrosion. Rhodium is expensive, however, and use of sufficient amounts to develop an adequate depth or thickness for practical application, the coating "case" necessitated use of rhodium plate at from 5 to 35% of the intended depth of diffusion coating. Additionally, the corrosion benefits were related to the development of a "spike" of rhodium concentration in the coating which is process related and limits processing flexibility.

In addition, platinum was found to be deficient in the Baladjanian process and product, but the properties of platinum are such that in other processes its use is highly desired. Similarly, use of palladium is sometimes useful but its use is not suggested in the Baladjanian et al patent.

Although greatly improved in corrosion resistance, the Baladjanian et al products are not especially resistant to erosion and wear. Increasingly, the need in turbine components, valving, and fluid
control equipment of all types is for erosion and wear
resistance, as well as corrosion resistance, since fuels
and other fluids with which these parts must deal
frequently contain particles and larger détritus, which
impinge on the wearing surfaces, exacerbating the
chemical corrosion problem by mechanically destroying the
corrosion resistant layer.

Moreover, the cost of obtaining adequate depth of
case using rhodium technology as disclosed by Baladjian
et al, is such that only limited markets where
performance requirements overrode cost, such as aircraft
engines, were available. Promising markets such as power
plant turbines, oil field equipment and the like were
essentially foreclosed on cost grounds. By the present
invention, however, the quantities of precious metal,
such as rhodium, platinum or palladium required is
substantially reduced, lowering costs appreciably, for
the same depth of diffusion coating case.

This benefit is unexpectedly realized from the
use of an added discrete particulate component to the
diffusion coating which replaces metallic phase in the
coating with an interdispersed phase, thus reducing the
need for precious metal while maintaining corrosion
resistance, and as well adds its own distinctive
beneficial properties, such as erosion and wear
resistance. The use of discrete particulate matter in
diffusion coatings is broadly known, although not in
connection with improving the corrosion resistance of an
alloy structure while obtaining the case depth with the
use of reduced amounts of precious metal.

U.S.P. 3,345,197, to Martini et al, teaches the
incorporation by codiffusion with aluminum, of undissolved materials, or interdispersed phases such as aluminum oxide, for particular purposes involved with improvements in the properties of the final coating. To accomplish this Martini finely grinds the aluminum oxide, e.g. to a size as fine as 5 microns, and mixes the resultant "colloidal" material with aluminum to form a powder, and then heats the part in the powder to achieve an aluminide coating with interdispersed aluminum oxide, some of which has migrated out of the powder into the surface of the part. Martini is limited in his pack composition to the extremely finely ground aluminum oxide, and to the use of aluminum as the diffusing metal. Thus limited, the Martini method is of limited utility, although the product realized has potential.

Important among the disadvantages of Martini is the alteration of conventional pack compositions, as by requiring quantities of finely ground aluminum oxide as a necessary part of the pack, at the risk of not achieving the desired incorporation of refractory oxide material in the final coating, where the particle size is excessive.

The flexibility of result in Martini is quite limited, since incorporation of the oxide from within the pack is restricted to but one refractory material and a single value of refractory material density in the diffusion coating and dependent on the original pack composition.

Summary of the Invention

There is a need in the art for corrosion, erosion and wear resistant structures, and for methods for imparting these qualities simply, repeatably, and more
economically than has been possible heretofore.

It is accordingly an object of the present
invention to provide improvements in diffusion coating
technology overcoming the limitations and disadvantages
of the prior art, and to provide the resulting products
having tailored chemical corrosion resistance with
reduced use of precious metals, and erosion and wear
properties characteristic of particular additives.

The foregoing and other objects of the invention
to become apparent hereinafter, are realized in the
method of forming on a nickel, cobalt or iron base metal
structure a diffusion coating case of a preselected
thickness and containing a precious metal ternary alloy
and an interdispersed phase to impart improved corrosion,
erosion and wear properties to a surface of the
structure, which includes applying onto the structure
surface an adherent layer of a precious metal in an
amount less than normally required for a case of the
preselected depth, applying a layer of an interdispersed
phase-forming discrete particulate matter to the surface
in a predetermined amount, forming a ternary alloy of the
base metal, the precious metal and an alloying element by
interdiffusing under nonoxidizing conditions the
layer-applied structure surface from a diffusion pack
containing the alloying element, and distributing and
maintaining the predetermined amount of interdispersed
phase-forming matter as discrete particulate matter
through the ternary alloy sufficient to increase the
thickness of the ternary alloy containing case on the
structure surface to the preselected thickness, whereby
the case has the corrosion resistance properties
characteristic of the ternary alloy, and the erosion and
wear properties characteristic of the interdispersed
phase matter, with the use of reduced amounts of the
precious metal.

In particular embodiments, the method includes:
selecting aluminum as the alloying element; selecting
rhodium, platinum and/or palladium as the precious metal;
applying the precious metal to the surface by depositing
from a bath thereof or by vapor deposition or by physical
deposition; subjecting if desired, the surface applied
precious metal to heating for a time and at a temperature
prediffusing the precious metal into the surface; and
maintaining a substantially oxygen-free atmosphere at the
surface during the precious metal heating.

In preferred embodiments, the invention includes
maintaining the predetermined amount of interdispersed
phase-forming discrete particulate matter separate from
the pack constituents and relatively richly concentrated
at the structure surface, e.g. as an adherent film on the
structure surface, suitably by binding the discrete
particulate matter into a film with an organic binder;
selecting as the interdispersed phase-forming matter a
hard carbide, a silicide, oxide or nitride as the
interdispersed phase-forming matter, e.g. selecting as
the hard carbide tungsten carbide, tantalum carbide,
zirconium carbide, titanium carbide or chromium carbide,
as the silicide molybdenum disilicide, or as the nitride
silicon nitride; or selecting as the interdispersed
phase-forming matter a metal having an atomic number of
24 or higher and which does not form ternary alloys with
the precious metal and the base metal, e.g. as the
interdispersed phase-forming matter a metal such as tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium or chromium; or selecting as the interdispersed phase-forming matter a refractory oxide such as zirconia, alumina, titania, magnesia, yttria or hafnia refractory oxides having a particle size of less than about 25 microns.

In a particularly preferred embodiment, the invention contemplates the method of forming on a nickel or cobalt base metal structure a diffusion coating case of a preselected thickness and containing a rhodium or platinum ternary alloy and an interdispersed phase to impart improved corrosion, erosion and wear properties to a surface of the structure, which includes applying onto the structure surface a first adherent layer of rhodium and/or platinum in an amount less than normally required for a case of the preselected depth, applying over the first adherent layer a second adherent layer of an interdispersed phase-forming discrete particulate matter onto the surface in a predetermined amount, forming a ternary alloy of the base metal, the platinum or rhodium, and aluminum by immersing the layer-applied structure surface in an aluminizing pack containing a refractory oxide and aluminum and diffusing under non-oxidizing conditions and simultaneously distributing the predetermined amount of interdispersed phase-forming matter as discrete particulate matter through the ternary alloy sufficient to increase the thickness of the ternary alloy containing case on the structure surface to the preselected thickness, whereby the case has the corrosion resistance properties characteristic of the ternary
alloy, and the erosion and wear properties characteristic of the interdispersed phase matter, with the use of reduced amounts of the rhodium or platinum.

As in the previous embodiments, in this embodiment the method further includes applying the rhodium or platinum metal to the surface by depositing from a bath or vapor thereof, or by physical deposition; maintaining the predetermined amount of interdispersed phase-forming discrete particulate matter relatively richly concentrated at the structure surface; binding the discrete particulate matter into an adherent layer on the structure surface with a binding agent, e.g. with an organic binder as binding agent; selecting as the discrete particulate matter tungsten carbide, tantalum carbide, zirconium carbide, titanium carbide or chromium carbide among the hard carbides, tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium or chromium among metals having an atomic number above 24 which do not form ternary alloys with the precious metal and alloying element under the operating conditions of the method, and selecting as a refractory zirconia, alumina, titania, magnesia, yttria or hafnia refractory oxides having a particle size of less than about 25 microns. One or more of the mentioned discrete particulate matter elements and compositions can be used from the foregoing groups, and from various combinations of groups in a particular application of the invention, depending on the final properties desired in the product.

In a highly preferred embodiment, the invention comprises the method of forming on a nickel or cobalt base metal structure a diffusion coating case of a
preselected thickness and containing a rhodium or platinum ternary alloy and an interdispersed phase to impart improved corrosion, erosion and wear properties to a surface of the structure, which includes depositing onto the structure surface a first adherent layer of rhodium and/or platinum to a depth equal to from 2.5 to 17% of the ultimate case depth and less than normally required for a case of the preselected depth, applying over the first adherent layer a second adherent layer of an interdispersed phase-forming discrete particulate matter and an organic binder onto the surface in a predetermined amount, forming a ternary alloy of the base metal, the platinum or rhodium, and aluminum by immersing the layer-applied structure surface in an alumining pack containing a refractory oxide and aluminum and diffusing under non-oxidizing conditions and simultaneously distributing the predetermined amount of interdispersed phase-forming matter as discrete particulate matter through the ternary alloy sufficient to increase the thickness of the ternary alloy containing case on the structure surface to the preselected thickness, whereby the case has the corrosion resistance properties characteristic of the ternary alloy, and the erosion and wear properties characteristic of the interdispersed phase matter, with the use of reduced amounts of the rhodium or platinum.

The invention further contemplates provision of new compositions of matter shaped into alloy structures of final or intermediate configuration. Thus there is provided in accordance with the invention, a cobalt, nickel or iron base alloy structure having a diffusion
coating, the coating comprising a ternary alloy of aluminum, base metal and rhodium, platinum and/or palladium effective to improve the corrosion resistance properties of the structure, and distributed within the coating an interdispersed phase of discrete particulate matter in an amount effective to improve the erosion and wear properties of the structure without reducing the corrosion resistance imparted by the ternary alloy. Preferably, the ternary alloy consists of rhodium, nickel or cobalt and aluminum, or platinum, nickel or cobalt and aluminum. Quaternary alloys of e.g. nickel or cobalt, platinum, rhodium and aluminum are obtained where two precious metals are used. The term "ternary" herein refers to alloys of three (ternary alloy per se), or four (sometimes herein referred to as quaternary alloys) or more metals, as obtained by the present method. Typically, the alloy structure further comprises discrete particulate matter in the form of a refractory oxide, such as aluminum oxide or zirconium oxide, or a hard carbide, particularly tungsten carbide., or a metal such as tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium, or chromium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

"Interdispersed" and its cognitives herein refer to a condition of a particulate higher atomic number metal, i.e. having an atomic number of 24 or above, or a refractory oxide, nitride, or silicide material, or a hard carbide material, being incorporated as a discrete
entity defining a separate phase within a diffusion-formed alloy or intermetallic compound.

EXAMPLE I

A nickel base alloy structure containing chromium, cobalt, molybdenum, tantalum, aluminum and titanium, was cleaned for plating and electroplated with 0.00004 inch of rhodium (about 10% of the ultimate case depth) from a rhodium sulfate solution. The part was then coated to a thickness of about 0.010 inch with a slurry of mixed 5 and 10 micron aluminum oxide particles dispersed in an acrylic lacquer. After the coating dried, the part was packed in a diffusion pack comprising 9% aluminum mixed with 91% aluminum oxide of -100 mesh, and a small amount of ammonium chloride. The pack was heated at 1900°F. for 4 hours. After the part cooled the coating was examined and found to be smooth, approximately 0.0035 inch in depth. Aluminum oxide particles were included in large numbers in the outer half of the coating.

In subsequent testing for erosion and wear by subjecting the part to a fluid stream containing fine particulate, it is noted that erosion is reduced substantially over an uncoated control part. Similar testing in a corrosive environment with sulfur-laden jet fuel reveals that corrosion resistance is excellent indicating the presence of an effective ternary alloy within the coating. Lower amounts of rhodium, e.g. 2.5% of the intended ultimate coating depth are effective when applied and followed by the mentioned interdiffusion in accordance with the invention, and use of more than 17.5% rhodium, platinum, rhodium-platinum, or palladium is not
usually required in accordance with the present method to obtain effective corrosion resistance by ternary or quaternary alloy formation and a case depth of adequate size unlike precious metal diffusion coatings effected without conjoint use of an interdispersed phase.

EXAMPLE II

Example I is duplicated but using both rhodium electroplate (0.00001 inch thick) and platinum electroplate (0.00004 inch) atop the rhodium. Processing is identical. The resultant part has a coating containing a quaternary alloy of nickel, rhodium, platinum and aluminum. Simultaneous fluid abrasion and corrosion testing reveals the coating has excellent properties against these environments.

EXAMPLE III

A conventional diffusion pack comprising per 100 parts by weight, 6 parts of aluminum powder, —200 mesh, and 94 parts of aluminum oxide powder, 100 to 325 mesh, is prepared. A jet engine blade comprised of nickel superalloy of the percent composition:

- 0.12 Carbon
- 12.5 Chromium
- 4.2 Molybdenum
- 2.0 Columbiium
- 0.8 Titanium
- 6.1 Aluminum
- 0.012 Boron
- 0.1 Zirconium
- Bal. Nickel
is surface deposited with rhodium by physical deposition to a depth of 0.00001 inch. The covered surface is then coated with an adherent layer of 10 micron powder aluminum oxide, by painting onto the part the oxide suspended in a lacquer binder. After the binder dries, the aluminum oxide is firmly bound to the part surfaces and the part, thus coated, is immersed in the mentioned pack. The pack is heated to 1050-1100° Centigrade, in a hydrogen atmosphere, for 4-5 hours. A second engine blade of identical composition, also placed in the pack during the heat, is also diffused but without first precoating with rhodium, as a Control. Microsections of the Example III and Control parts are compared by microscopic examination. Comparison of the Example and Control parts reveals that each has a diffusion coating which extends both inwardly and outwardly from the nominal surface of the part before diffusion and exhibits an oxide dispersion characterized by uniform distribution of an interdispersed phase of aluminum oxide particulate, which will greatly enhance erosion resistance of the part. The Example part is microscanned for the presence of alloy of rhodium, nickel and aluminum and its presence is confirmed. Corrosion resistance to sulfurous jet fuel is excellent. Simultaneous subjection of the part to carbon particulates shows excellent resistance to erosion and wear in comparison with an untreated part of like configuration.

EXAMPLE IV

Example III is duplicated using as the pack composition, in lieu of the aluminum powder in the pack,
titanium powder, -200 mesh (Example IVa); boron powder, 
-325 mesh (Example IVb); and silicon powder, -200 mesh 
(Example IVc). The interdispersed material is also varied 
using tungsten carbide (Example IVd), tantalum carbide 
(Example IVe), zirconium carbide (Example IVf); titanium 
carbide (Example IVg); silicon carbide (Example IVh); 
chromium carbide (Example IVi). The interdispersed 
material is also varied using tungsten (Example IVj), 
tantalum (Example IVk), molybdenum (Example IVl); 
zirconium (Example IVm); titanium (Example IVn); hafnium 
(Example IVo); yttrium (Example IVp); molybdenum 
disilicide (Example IVq); silicon nitride (Example IVr); 
all powdered and held on with organic binder, and 
plated-on chromium (Example IVs) as the metal coating on 
the blade part; and in lieu of the aluminum oxide 
refractory coating on the part, zirconia (Example IVt); 
titania (Example IVu); magnesia (Example IVv); yttria 
(Example IVx); and hafnia (Example IVz). The parts were 
first surface covered with an adherent layer of rhodium, 
platinum or palladium, in an amount less than normally 
required for the case depth obtained. The rhodium is not 
required to be prediffused into the part being treated, 
and this extra step is generally avoided. The 
anti-corrosion benefits of the rhodium addition are 
realized whether or not the rhodium is relatively richly 
concentrated near the interface of the diffusion coating 
layer on the part substrate.

The products of Examples IVa-z are improved in 
corrosion, erosion and/or wear performance over controls 
produced at the same time, but without use of the 
rhodium, platinum or palladium coating, or maintaining
the particular interdispersed material at the
interdiffusion locus by the expedient of coating the part
surface with the interdispersed material, in advance of
subjecting the part to pack diffusion. Also, it will be
noted that the pack compositions need not be specially
formulated, either as to constituents or particle size of
constituents. The disclosed method therefore affords a
product of variously improved properties with only the
coating on the part to be diffused being varied, for a
given pack composition.

The reason for the improvement in properties of a
part diffused with an interdispersed phase over a part
without such a phase appears to be that the dispersed
phase can stabilize a protective oxide phase formed in
part use, provide some protection against impinging
particles, or change the macroscopic hardness of the
coating. The improvement in corrosion properties of an
interdiffused part over a part without such a phase with
reduced amounts of precious metal is evidently resultant
from the formation of ternary or quaternary alloys of the
precious metals, the base metal, e.g. nickel, cobalt or
iron, and aluminum form the diffusion pack and the
replacement of some of the coating metallic phase with
the interdispersed phase.

The interdispersed phase may be a refractory
oxide, as indicated above whereby the property
improvements are typically improved erosion resistance, a
hard carbide, nitride or silicide whereby the property
improvements are typically wear resistance, or a metal
whereby the property improvements are typically in
corrosion resistance.
Typical pack diffusion conditions for carrying out the present method are temperatures between 760° C. to 1100° C. and heating for 2 to 20 hours in an inert, oxygen-free atmosphere.

Suitable binders, if used, are synthetic organic polymeric materials suitably soluble in organic vehicles which will evaporate at a satisfactory rate for formation of adherent coating on a part to be diffused, or a portion of such part, where specifically varied properties are desired.

The term "nickel base", "cobalt base", and "iron base" respectively refer to alloys in which nickel, cobalt, or iron is the largest single ingredient, in weight per cent, although not necessarily a major weight amount of the entire alloy. Suitable alloys herein contain in addition to the base metal at 35% and more, effective, minor amounts by weight of one or more of tungsten, manganese, molybdenum, iron, nickel, cobalt, carbon, vanadium, titanium, aluminum, tantalum, columbium, chromium, boron, and/or zirconium and the like conventionally present in superalloys.
I CLAIM:

1. Method of forming on a nickel, cobalt or iron base metal structure a diffusion coating case of a preselected thickness and containing a precious metal ternary alloy and an interdispersed phase to impart improved corrosion, erosion and wear properties to a surface of said structure, which includes applying onto said structure surface an adherent layer of a precious metal in an amount less than normally required for a case of said preselected depth, applying a layer of an interdispersed phase-forming discrete particulate matter to said surface in a predetermined amount, forming a ternary alloy of said base metal, said precious metal and an alloying element by interdiffusing under nonoxidizing conditions said layer-applied structure surface from a diffusion pack containing said alloying element, and distributing said predetermined amount of interdispersed phase-forming matter as discrete particulate matter through said ternary alloy sufficient to increase the thickness of said ternary alloy containing case on said structure surface to said preselected thickness, whereby said case has the corrosion resistance properties characteristic of said ternary alloy, and the erosion and wear properties characteristic of said interdispersed phase matter, with the use of reduced amounts of said precious metal.

2. The method according to claim 1, including also selecting an iron base alloy structure as said structure to be diffusion coated.
3. The method according to claim 1, including also selecting a cobalt base alloy structure as said structure to be diffusion coated.

4. The method according to claim 1, including also selecting a nickel base alloy structure as said structure to be diffusion coated.

5. The method according to claim 1, including also selecting aluminum as said alloying element.

6. The method according to claim 1, including also selecting rhodium as said precious metal.

7. The method according to claim 1, including also selecting platinum as said precious metal.

8. The method according to claim 1, including also selecting palladium as said precious metal.

9. The method according to claim 1, including also applying said precious metal to said surface by depositing from a bath thereof.

10. The method according to claim 1, including also applying said precious metal to said surface by vapor deposition.

11. The method according to claim 1, including also applying said precious metal to said surface by physical deposition.
12. The method according to claim 1, including also subjecting said surface applied precious metal to heating for a time and at a temperature prediffusing said precious metal into said surface.

13. The method according to claim 12, including maintaining a substantially oxygen-free atmosphere at said surface during said precious metal heating.

14. The method according to claim 1, including also maintaining said predetermined amount of interdispersed phase-forming discrete particulate matter separate from said pack constituents and relatively richly concentrated at said structure surface.

15. The method according to claim 14, including maintaining said discrete particulate matter as an adherent film on said structure surface.

16. The method according to claim 15, including also binding said discrete particulate matter into a film with an organic binder.

17. Method according to claim 1, including also selecting a refractory oxide, a hard carbide, a silicide, or nitride as said interdispersed phase-forming matter.

18. The method according to claim 17, including also selecting as the hard carbide tungsten carbide, tantalum carbide, zirconium carbide, titanium carbide or chromium carbide, as the silicide molybdenum disilicide,
or as the nitride silicon nitride.

19. Method according to claim 1, including also selecting a metal having an atomic number of 24 or higher and which does not form ternary alloys with said precious metal and said base metal as said interdispersed phase-forming matter.

20. The method according to claim 19, including also selecting as said interdispersed phase metal tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium or chromium.

21. Method according to claim 1, including also selecting as said interdispersed phase-forming matter zirconia, alumina, titania, magnesia, yttria or hafnia refractory oxides having a particle size of less than about 25 microns.

22. Method of forming on a nickel or cobalt base metal structure a diffusion coating case of a preselected thickness and containing a rhodium or platinum ternary alloy and an interdispersed phase to impart improved corrosion, erosion and wear properties to a surface of said structure, which includes applying onto said structure surface a first adherent layer of rhodium and/or platinum in an amount less than normally required for a case of said preselected depth, applying over said first adherent layer a second adherent layer of an interdispersed phase-forming discrete particulate matter onto said surface in a predetermined amount, forming a
ternary alloy of said base metal, said platinum or rhodium, and aluminum by immersing said layer-applied structure surface in an aluminizing pack containing a refractory oxide and aluminum and diffusing under non-oxidizing conditions and simultaneously distributing said predetermined amount of interdispersed phase-forming matter as discrete particulate matter through said ternary alloy sufficient to increase the thickness of said ternary alloy containing case on said structure surface to said preselected thickness, whereby said case has the corrosion resistance properties characteristic of said ternary alloy, and the erosion and wear properties characteristic of said interdispersed phase matter, with the use of reduced amounts of said rhodium or platinum.

23. The method according to claim 22, including also applying said rhodium or platinum metal to said surface by depositing from a bath or vapor thereof.

24. The method according to claim 23, including also applying said rhodium or platinum to said surface by physical deposition.

25. The method according to claim 23, including also maintaining said predetermined amount of interdispersed phase-forming discrete particulate matter and relatively richly concentrated at said structure surface.

26. The method according to claim 25, including binding said discrete particulate matter into an adherent
layer on said structure surface with a binding agent.

27. The method according to claim 26, including also binding said discrete particulate matter with an organic binder as binding agent.

28. The method according to claim 27, including also selecting as said discrete particulate matter tungsten carbide, tantalum carbide, zirconium carbide, titanium carbide or chromium carbide.

29. The method according to claim 27, including also selecting as said discrete particulate matter tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium or chromium.

30. The method according to claim 27, including also selecting as said discrete particulate matter zirconia, alumina, titania, magnesia, yttria or hafnia refractory oxides having a particle size of less than about 25 microns.

31. Method of forming on a nickel or cobalt base metal structure a diffusion coating case of a preselected thickness and containing a rhodium or platinum ternary alloy and an interdispersed phase to impart improved corrosion, erosion and wear properties to a surface of said structure, which includes depositing onto said structure surface a first adherent layer of rhodium and/or platinum to a depth equal to from 2.5 to 17% of the ultimate case depth and less than normally required
for a case of said preselected depth, applying over said first adherent layer a second adherent layer of an interdispersed phase-forming discrete particulate matter and an organic binder onto said surface in a predetermined amount, forming a ternary alloy of said base metal, said platinum or rhodium, and aluminum by immersing said layer-applied structure surface in an aluminizing pack containing a refractory oxide and aluminum and diffusing under non-oxidizing conditions and simultaneously distributing said predetermined amount of interdispersed phase-forming matter as discrete particulate matter through said ternary alloy sufficient to increase the thickness of said ternary alloy containing case on said structure surface to said preselected thickness, whereby said case has the corrosion resistance properties characteristic of said ternary alloy, and the erosion and wear properties characteristic of said interdispersed phase matter, with the use of reduced amounts of said rhodium or platinum.

32. Cobalt, nickel or iron base alloy structure having a diffusion coating, said coating comprising a ternary or quaternary alloy of aluminum, base metal and rhodium, platinum or palladium effective to improve the corrosion resistance properties of said structure, and distributed within said coating an interdispersed phase of discrete particulate matter in an amount effective to improve the erosion and wear properties of said structure without reducing the corrosion resistance imparted by said ternary alloy.
33. The alloy structure according to claim 32, in which said ternary or quaternary alloy contains rhodium and/or platinum, nickel or cobalt and aluminum.

34. The alloy structure according to claim 33, in which said ternary or quaternary alloy contains of rhodium and/or platinum, nickel or cobalt and aluminum.

35. The alloy structure according to claim 33 or 34, in which said discrete particulate matter comprises a refractory oxide.

36. The alloy structure according to claim 35, in which said refractory oxide is aluminum oxide or zirconium oxide.

37. The alloy structure according to claim 33 or 34, in which said discrete particulate matter comprises a hard carbide.

38. The alloy structure according to claim 37, in which said hard carbide is tungsten carbide.

39. The alloy structure according to claim 33 or 34, in which said discrete particulate matter comprises tungsten, tantalum, molybdenum, zirconium, titanium, hafnium, yttrium, or chromium.
## INTERNATIONAL SEARCH REPORT

### I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ①

According to International Patent Classification (IPC) or to any 'National Classification' as Int. Cl. B21D 39/00; B22C 23/02; B32B 15/02; C23C 9/10, 11/00

U.S. Cl. 427/252; 428/615, 621, 627,652

### II. FIELDS SEARCHED

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
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<tbody>
<tr>
<td>U.S.</td>
<td>427/202,250,252,253,255.2,255 3,328</td>
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<td>427/372.2,383.7,383.9,405,419.1,419.2,419.7,436,</td>
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<td>428/615,621,627,652</td>
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</table>

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched ④

### III. DOCUMENTS CONSIDERED TO BE RELEVANT ④

<table>
<thead>
<tr>
<th>Category ⑤</th>
<th>Citation of Document, ⑥ with indication, where appropriate, of the relevant passages ⑦</th>
<th>Relevant to Claim No. ⑧</th>
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<tbody>
<tr>
<td>Y</td>
<td>U $3,345,197 Published 3 Oct. 1967 Martini et al</td>
<td>1-39</td>
</tr>
<tr>
<td>Y</td>
<td>U $3,573,963 Published 6 April 1971 Maxwell</td>
<td>1-39</td>
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<tr>
<td>A</td>
<td>U $3,677,789 Published 18 July 1972 Bungardt et al</td>
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</tr>
<tr>
<td>A</td>
<td>U $3,692,554 Published 19 Sept. 1972 Bungardt et al</td>
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<tr>
<td>Y</td>
<td>U $3,961,910 Published 8 June 1976 See col. 2 line 33 to col. 3 line 17 col. 4 line 33 to col. 5 line 48, Baladjanian et al</td>
<td>1-39</td>
</tr>
<tr>
<td>A</td>
<td>U $3,978,251 Published 31 Aug. 1976 Stetson et al</td>
<td>1-39</td>
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</table>

① Special categories of cited documents: ⑤

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

④ Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

⑤ Document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

⑥ Document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

⑦ "A" document member of the same patent family

### IV. CERTIFICATION

Date of the actual completion of the International Search ⑨

20 July 1983

Date of Mailing of this International Search Report ⑩

05 Aug 1983

International Searching Authority ①

Signature of Searching Authority P.A.

S. L. Childs

Form PCT/ISA/210 (second sheet) (October 1981)
### FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

<table>
<thead>
<tr>
<th>A</th>
<th>U.S.A. 3,979,273 Published 7 Sept. 1976 Panzera et al</th>
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<tr>
<td>A</td>
<td>U.S.A. 4,070,507 Published 24 Jan. 1978 Stueber et al</td>
<td>1-39</td>
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<tr>
<td>A</td>
<td>U.S.A. 4,156,042 Published 22 May 1974 Hayman et al</td>
<td>1-39</td>
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</table>

### OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. **Claim numbers** , because they relate to subject matter not required to be searched by this Authority, namely:

2. **Claim numbers** , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

### OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. **As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.**

2. **As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:**

3. **No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:**

4. **As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.**

**Remark on Protest**

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.