

[54] **MULTI-METAL CORROSION-RESISTANT
DIFFUSION COATINGS**

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[22] Filed: **July 28, 1971**
[21] Appl. No.: **167,030**

Related U.S. Application Data

- [62] Division of Ser. No. 733,303, May 31, 1968, Pat. No.
3,642,457.
[52] U.S. Cl. **117/71 M**, 29/196.2, 29/196.5,
29/196.6, 117/130 R, 204/37 R, 204/147
[51] Int. Cl. **B44d 1/46**
[58] Field of Search 204/148, 147, 35, 37 R;
117/71, 109, 22, 130 R; 29/196.2, 196.5,
196.6; 148/31.5

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[57] **ABSTRACT**

A method is provided herewith for the production of multi-metal diffusion coatings on metal articles providing prolonged protection against chemical or galvanic corrosion of the surface of the coated article during prolonged exposure to corrosive conditions, and particularly high saline content marine atmospheres, especially where the protective coating is also subjected to mechanically erosive and abrasive environments, with the multiplicity of coating metals being selected so that the combination thereof provides a coating varying through the thickness thereof from outer surface toward the interface of coating layer and coated article so that the mechanical resistance to chemical corrosion is greatest at the outer surface but decreases as the coating thickness is eroded away, while the components of the coating offering sacrificial or cathodic protection are more concentrated adjacent the coating-article interface so that cathodic protection of the coated article increases as the coating is removed by abrasion or erosion. As illustrative, the outer coating surface includes a high concentration of metallic components inherently resistant to saline corrosion and/or abrasion, although offering less cathodic protection for the coated article; while inner layers of the coating are rich in metallic components offering high sacrificial or cathodic protection, although less erosion or saline corrosion resistance.

5 Claims, No Drawings

MULTI-METAL CORROSION-RESISTANT DIFFUSION COATINGS

This is a division of application Ser. No. 733,303, filed May 31, 1968, now U.S. Pat. No. 3,642,457.

This invention relates to the protection of metal articles from corrosion in highly saline and/or marine atmospheres despite the fact that such articles are also to be used under circumstances where severe mechanical erosion or abrasion of the protective coating is likely to be experienced and, more particularly, to multi-component diffusion coatings in which the extent of sacrificial protection of the coated article from components in the coating increases as the thickness of the protective coating is eroded away by mechanical abrasion by utilizing for the outer surface of the coating components which have marked erosion and corrosion resistance, although little potential for cathodic protection, while utilizing in inner layers of the coating adjacent the coated article components with a high potential for cathodic protection although being of reduced erosion or corrosion resistance.

As purely illustrative of certain applications to which this invention is particularly related, and the problems incident thereto, one may note the circumstances and environments incident to the operation of certain components of jet aircraft engines in highly saline atmospheres (such as low flying aircraft, particularly helicopters, adjacent seaports and seacoasts), particularly where the highly saline marine atmosphere also includes substantial amounts of erosive particles of sand, coral dust, etc. Whereas the anti-corrosion problems of turbine components (as compared to compressor components) of such jet aircraft engines subjected primarily to only the impingement of extremely high-temperature combustion gases may relate so much to oxidation resistance at such high temperatures that other possible sources of corrosion become insignificant, the compressor components of such jet engines experience quite different problems. For example, the compressor components, while rarely subjected to operating temperatures above 900° F, are subjected to direct impingement of highly saline atmospheres at the air intake, which may also include substantial amounts of abrasive particulate material, in addition to being subjected to tremendous mechanical stresses from centrifugal forces, thermal shock, vibration etc., and under circumstances (particularly with single-engine aircraft) where premature failure of the compressor parts for whatever reason may be catastrophic, regardless of the fact that the greater problem of extremely high temperature oxidation-resistance of the hot turbine components may have otherwise been solved.

Thus, if the particular materials (such as high strength ferrous alloys like those designated in the Aerospace Material Specifications of the Society of Automotive Engineers as AMS 5508, AMS 5616, AMS 6304, etc.) are utilized for their mechanical strength in the compressor, they may have inadequate saline resistance or erosion resistance, without some protective surface treatment, and to an extent which cannot assure a useful and failure-free life comparable to that of the high temperature refractory metals or superalloys utilized in the hot turbine components of the same jet engines.

But jet engine compressor components must function and maintain their functioning within very low toler-

ances and clearances which do not admit of a substantial build up of corrosion products (rust, pulverous oxides, etc.), and even miniscule pitting from saline corrosion (characteristic of virtually all stainless steel parts subjected to saline atmospheres) may reduce the mechanical strength factor many-fold and to an extent which is inimical with adequate performance in such highly stressed parts as compressor blades, compressor rotors, and, particularly, the junctures therebetween subjected to great centrifugal and other vibrational and mechanical forces in a rotating manner and at speeds which cannot tolerate substantial radial imbalances.

If it is attempted to protect against the saline corrosion to be expected in such applications in marine atmospheres by, for example, a diffused nickel-cadmium electroplated protective coating (as set forth in AMS procedure 2416 D) or by the diffusion coating of metallic zinc into the surface of the ferrous structures to be protected, less than optimum results may be encountered. For example, considering a nickel-cadmium coating in which the nickel is adjacent the ferrous substrate (as is almost inevitable because cadmium is virtually insoluble in iron and, thus, is difficult satisfactorily to diffuse into a ferrous surface), neither component is sufficiently anodic relative to the substrate to assure absolute sacrificial protection in local areas where the electroplated nickel has not adhered to the ferrous substrate; and, furthermore, when the surface layer of cadmium is removed or penetrated by the inevitable erosion or abrasion encountered in such specific applications as noted above, the exposed sublayer of nickel is electrochemically noble relative to the ferrous substrate so that saline galvanic corrosion is actually intensified to an extent even greater than that which would occur in the same atmosphere with uncoated ferrous substrates.

Similarly, relying on a protective diffusion coating of zinc may eliminate or curtail the exaggeration of electrochemical saline corrosion of the ferrous substrate, but zinc is itself highly corrosive in saline atmospheres producing voluminous quantities of "white rust" deposit (such as complexes of zinc hydroxide and zinc chloride) which build up on the surface of the parts and diminish the mechanical tolerances and aerodynamic effectiveness of the surfaces thereof.

As will be understood, the foregoing difficulties are not necessarily disastrous in various types of hardware, even for the aforementioned applications. For example, the blades and shroud vanes of a jet engine compressor may be considered much more susceptible to mechanical erosion or abrasion by air-borne sand or coral dust particles than is the compressor rotor disc around the periphery of which the blades are fastened. Yet all are subjected to whatever electrochemical corrosion is inherent in such saline environments, and it is believed unrealistic to attempt to design a chemically or electrochemically or cathodically protective coating without recognizing that it may be subjected to mechanical erosion or abrasion onslaught at a rate which far exceeds the expected life of the coating even if it be considered as wholly electrochemically sacrificial. By the same token, if the protective coating be subjected both to mechanical erosion and sacrificial cathodic protection, particularly under circumstances where the rate of erosion exceeds that of cathodic sacrifice, then the need for cathodic protection increases the more the thickness of the coating diminishes by erosion — at

least to the extent that the less the coating mechanically protects against erosion and corrosion (i.e., the thinner the coating becomes), the greater is the need for cathodic protection of the substrate.

In accordance with this invention, by contrast to previous suggested solutions of such problems, there is provided a multi-component diffusion coating for ferrous metal articles or substrates having a composition gradient through the thickness of the coating from outer surface to coating-substrate interface varying in chemical and mechanical properties whereby, regardless of the resistance of the coating layers to mechanical erosion or abrasive wear, the outer surface has concentrated therein components particularly resistant to saline corrosion (although of less potential for cathodic protection of the substrate), while inner portions of the coating adjacent the substrate to be protected have concentrated therein components of increased potential for cathodic or sacrificial protection of the substrate (although perhaps less than maximally resistant to either mechanical erosion or direction chemical corrosion by the saline atmosphere). Yet all such components are applied in accordance herewith, and integrated with the metal article substrate to be protected by diffusion techniques producing substantially complete integration of the various coating components with the substrate article to be protected in a manner which substantially eliminates mechanical cracking or separation of the coating relative to the substrate despite intense mechanical or thermal shock stresses which may be encountered in use. As a further feature of this invention, there are provided a plurality of techniques for applying such a multi-component protective coating, either in one or more stages of application, to provide segregated but metallurgically unified areas through the coating of varying compositions and specifically located with regard to the nobility, sacrificial potentials, cathodic protection characteristics, and corrosion and erosion resistances to achieve optimal mechanical and electrochemical or cathodic protection of the metal article being coated.

With the foregoing and additional objects in view, this invention will now be described in more detail, and other objects and advantages will be apparent from the following description and the appended claims.

In attempting to select and devise the appropriate combinations of multi-metallic systems for achieving adequate or optimum protective coatings in accordance herewith, a number of independently variable, and often inconsistent, criteria need be kept in mind. For example, in order to avoid mechanical failures or separation under thermal shock or physical cracking of the coating materials, it is preferred that an actual diffusion of the coating material into the substrate be obtained (as compared, for example, to merely an electro-deposition or plating, although that may be an appropriate means for preliminary deposition of the coating metal provided it can be subsequently diffused into the substrate). Yet, there are some metals which might provide desired electrochemical protection but which are not susceptible to actual diffusion into a ferrous substrate (cadmium, for example, is virtually insoluble in iron and, thus, not susceptible for solid state diffusion thereinto).

Similarly, some metals are available for good initial corrosion protection or resistance to corrosion in saline atmospheres and adequately diffusible into iron, but

which do not render the desired cathodic or sacrificial protection of iron in a saline atmosphere (nickel, for example, which, being more noble than iron, actually increases the iron corrosion in any area where the nickel protective coating may have been worn away sufficiently to expose the iron substrate surface). Other metals which may be readily diffusible into iron and electrochemically appropriate for sacrificial protection thereof may not be sufficiently initially resistant to saline corrosion or mechanical erosion to last as a protective coating long enough for their sacrificial protection to be realized (zinc, for example, is readily diffused into ferrous substrates and sacrificially protective thereof, but so susceptible to initial saline corrosion as to produce such large initial quantities of "white rust" as frequently to outweigh the ultimate or subsequent protection which might be afforded).

Nevertheless, considering the foregoing criteria, and others as will be noted hereinafter, multi-component protective coatings have been devised in accordance herewith to give satisfactory or enhanced protection under the saline-corrosive and mechanically erosive environments noted by utilizing a combination of various metals to form a multi-layer coating where all components are diffused or interdiffused with a ferrous substrate and under circumstances where the composition gradient through the coating is such as to maximize initial saline corrosion and mechanical erosion when the coated article is put into use, while later maximizing cathodic sacrificial protection as outer layers of the coating are eroded or corroded away.

Merely as illustrative of the teachings hereof, one such protective coating system may be noted as a combination of cadmium and zinc supplied as a diffusion coating over the surface of a ferrous substrate under such circumstances that approximately the outer one-third of the coating thickness is rich in cadmium, while the inner two-thirds is rich in zinc. In this manner, initial saline corrosion of zinc is minimized by having the cadmium outer layer, while the cadmium-rich outer layer produces far less saline corrosion products than does zinc. Although cadmium is virtually insoluble in iron (thus minimizing its utility for direct diffusion coating into an iron substrate), it is readily soluble in zinc, and zinc is readily soluble in iron, so that the combination provides for an integrated diffusion coating of zinc into the iron substrate and then cadmium into the zinc coating.

It is not, however, necessary that the process be carried out in the above two-stage fashion. For example, satisfactory results were obtained in accordance herewith in the protective coating of steel articles fabricated from a ferrous material such as AMS 5616 (characterized in the Aerospace Material Specifications of the Society of Automotive Engineers as steel including about 13 percent chromium, 2 percent nickel, and 3 percent tungsten) by heating the articles to be coated at about 730°F. for about 12 hours embedded in a powder pack including, by weight, about 10 percent metallic zinc powder (-325 mesh), about 10 percent cadmium powder (-325 mesh) with a balance of about 80 percent tabular alumina as an inert filler. After such treatment, the articles, still embedded in the pack, were additionally heated to a temperature of about 830°F. for an additional half hour, and then air cooled. Because of the ready solubility of zinc into iron and the lack of solubility of cadmium, the foregoing process re-

sults in a protective coating with the outer surface primarily cadmium and the inner portion adjacent the coating-substrate interface rich in zinc in a manner which provides for a cadmium-zinc protective outer surface and a layer reservoir of zinc adjacent the substrate interface for cathodic sacrificial protection of the ferrous article when ultimate erosion of the outer surface of the coating occurs.

Somewhat similar results were obtained in accordance herewith in a two-stage pack impregnation process by first producing a preliminary coating of zinc (about 0.8 mil thick and comprising approximately 13 percent iron and 87 percent zinc) on the ferrous article to be coated by embedding it in a powdered pack including about 10 percent zinc, a vaporizable halogen or halide energizer (0.25 percent ammonium iodide and 0.125 percent iodine), and alumina as an inert filler, and heating at about 830°F. for 12 hours in a closed retort (all in known and well understood manner). Thereafter the thus coated article was embedded in a powdered pack comprising about 3.4 percent zinc powder (-325 mesh), 16.6 percent cadmium powder (-325 mesh) and the balance tabular alumina for an additional coating cycle at about 730°F. for 12 hours to provide an outer cadmium coating layer integrally and diffusion-bonded with the ferrous article and the preliminary zinc coating.

Although, as noted above, electroplating of the protective coating may not give optimum results because of a lack of integrity which may develop between the electroplated layer and the substrate, such techniques are appropriate for the preliminary deposition of various components of the protective coating in accordance herewith provided they can be subsequently integrated by diffusion or interdiffusion of the various components. For example, satisfactory results have been achieved in accordance herewith by diffusion coating a zinc layer on a ferrous substrate (such as AMS 5616) by the technique noted above (embedding in a pack comprising alumina, 10 percent zinc powder, 0.25 percent ammonium iodide and 0.125 percent iodine for a heating cycle of 12 hours at 830°F.) and thereafter electroplating cadmium over the thus coated ferrous article from a conventional cyanide electroplating bath. Thereafter, the plated article was heated in an inert powdered pack at about 650°F. for 4 hours to promote diffusion of the plated cadmium layer into the zinc-coated surface of the ferrous article for ultimate diffusion integration of the several components of the protective coating and to provide a cadmium-rich outer surface under which was a zinc-rich sacrificially protective layer bonded to the ferrous substrate.

As will be understood from the disclosure thereof, cadmium-zinc combinations are particularly attractive for multi-component protective coatings in accordance herewith because both such metals have high vapor pressures at relatively low temperatures and thus satisfy one of the requirements for direct vapor deposition in a powder pack cementation process. Furthermore, the vapor pressures of these two metals are adequately high for satisfactory deposition at treating temperatures which do not adversely affect the mechanical properties of the hardened and tempered steels of the types referred to earlier from which the ferrous metal articles are likely to be fabricated for applications to which this invention is particularly related (e.g., coating temperatures less than 900°F.).

Furthermore, the cadmium-zinc combination is particularly interesting in this connection because the physical vapor phase deposition of a metal (as opposed to a volatile compound of that metal) in a thermally homogenous powdered cementation pack is appropriate if the metal dissolves in the substrate to form an alloy therein the vapor pressure of which at coating temperature is lower than that of the metal being deposited. Although cadmium does not bear this relationship with iron, zinc does behave in this manner with respect to the ferrous substrate, and cadmium is soluble enough in zinc to be satisfactorily deposited simultaneously with zinc into a ferrous substrate and/or into a ferrous substrate previously coated with zinc.

Additionally, as noted above, these two metals are particularly attractive regarding the erosion and sacrificial protection of ferrous articles because zinc is highly cathodically protective of ferrous substrates (although not itself sufficiently resistant to direct saline corrosion) and cadmium is highly resistant to saline corrosion (although not itself sufficiently sacrificial to protect fully a ferrous substrate as with zinc, and the cadmium-zinc combination is more resistant to mechanical abrasion than either component alone. Similarly, the relative solubilities of cadmium and zinc in either zinc or iron automatically control the concentration gradient through the coating so as to concentrate cadmium on the outer surface while the inner layer of the coating adjacent the substrate interface is primarily rich in sacrificially protective zinc.

As will be apparent from the foregoing, a diffusion coating having a cadmium-rich surface and a zinc-rich undercoat is capable of affording adequate cathodic protection of the ferrous substrate while, at the same time, avoiding severe surface corrosion or "white rust" formation in a highly saline atmosphere. As the outer (cadmium) surface becomes partially or wholly removed by erosion or abrasion so as to reduce the coating thickness and even locally expose the substrate, then the zinc-rich undercoat thus exposed will afford increased cathodic sacrificial protection in the weakened areas. Even under such conditions, "white rust" deposits from the zinc form only in those areas where the zinc undercoat is exposed by erosion, not over the entire coating surface, and additional protection against saline corrosion and pitting of the ferrous substrate is extended by the cathodic or sacrificial protection of the zinc increasingly at the end of the expected service life of the coating where such protection is most crucial as the thickness of the coating becomes more and more eroded to the point of ultimate necessary replacement, repair, or recoating of the ferrous article.

Cadmium-zinc coatings of the type described above have been tested in a salt spray cabinet in accordance with Federal Test Method No. 811.151a to assess the protectability thereof, and in all such official testing, as well as other experience evaluations, the protectiveness of such coatings and the prolonged useful life thereof has far exceeded results with other previously acceptable zinc or cadmium or nickel coatings utilized for similar applications as discussed above.

Considering another multi-component coating system with which satisfactory results are achieved in accordance herewith, one may note a technique involving first coating the ferrous substrate with a diffusion coating of zinc, thereafter electroplating a thin layer of nickel on to the zinc-coated surface, and thereafter ad-

ditionally applying a diffusion coating of zinc with interdiffusion of all three layers for diffusion-bonding to the ferrous substrate and for driving the outer zinc layer into and through the nickel layer so as to provide an outer coated surface rich in nickel (for initial corrosion and abrasion resistance) and an inner layer rich in zinc for sacrificial protection upon eroding of the outer layer. In accordance with this embodiment, the ferrous article is first coated by impregnation in a zinc-containing cementation pack, as noted above, for 12 hours at 830° F., after which a thin layer of nickel is electroplated on to the thus coated surface by any of known means such as utilizing a conventional nickel sulphamate bath employing a current density of about 0.4 amps per square inch and a plating time of about 4 minutes. Thereafter the plated article is again embedded in the zinc cementation powdered pack for an additional 2 hours' heating at about 830° F.

The above noted treatment cycles are particularly designed to facilitate interdiffusion and bonding between all layers of the coating and between the zinc undercoat and the substrate. In this way, an efficient metallurgical bond is assured at all compositional interfaces, thereby reducing the possibility of layer spalling in use. The coating produced in accordance with this embodiment has a composition profile or a concentration gradient through the coating such that the zinc content of the coating drops from about 60 percent at a point approximately one-third of the way into the coating, and then rises to a constant level of about 88 percent over the inner one-third of the coating. The nickel content, on the other hand, rises steadily from the surface to reach a maximum (corresponding to the zinc minimum) at about one-third the thickness of the coating, and thereafter decreases toward the substrate-coating interface at which point it approximates whatever is the original nickel content (if any) of the base metal being coated.

Although a substantially pure zinc diffusion coating was applied as the last step to the outer surface of the above example, the diffusion conditions of the application of the zinc layer are such as to cause the zinc to diffuse into and through the nickel layer, thus uniting the electroplated nickel and decreasing the surface content of zinc. For this reason, the third step involves a diffusion coating of zinc for no more than about 2 hours, because a heavier application of zinc would result in too high zinc concentration on the outer surface and, thus, have little or no advantage over merely a zinc coating over the entire article. Indeed, for many applications, the first zinc coating step may be eliminated, with satisfactory results in accordance herewith having been achieved by directly electroplating nickel on the ferrous article, and then applying an outer zinc diffusion coating from a cementation pack with diffusion of the zinc into and through the electroplated layer to bond it to the surface of the ferrous article but still maintaining the concentration gradient of high nickel content at the surface and high zinc content for sacrificial protection adjacent the coating-substrate interface. Satisfactory results have been achieved by applying the zinc diffusion coating over the electroplated nickel from a pack such as noted above at a temperature of 750°-850° F. for about 12 hours. The presence of highly sacrificial zinc between the outer nickel layer and the ferrous substrate eliminates the above-noted difficulties with cadmium-nickel systems whereby ero-

sion of the coating and exposure of adjacent areas of nickel and ferrous substrate actually increases electrochemical corrosion because of the fact that nickel is noble with respect to ferrous metals in saline atmospheres and, consequently, not cathodically sacrificially protective thereof.

A further illustrative of multi-metal coating systems embodying and for practising this invention may be noted the diffusion coating obtained with satisfactory results on AMS 6304 steel utilizing a combination of zinc and lead. Such coatings were produced from a single-stage cementation process using a powdered pack including, by weight, 5 percent lead, 5 percent zinc, 90 percent tabular alumina, and 0.5 percent ammonium iodide, in which pack the AMS 6304 articles were heated at about 900° F. for 20-30 hours. The resulting coating provided a high concentration of lead at the outer surface, with a preponderance of zinc and very little lead in the undercoating adjacent the substrate surface. Here again, the surface concentration of lead decreases the immediate saline corrosion of zinc (with the undesirable "white rust" formation characteristic of such corrosion), while the internal concentration of zinc affords enhanced sacrificial protection when the outer surface of the coating begins to show the effect of mechanical erosion or abrasion.

In saline atmospheres, lead is considerably less anodic than zinc, as desired in accordance herewith, and relatively insoluble in the iron of the ferrous substrate, but soluble in the alloy produced between the ferrous substrate and zinc.

As will be apparent from the foregoing examples, satisfactory results have been achieved with coatings on steel materials and using the zinc-cadmium, zinc-nickel, or zinc-lead systems as disclosed, by producing the coatings at treating temperatures no higher than about 900° F. or less. With the types of steel-base articles noted above, as is well understood, a significant change or deterioration in metallurgical and mechanical properties (particularly fatigue life, tensile strength, and thermal shock resistance) may occur with metal articles fabricated from such materials if the articles are subjected to a post-fabrication temperature treatment above 900°-1,000° F. When the continued maintenance of high mechanical properties is an important consideration in the article being coated (as with the jet aircraft engine compressor components referred to above), it is of some significance to be able to provide whatever post-fabrication surface coating may be desired for corrosion protection at coating or treating temperatures below those at which the base metal article itself undergoes undesired crystallographic or metallurgical transformations, and it is in this area, among others, where the corrosion-resistant coatings according to this invention are particularly advantageous, in addition to the above-noted quality of providing preliminary corrosion and erosion protection at the surface with increased cathodic sacrificial protection as the coating is inevitably worn away.

It has been possible to devise diffusion coating systems and accelerators therefor which permit the diffusion coating of metal such as aluminum at coating temperatures far below those conventionally required for aluminum-base diffusion coatings (as disclosed in copending application Docket No. 24-669, filed of even date herewith) to avoid the above noted metallurgical difficulty, and some of such systems (notably those

combining aluminum and zinc) may be considered as having an electrochemical potential in saline atmospheres which would be cathodically sacrificially protective of ferrous substrates. Similarly, as disclosed in co-pending application Docket No. 24-670, filed of even date herewith, other aluminum-base diffusion coatings are provided to provide cathodic protection of ferrous substrates in saline atmospheres and at relatively low coating temperatures. In some of such other types of coatings, moreover, there is also to be found the additional feature here whereby the outer surface of the coating is rich in metal preliminarily resistant to saline corrosion and mechanical erosion, while inner layers of the coating are rich in a metal providing cathodic protection of the substrate although, perhaps, itself deficient in direct or initial corrosion resistance in the saline atmosphere against which protection is desired.

For example, utilizing a pack comprising 20 percent aluminum, 1 percent each cadmium and zinc, 0.5 percent ammonium iodide, and 0.25 percent urea, with the balance being tabular alumina, AMS 6304 articles were coated at 900°F. during a 30^o hour heating cycle to produce coatings of about 1 mil in thickness and having the composition of about 1-10 percent zinc and 60-65 percent aluminum at the substrate-coating interface, the balance being iron. The zinc content decreased to zero away from the substrate-coating interface, while the aluminum content increased toward the surface, thus producing the desired concentration gradient in accordance herewith whereby initial protection of the outer surface from both corrosion and erosion is attributable to the aluminum, while a zinc concentration near the substrate produces a potential for cathodic protection as the thickness of the coating is eroded or corroded away in use. Nevertheless, as noted below, the total potential difference between such coatings and substrate may not be as great as with the zinc-cadmium coatings in accordance herewith, but, with certain substrate materials, the aluminum-zinc coatings are sufficiently anodic to give the desired cathodic protection as the coating is worn thinner in use.

Also, as will be apparent from the foregoing, the coating systems embodying and for practicing this invention utilize the combination of a highly sacrificial metal of greater solubility in the substrate and a less sacrificial metal of less solubility in the substrate, and, preferably, also greater resistance to preliminary corrosion and erosion, with, of course, the further admonition that the two metals must be compatible with each other in the coating environment and susceptible of being diffusion coated as desired. It may also be noted that the more sacrificial of the two elements should possess an electrochemical potential with respect to the substrate sufficiently high to provide the desired cathodic protection thereof in saline atmospheres, but, preferably, no higher than is practically necessary to do so.

That is, if the more sacrificial coating metal is unnecessarily highly anodic with respect to the substrate, the principal result will be that it will be sacrificed, when electrochemical corrosion commences, at an unnecessarily high rate (however much it may protect the substrate), thus ultimately decreasing the total service life of the whole protective coating. As illustrative of the foregoing, one may note some comparative electrode

potential data regarding a number of the foregoing illustrative examples.

The electrode potentials of a number of samples were measured in a 3 percent NaCl solution at 22° C. with reference to a standard saturated calomel electrode ($E = 0.242$ volts on the hydrogen scale) after five minutes of immersion in the salt solution, with the specimens being cylinders 1 inch long and 7/16 inch in diameter. As will be understood, the more anodic surface was indicated by a higher negative electrode potential, which indicates a greater tendency for the surface metal to dissolve in or be corroded by the saline environment or atmosphere. Merely as illustrative of data obtained in such determinations, it may be noted that uncoated specimens of AMS 5616 and 6304 showed potentials of, respectively, -0.29 v. and -0.57 v., with such substantial variations apparently being attributable to the fact that the higher proportion of chromium in AMS 5616 substantially lowers the negative potential.

An AMS 5616 specimen with a diffusion coating of zinc alone showed a potential of -0.92 v., thus confirming the tremendous propensity for the zinc to combine with the saline atmosphere, however cathodically protective the zinc might be for the ferrous substrate. It was found that such high negative potential of the zinc coating could be substantially reduced (e.g., down to -0.83 v.) by chemical conversion of the diffused coating by immersion of the coated specimens in a bath of zinc phosphate in known manner, but the results of such conversion, particularly in atmospheres producing excessive erosion or mechanical abrasion, may be short lived. A specimen coated with a zinc-cadmium coating in accordance herewith (produced by the single-stage pack cementation process noted above) gave a potential of -0.81 v.

Similarly, regarding AMS 6304 specimens, a diffusion coating of zinc alone had a potential of -0.91 v., which was reduced to -0.82 v. by chemical conversion in a zinc phosphate bath. A zinc-cadmium diffusion coating in accordance herewith and produced by a single-stage pack cementation process had potential of -0.81 v. Additional specimens of AMS 5616 and 6304 coated with the aluminum-zinc diffusion coating noted above had potentials of, respectively, -0.78 v. and -0.77 v., which were further somewhat reduced by chemical conversion of the coated surface in aluminum chromate solutions (such as Alodine) to give, respectively, -0.74 v. and -0.72 v.

As will be apparent from the foregoing data, all the various coatings indicated are considerably more anodic than the ferrous substrate, thus offering sacrificial protection. Nevertheless, the pure zinc coatings exhibit such high negative potential that corrosion thereof in saline atmospheres would be excessively rapid, even if there were not the additional disadvantage of the excessive formation of "white rust" deposits on the article. Even reducing this negative potential by additional chemical treatment of the coated article produces no particular advantage over the zinc-cadmium coatings in accordance herewith, lacks the permanence thereof due to the interdiffusion of both metals, and requires an additional treatment step, while lacking the concentration gradient through the coating which provides for erosion and corrosion resistance at the coated surface and increased sacrificial protection nearer the substrate as the coating thickness becomes eroded away.

It has been developed in accordance herewith that adequate sacrificial protection of the substrate is obtained if the negative potential of the protective coating is at least 0.2 -0.3 v. higher than that of the substrate. Such a variance is preferred for applications to which this invention particularly relates because, with local erosion of the coating and/or pinholes or cracks therein, the exposed area of sacrificial metal, as compared to the exposed area of substrate, may not be expected to be large enough to offer satisfactory cathodic protection if the potential difference between the two metals is less than about 0.2 v. As noted above, however, it is not preferred to have this potential difference substantially above the minimum because, in that event, the principal result is merely to accelerate the rate of loss of the protective metal by corrosion without increasing the amount of sacrificial protection afforded. Generally, and as a practical matter, satisfactory results have been achieved in accordance herewith if the potential difference between the substrate and the protective coating is within the range of about 0.3-0.7 v. for coating thicknesses within the 1-2 mil range.

Considering the foregoing, the above electrode potential data indicate that, whereas the aluminum-zinc coating noted above might give substantial sacrificial protection on AMS 5616 steel articles, it falls far below the protection afforded by the zinc-cadmium coatings on AMS 6304 articles, undoubtedly because of the much lower proportion of zinc in the coating and notwithstanding the fact that most of the zinc is concentrated toward the substrate. Thus, although the aluminum-zinc coatings may offer enhanced overall protection against corrosion and erosion in saline atmospheres, such protection must largely be attributable to coating integrity or resistance other than cathodic protection — as contrasted with the zinc-cadmium coatings where total protection is achieved first by the inherent resistance of the cadmium-rich surface and, thereafter, by sacrificial protection of the zinc-rich interior of the coating as the coating thickness becomes eroded or corroded away.

As will be apparent from the foregoing, there are provided in accordance herewith coating materials and techniques for providing multi-component diffusion coatings on metal articles by simple, even one-step pack cementation procedures for protection of the metal article from erosive and corrosive saline environments. The coatings embodying and for practicing this invention are readily applied at temperatures low enough so that the coating step does not induce crystallographic or metallurgical transformations in the article being coated which might affect the mechanical properties thereof.

Furthermore, these multi-component coatings are produced on the base metal article in such fashion that the coatings become more anodic toward the substrate-coating interface for increased cathodic sacrificial protection of the substrate as the surface of the coatings becomes eroded away. Thus, the surface of the coating is rich in a component of increased corrosion and ero-

sion resistance, while the inner portions of the coatings are rich in a component offering greater sacrificial protection of the substrate although that component may have considerably less corrosion or erosion resistance. In any event, if there are components of the coating which are not anodic with respect to the substrate, electrochemical contact between the substrate and such less noble components is avoided despite the interdiffusion of all components and the substrate for complete unification and integration thereof against a possibility of fractures or spalling or separation of coating and substrate even under intense mechanical strain and thermal shock conditions.

While the methods and compositions set forth above form preferred embodiments of this invention, this invention is not limited to these precise methods and compositions, and changes may be made therein without departing from the scope of this invention which is defined in the appended claims.

What is claimed is:

1. A method of providing a ferrous metal article with a multi-component surface diffusion coating for both mechanical and cathodic protection against erosion by abrasion and corrosion by saline environments which comprises,

coating said article with a first coating metal of zinc which is both diffusably soluble in the surface of said article and substantially anodic electrochemically with respect thereto when diffused into the surface thereof and a second coating metal selected from the group consisting of cadmium, nickel and lead which is both less anodic than zinc and more resistant than zinc to said saline environment,

and diffusing both said coating metals thereon embedded in a powdered coating pack at a temperature ranging up to about 900°F. to effect metallurgical integration and bonding of said coating metals and said article forming said multi-component surface diffusion coating on said article with said zinc being concentrated adjacent the article-coating interface and said second coating selected from the group cadmium, nickel and lead being concentrated adjacent the outer surface of said multi-component coating.

2. The method of claim 1, wherein said first and second coating metals are applied by embedding said article in a pack containing said first and second coating metals dispersed through an inert filler, and diffusion coating said metals from said pack into the surface of said article such that the first coating metal is concentrated adjacent the metal substrate and said second coating metal is concentrated adjacent the outer surface of said multi-component coating.

3. The method of claim 1, wherein said second coating metal is cadmium.

4. The method of claim 1, wherein the second coating metal is lead.

5. The method of claim 1, wherein the second coating metal is nickel.

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