

[54] **PROCESS FOR PRODUCING A CORROSION RESISTANT DUPLEX COATING**

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3,705,818 12/1972 Grosseau ..... 117/93.1 PF

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[57] **ABSTRACT**

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A process for producing a corrosion resistant duplex coating having a metallurgically sealed undercoat, said undercoat being obtained by plasma depositing two or more materials onto a substrate in a substantially unreacted state so that when the coated substrate is heat treated in a non-oxidizing atmosphere, reaction/diffusion will occur between the materials thereby forming a metallurgically sealed undercoat securely bonded to the substrate and to a primary overcoat.

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[58] **Field of Search** ..... 117/93.1 PF, 105.2, 70 A, 117/70 C, 71 M, 131, 105; 29/195 M, 195 A, 196.2, 196.6; 148/31.5

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**UNITED STATES PATENTS**

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**10 Claims, No Drawings**

## PROCESS FOR PRODUCING A CORROSION RESISTANT DUPLEX COATING

### FIELD OF THE INVENTION

This invention relates to a process for producing a metallurgically sealed undercoat for a primary coated substrate which effectively protects the substrate from oxidation and/or corrosion attack.

### BACKGROUND OF THE INVENTION

There are many excellent coatings available for providing a substrate with a surface having specific characteristics suitable for a particular end use application. The coating may be applied to increase the wear-resistant characteristics of the substrate, decrease the contact-friction characteristics of the substrate, electrically or thermally insulate the substrate, or protect it from oxidation or other corrosive attack. Many such coatings, however, are inherently porous, as are the plasma deposited and detonation gun coatings, and thereby allow liquid or gas mediums in an end use environment to permeate to the substrate where the medium can attack and corrode the substrate. Thus an otherwise perfectly good coating for a particular purpose may be ineffective due to inherent porosity.

Several methods have been developed for sealing the inherent porosity of many coatings so as to provide an effective barrier to protect the substrate from attack by corrosive elements. One such method is to impregnate the coating with a silicone, an epoxy resin or a similar material which is highly resistant to many aqueous corrosive environments. This technique, however, requires a delicate process procedure for infiltrating the sealants into the pores of the coating and in addition, the sealants are unsuited for high temperature, highly corrosive environments, such as molten zinc, molten aluminum and the like, because of decomposition, oxidation and/or melting of the sealant.

Another method for sealing a porous type coating is to impregnate the coating with a low-melting metal which may effectively retard attack in some environments but would be ineffective in high temperature corrosive environments where it would very likely decompose, oxidize and/or melt. It may also react with and degrade the properties of either the coating or the substrate.

Other methods that have been developed include the flame spraying of two or more selected metals that will react exothermally during spraying to produce an intermetallic compound that will effectively bond to the substrate. These coatings may have less porosity than that of conventional type flame sprayed coatings, such as metals, alloys or ceramic coatings, but are not completely sealed.

The present invention differs from the above approaches which attempt to effectively produce an overall impervious coating, by being directed to the introduction of a plasma-deposited metallurgically sealed undercoat between a primary coating and a substrate. The undercoat comprises the simultaneous plasma-deposition of at least two materials which are deposited in the unreacted state so that when subjected to a heat treatment in a non-oxidizing atmosphere, a reaction-diffusion will occur between the materials.

### SUMMARY OF THE INVENTION

This invention is directed to a process for producing a coating having a metallurgically sealed undercoat. Specifically, the invention relates to a process for producing a coating by simultaneously depositing, by plasma-spraying or detonation gun techniques, a first layer of two or more materials, each of which is selected from at least one of the groups consisting of metals, alloys, and intermetallics, onto a substrate so as to form an interlocking lamellar structure composed of splats of the individual materials in a substantially unreacted state; followed by depositing a primary surface layer selected from at least one of the groups consisting of metals, metal alloys, intermetallics, metal oxides, metal nitrides, metal borides, metal silicides, metal carbides, and cermets, onto said first deposited layer; and thereafter subjecting the duplex deposited coating to an elevated temperature in a non-contaminating atmosphere for a time period sufficient to react/diffuse the materials in said first layer to produce a metallurgically sealed undercoat of a substantially homogeneous alloy and/or intermetallic. The undercoat produced between the primary coating and the substrate will effectively provide a barrier that will be inert or highly corrosion resistant in high temperature corrosive environments, such as air and other oxidizing gases at high temperatures. High temperature is intended to mean a temperature above which corrosion of an uncoated substrate material would begin, and which would rapidly continue. This temperature is a function of the medium in the environment and the composition of the substrate, and once both are known, an artisan can readily determine its numerical value.

The coated articles of this invention can also admirably be used in lower temperature environments presenting a severe corrosion problem, but, however, economics may limit the use of such coated articles under such conditions.

The coating applied according to this invention would also be admirably suited for environments where the coated article would be subjected to thermal fatigue since the surface bond phenomenon of the plasma-deposited coating would be sufficient to substantially secure the coating to the substrate and thus effectively eliminate spalling which usually occurs with conventional types of coatings.

The coated articles of this invention are also admirably suited for environments such as exist in the steel industry wherein the reaction between a steel substrate and molten zinc or aluminum is so great that any permeation of the molten medium or its vapor, through a porous type coating on the steel substrate will cause chemical attack at such a rate that the steel substrate will be rendered ineffective in a short time.

The metallurgical undercoat layer of this invention is essentially an as-deposited layer, applied by plasma or detonation gun techniques, comprising a mechanical mixture of two or more materials with significantly different chemical activity, such chemical activity being defined beginning on Page 91 of the text titled "The Theory of Transformation in Metals and Alloys" by J. W. Christian, Pergamon Press-Oxford, 1965 edition. Thus there exists in the undercoat a driving force, over and above the ordinary driving force of surface free energy that causes conventional sintering. In such an as-deposited coating, this additional energy appears to be

necessary to achieve densification and sealing at temperatures and within reasonable time periods. Conventional plasma-deposited coatings, and similar coatings, usually have a significantly lower coefficient of thermal expansion than the usual metallic substrates and thus when a coated substrate is heated, the coating tends to crack perpendicular to the surface and to shear the bond line with the surface. Moreover, this problem is compounded by the high residual tensile stress frequently present in an as-deposited coating. During the heat treatment of the metallurgical undercoat of this invention, the shrinkage that occurs due to reaction/diffusion between the materials tends to relieve the residual stress, and on subsequent thermal cycling in end use applications, the undercoat serves as a buffer between the primary coating and the substrate. In some cases this buffering is insufficient to prevent the perpendicular cracking of the primary coating, but it does prevent corrosive attack since the undercoat itself does not crack. In addition, the strong bond between the primary coating and the undercoat, and between the undercoat and the substrate, substantially eliminates failure due to shearing at these bonding lines.

The selection of a primary coating and the substrate will usually be somewhat dictated by the end use application of the coated article. The primary coating can be deposited by conventional plasma-spraying as disclosed in U.S. Pat. Nos. 2,858,411 and 3,016,447; by Detonation-Gun techniques as disclosed in U.S. Pat. Nos. 2,714,563, 2,950,867 and 2,964,420; by flame spraying techniques, by electro-deposition techniques, electrophoresis techniques, by slurry techniques, or the like. The similarity in a final coating obtained by these techniques is that the coating has inherent porosity that makes the substrate vulnerable to attack by a corrosive medium. For example, in the steel industry, a steel substrate, such as a roll, coated with alumina by conventional techniques, and then employed in a molten zinc or aluminum environment, will last only a relatively short time since the zinc or aluminum will permeate the alumina coating and attack the substrate. Thus the useful life of alumina coated rolls in the steel industry is relatively short when exposed to a molten zinc or aluminum environment even though alumina does not react with either molten zinc or aluminum.

Some examples of substrate materials used in various corrosive environments include, but not limited to, metals and alloys, such as steel, stainless steel, iron base alloys, aluminum, aluminum base alloys, nickel, nickel base alloys, cobalt, cobalt base alloys, copper, copper base alloys, chromium, chromium base alloys, refractory metals, and refractory base alloys. Likewise some primary coating materials suited for use in corrosive environment, include, but not limited to the following: metal, metal alloys, intermetallics, cermets, metal oxides, metal nitrides, metal carbides, metal borides, and metal silicides in a combination known to produce a good coating. Suitable metals include nickel (Ni), cobalt (Co), chromium (Cr), gold (Au), silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru) and the refractory metals. Suitable alloys would include the alloys of the above metals, and a suitable cermet would be a tungsten carbide cobalt composite or the like. Suitable metal oxides would include alumina ( $Al_2O_3$ ), silica ( $SiO_2$ ), chromium sesquioxide ( $Cr_2O_3$ ), hafnium oxide ( $HfO_2$ ), beryllium oxide ( $BeO$ ), zirconium oxide ( $ZrO_2$ ), stannic oxide ( $SnO_2$ ),

magnesium oxide ( $MgO$ ), yttrium oxide ( $Y_2O_3$ ), rare earth oxides, titanium dioxide ( $TiO_2$ ), and magnesium-zirconium oxide ( $MgZrO_3$ ). Suitable metal carbides include silicon carbide ( $SiC$ ), boron carbide ( $B_4C$ ), hafnium carbide (HfC), columbium carbide (CbC), tantalum carbide (TaC), titanium carbide (TiC), zirconium carbide (ZrC), molybdenum carbide ( $Mo_2C$ ), chromium carbide ( $Cr_3C_2$ ) and tungsten carbide (WC). Suitable metal borides include titanium boride ( $TiB_2$ ), zirconium boride ( $ZrB_2$ ), columbium boride ( $CbB_2$ ), molybdenum boride ( $MoB_2$ ), tungsten boride ( $WB_2$ ), tantalum boride ( $TaB_2$ ) and chromium boride (CrB). Suitable metal nitrides include aluminum nitride (AlN), silicon nitride ( $Si_3N_4$ ), titanium nitride (TiN), zirconium nitride (ZrN), hafnium nitride (HfN), vanadium nitride (VN), niobium nitride (NbN), tantalum nitride (TaN) and chromium nitride (CrN). Suitable silicides include molybdenum silicide ( $MgSi_2$ ), tantalum silicide ( $TaSi_2$ ), tungsten silicide ( $WSi_2$ ), titanium silicide ( $TiSi_2$ ), zirconium silicide ( $ZrSi_2$ ), vanadium silicide ( $VSi_2$ ), niobium silicide ( $NbSi_2$ ), chromium silicide ( $CrSi_2$ ) and boron silicide ( $B_4Si_2$ ).

The undercoat layer of this invention must be composed of at least two materials, each of which is selected from at least one of the groups consisting of elemental metals, alloys, and intermetallics, and such materials must be deposited on the substrate in an unreacted state; i.e., an interlocking lamellar structure composed of splats of the individual materials. The selection of the two or more materials for the undercoat is important since they must react/diffuse together at an elevated temperature so as to form a substantially homogeneous alloy and/or intermetallic; be compatible with the substrate such that they form a good bond while not significantly interdiffusing with the substrate upon being subjected to a heat treatment or when subjected to a particular end use environment; they must be compatible with the primary coating such that they do not significantly react and/or diffuse with such coating; and after reaction/diffusion has occurred, they must be capable of forming a substantially effective barrier between the substrate and any corrosive type medium that may exist in its intended end use environment which can permeate through the primary coating. Thus the reaction/diffusion that occurs during the heat treatment in a non-contaminating atmosphere will effectively seal the undercoat and provide a barrier for the substrate from corrosive attack. Although a substantially homogeneous alloy or intermetallic may be formed at the elevated temperature during the heat treatment, a precipitation may occur during cooling to ambient temperature whereby the precipitate would be distributed in a solid or alloy matrix, such precipitate being an alloy/or intermetallic formed from the deposited materials of the undercoat. Also, a transient intermetallic compound may form during the heat treatment which would convert to an alloy upon completion of the heat treatment. Thus at any particular time during the heat treatment, an intermetallic compound and an alloy, both formed from the materials of the undercoat, may exist simultaneously. However, in the preferred embodiment, an undercoat composed of a substantially homogeneous alloy or intermetallic would be desirable although an undercoat composed of an intermetallic compound distributed substantially throughout an alloy matrix would be suitable in certain applications.

The heat treatment and temperature required to achieve substantial homogenization and sealing during the reaction/diffusion step are a function of the materials of the undercoat. It is essential, however, that during deposition by plasma or detonation gun techniques, a minimum of oxidation of the materials occurs, and that the as-deposited composition consists of a mechanical mixture of discrete, essentially unreacted materials. If these requirements are not substantially met, the interaction between the materials during the reaction/diffusion step will be impeded and complete sealing will not occur. Although interdiffusion between the undercoat and the substrate or the primary coating should be very small in most cases, a minor amount may tend to increase the bond strength.

The particular materials selected for the undercoat on a substrate should, after the reaction/diffusion step, be resistant to the corrosive medium that will exist in the intended end use environment of the coated substrate. In some applications the selected reacted undercoat material may not possess the corrosion resistant characteristics necessary for a particular end use application and therefore an additional process step may be required for enhancing such characteristics. A conventional oxidizing, carburizing, nitriding, boriding, siliciding or the like, step may be sufficient to develop a corrosion resistant oxide, carbide, nitride, boride, silicide, or the like, respectively, on the undercoat segmented areas exposed to the exterior through the inherent porosity of the primary coating. This process treatment of the exposed segmented areas on the undercoat layer may be carried out in a controlled environment so as to react only one of the materials in the undercoat and thereby control the formation of the layer thickness on said segmented areas, or produce a layer on the segmented areas which has sufficient corrosion resistance. The formation of a thicker layer than necessary, may result in the spalling of the primary coating. If the end use or service environment is an oxidizing, nitriding or similar environment, then the particular oxide, nitride or similar compound chosen, respectively, should be a very slowly developing compound; i.e., growth controlled by slow diffusion as occurs in  $Al_2O_3$ .

Suitable materials for use in the undercoated layer include elemental metals such as nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, titanium, antimony, calcium, manganese, zirconium, vanadium, hafnium, magnesium, zinc and palladium, and alloys or intermetallics of the above elemental metals such as nickel-chromium, iron-chromium, cobalt-chromium, iron-chromium alloys containing rare earth additions, nickel-chromium alloys containing rare earth additions, cobalt-chromium alloys containing rare earth additions, and copper-aluminum. For the purpose of this invention, yttrium is included as one of the rare earth metals.

Any artisan can determine the choice of the undercoat materials that can be deposited in an unreacted state and thereafter upon being subjected to a heat treatment produce a substantially homogeneous alloy and/or intermetallic impervious undercoat, once the substrate and primary coating materials are selected, and the intended end use environment is known. The temperature at which the reaction/diffusion occurs between the selected materials of the undercoat is a function of such materials and can be readily determined from any good metallurgical text reference.

A non-contaminating atmosphere is required during the heat treatment of this inventive process to prevent a layer, such as an oxide layer, from interfering with the reaction/diffusion step of the process. A suitable non-contaminating atmosphere would be an inert atmosphere such as argon, helium, or vacuum, or a reducing atmosphere such as hydrogen.

When the reacted undercoat layer is to be oxidized, carburized, nitrided, silicided, borided or the like, to increase its corrosion resistance, then conventional processing techniques can be used. For example, the segmented areas of the undercoat exposed to the exterior through the porosity of the primary coating can be oxidized by exposure to a mixture of  $H_2O$  and  $H_2$  in such ratios that only the desired component of the undercoat is oxidized, such as aluminum in a nickel-aluminum undercoat. Nitriding of the exposed areas of the undercoat can be accomplished by exposure to nitrogen or ammonia at elevated temperature. The exposed areas of the undercoat could be carburized by exposure to methane at elevated temperature. Likewise, siliciding or boriding of the exposed areas can be accomplished by conventional techniques. The degree of formation of the oxide, nitride, carbide, silicide, boride or the like layer should be sufficient to produce the desired corrosion resistant characteristics necessary for the undercoat when exposed in a particular environment, while insufficient to cause the primary coating to spall.

A general procedure for implementing this invention will be illustrated by the following example. In the manufacture of a hot dip galvanized steel sheet, rolls are submerged in a molten zinc bath to guide the steel sheet through the bath in a particular manner. Since molten zinc is a very corrosive medium, the rolls are presently fabricated using expensive alloys such as special stainless steels. The useful life of such rolls are relatively short, about 5 to 20 days, before they are excessively damaged by the molten zinc bath. In addition, the reaction products produced therefrom have the detrimental effect of marking the steel sheet. Resorting to an alumina coating on a plain carbon steel roll would not only prevent the marking of the steel sheet since alumina does not react with zinc, but would also reduce both the initial cost and maintenance costs of the roll. However, without a means of sealing the porous coating and increasing its bond strength, the coating spalls due to thermal fatigue, and reaction of the zinc vapor with the carbon steel substrate occurs. Using the teaching of this invention, a mixture of 85 to 96% by weight of an iron-chromium alloy (80% iron, 20% chromium) and 4 to 15% by weight aluminum could be simultaneously plasma-deposited on the carbon steel roll and then over-coated with alumina by conventional techniques. The coated rolls could then be heat treated at a temperature between about 700°C. and about 900°C. in a hydrogen or argon atmosphere for a sufficient time period, about 4 to 20 hours, to allow reaction/diffusion of the components of the undercoat to seal the coating and form an essentially homogeneous alloy undercoat. This alloy, however, would not be completely resistant to attack by molten zinc since segmented areas of the alloy would be exposed to the exterior through the porosity of the primary alumina coating. To remedy this situation, the coated roll could be oxidized in an air atmosphere at a temperature of between about 700°C. and about 900°C. for a sufficient time period, about 4

hours, to from an oxide layer on the exposed areas of the undercoat. Since the oxide is not attacked by zinc, the coated roll is ideally suited for use in a molten zinc environment. Even though cracks, perpendicular to the surface of the substrate, may form in the alumina, the alumina will not spall from the undercoat due to the strong bond therebetween, and since the undercoat does not crack, the roll will be protected from attack by the zinc vapors. In some applications, it may be essential that only the aluminum in the undercoat be oxidized. To accomplish this requirement, the oxidation step should be performed in an atmosphere containing a partial pressure of oxygen, such oxygen being present only in an amount that would be sufficient to substantially oxidize the aluminum in the alloy, but not sufficient to effectively oxidize the iron or chromium.

It is also within the purview of this invention to have the undercoat layer heat treated prior to depositing the primary layer. Thus, after reaction/diffusion has occurred in the undercoat layer, the primary layer may be deposited by any conventional technique to produce a duplex coating having excellent corrosion resistant characteristics.

#### EXAMPLE 1

Two solid bars measuring 1 inch in diameter by one-half inch long, one of which was plain-carbon steel 1018 and the other a stainless steel 410, were given a plasma-deposited 0.0045 inch thick alumina coating. The two bars were subjected to a cyclic oxidation test consisting of exposing the bars to room temperature for one-half hour followed by subjecting them to an air environment heated to 900°C. for 2 ½ hours. After only 120 hours of this cyclic testing, the plasma-deposited alumina coating spalled from both samples. A conventional pre-alloyed undercoat of nichrome (Ni-80%; Cr 20%), 0.002-0.003 inches thick, was deposited on identical bars as described above, followed by a 0.0045 inch thick primary coating of alumina. The duplex coated bars upon being subjected to the same cyclic oxidation test and for the same duration as above, resulted in the cracking of both layers of the dual coating, and the exposed substrate was extensively oxidized.

Two bars, similar to the above, were given a 0.002 to 0.003 inch thick undercoat of a mixture of 95 wt/o nickel and 5 wt/o aluminum followed by a 0.0045 inch thick alumina primary coating. Again the duplex coated bars were subjected to the same cyclic oxidation test and for the same duration as above, and again the dual coating cracked exposing the substrate to the oxygen environment whereupon extensive substrate oxidation occurred as well as internal oxidation of the undercoat. In addition, most of the alumina spalled off the undercoat on the 410 stainless steel bar.

Two bars, similar to the above, were given a plasma deposited 0.002 to 0.003 inch thick undercoat of aluminum particles coated with nickel - intended to form a nickel aluminide undercoat-, followed by a primary 0.0045 inch thick coating of alumina. The duplex coated bars were subjected to the same cyclic oxidation test and for the same duration, and again the coating cracked exposing the substrate. Both the substrate and the undercoat were heavily oxidized and part of the alumina had completely spalled off on both bars.

Two bars similar to above, were plasma-sprayed with a mixture of 80 wt/o nickel and 20 wt/o chromium producing a 0.002 to 0.003 inch thick undercoat, followed

by a primary 0.0045 inch thick coating of alumina. The duplex coated bars were heat treated for 10 hours at 900°C. in hydrogen, and then selectively oxidized at 900°C. for 26 hours in a mixture of hydrogen and water vapor with a dew point of about -10°C., which was sufficient to form Cr<sub>2</sub>O<sub>3</sub>, but insufficient to form NiO, on the surface areas of the undercoat layer that were exposed through the porosity in the alumina primary coating. In a cyclic oxidation test as above, the metallurgically sealed undercoat on both bars showed no degradation after 120 hours.

A duplex coating, produced by plasma-depositing a 0.002 to 0.003 inch thick undercoat of a mechanical mixture of 76 wt/o iron, 20 wt/o chromium, and 4 wt/o aluminum, followed by a 0.0045 inch thick primary coating of alumina, was deposited on a 410 stainless steel bar and on a 1018 steel bar as above. The bars were then heat treated for 10 hours in hydrogen at 900°C. for 26 hours in a mixture of hydrogen and water vapor with a dew point of about -45°C., which was sufficient to form Al<sub>2</sub>O<sub>3</sub> but inhibit the formation of FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, or Cr<sub>2</sub>O<sub>3</sub> or their spinels. In a cyclic oxidation test for the same duration as above, the 410 stainless steel coated bar showed no degradation but the coating on the 1018 steel bar buckled due to thermal fatigue. A duplex coating, produced by plasma-depositing a 0.002 to 0.003 inch thick undercoat of a mechanical mixture of 65 wt/o iron, 20 wt/o chromium, and 15 wt/o aluminum, followed by a 0.0045 inch thick primary coating of alumina, was deposited on a 1018 steel bar. The coated bar was heat treated to 700°C. for 12 hours in hydrogen and then selectively oxidized at 700°C. for 8 hours in a hydrogen and water vapor mixture with a dew point of -45°C. The bar was subjected to the same cyclic oxidation test for the same duration as above, and upon being examined it exhibited no apparent damage as evidenced by metallographic examination.

#### EXAMPLE 2

Two 410 stainless steel rings and two 1018 steel rings, measuring 1 inch outside diameter, 0.9 inch inside diameter by 1/2 inch wide, were given either a conventional 0.002 to 0.003 inch thick nichrome undercoat or a 0.002 to 0.003 inch nickel aluminide undercoat as described in Example 1 so that each of the same type rings had a different undercoat. A primary plasma coating of alumina, 0.0045 inch thick, was then deposited on all four rings. The coated rings were then cut in half along a diameter and subjected to a 120 hour cyclic oxidation test as described in Example 1. Both the nichrome and nickel aluminide undercoated 410 stainless steel rings and the nickel aluminide undercoated 1018 steel ring failed in that the alumina/nichrome coating on the 410 stainless steel ring cracked and the substrate was oxidized, the alumina on the alumina/nickel-aluminide coated 410 stainless steel ring spalled off and the undercoat and substrate were badly oxidized, and both the alumina and undercoat on the alumina/nickel-aluminide coated 1018 steel ring spalled off and the substrate was severely oxidized. The nichrome undercoated 1018 steel ring appeared satisfactory except that a small amount of internal oxidation of the substrate did occur along with a few perpendicular cracks in the alumina that did not penetrate the undercoat.

Two 410 steel rings and two 1018 steel rings, similar to the above, were given either a plasma deposited 0.002 to 0.004 inch thick undercoat of a mechanical mixture of 76 wt/o iron, 20 wt/o chromium and 4 wt/o aluminum, or a mixture of 65 wt/o iron, 20 wt/o chromium and 15 wt/o aluminum, so that each of the same type rings had a different undercoat. The four rings were then plasma coated with a 0.0045 inch thick primary coating of alumina. The four rings were then heat treated in hydrogen at 800°C. for 4 hours. The duplex coated rings were thereupon cut in half along in diameter and subjected to a 120 hour cyclic oxidation test as described in Example 1 and upon being examined, they exhibited no significant damage whatsoever as evidenced by metallographic examination.

#### EXAMPLE 3

A 1095 steel substrate, measuring 1 inch diameter by 6 inches long with a hemispherical end, was given a plasma deposited 0.002-0.004 inch thick undercoat of a mixture of 80 wt/o nickel and 20 wt/o chromium, followed by a primary plasma coating, 0.004-0.006 inches thick. The coated substrate was heat treated for 8 hours at 900°C. in a hydrogen atmosphere and then heat treated at 800°C. for 4 hours in air. The coated substrate was placed in a molten zinc atmosphere at a temperature of 585°C. to 600°C. for 428 hours and upon being examined, it exhibited no evidence of failure. A plasma deposited alumina coating, without an undercoat, on a 1095 plain carbon steel substrate and on a 304 stainless steel substrate, both having the same measurements as above, lasted less than 250 hours when exposed to the same molten zinc environment.

#### EXAMPLE 4

A 0.0045 inch thick coating of alumina was plasma deposited on a 1018 steel substrate, a 1095 steel substrate and a 304 stainless steel substrate, each of which had the dimensions of the substrate in Example 3. The three coated specimens were then subjected to a cyclic corrosion test by being submerged in a molten aluminum at 700°C. The coated specimens were submerged in the aluminum bath for about 125 hours and then exposed to air at room temperature for 2 hours before resubmerging them back into the bath. The 1018 and 1095 steel coated specimens failed in less than 125 hours, such failure being the spalling of the alumina coating and attack of the substrate by the aluminum. In less than 400 hours of the cyclic testing, the 304 stainless steel specimen failed in the same manner.

Four 1018 steel specimens, identical to the one described above, were plasma-sprayed with different mixtures of materials as shown in the Table below. Over the 0.002 to 0.004 inch thick undercoats, a primary plasma coating of 0.0045 inch thick alumina was deposited. The duplex coated specimens were then subjected to a reaction/diffusion heat treatment followed by a preoxidation step as shown in the Table. The specimens were then subjected to a cyclic corrosion test as described above and after 900 hours specimens 1, 3 and 4 showed no sign of failure. The test for specimen 2 was terminated after 800 hours for testing convenience and at that time exhibited no apparent sign of failure as evidenced by visual and metallographic examinations.

TABLE

Specimens	Composition	Reaction/Diffusion Heat Treatment	Preoxidation
1	Fe+ 20wt/oCr+4wt/oAl	5 hrs at 800°C. in vacuum	5 hrs at 800°C in air
2	Ni+ 20wt/oCr*	6 hrs at 800°C. in hydrogen	2 hrs at 800°C. in air
3	Ni+ 31wt/oAl	4 hrs at 800°C. in hydrogen	4 hrs at 800°C in air
4	Ni+ 31wt/oAl	5 hrs at 800°C. in vacuum	5 hrs at 800°C in air

\* Test terminated at 800 hrs.

#### EXAMPLE 5

To determine the combined effects of externally applied loads and a high-temperature molten-metal environment on duplex coated substrate processed in accordance with this invention, a duplex coated article was prepared in the following manner. The clean face of a 20-inch diameter by 60-inch long low-alloy carbon steel roll (1080 steel), such as a pot roll (or sink roll) which in the steel industry keeps a steel sheet submerged in a molten aluminum pot for the purpose of aluminizing the surface of the steel strip, was degreased using N-D-150 degreasing fluid made by National Chem Search of St. Louis. The surface was mechanically roughened by grit-blasting with 60 mesh Al<sub>2</sub>O<sub>3</sub> abrasive (Fast-Blast 60). The roll was then positioned in a machine capable of rotating a piece at 159 rpm and traversing a plasma torch at 0.33 inch/second. A plasma torch fitted with a copper anode was used for spraying the undercoat material. An inert gas shield with argon was used to prevent oxidation of the material during spraying. The undercoat material was sprayed as a mechanical mixture of two powders, 96 w/o of an alloy of FeCr and 4 w/o of unalloyed Al. The FeCr alloy was 80w/o Fe and 20 w/o Cr. The thickness of the undercoat was 0.003 inch.

The overcoat, 0.0032 inch thick, was sprayed immediately after and on top of the freshly deposited undercoat and was composed of pure Al<sub>2</sub>O<sub>3</sub>. A plasma torch fitted with a copper anode was also used for this overcoat. The same rotation and traverse speeds used for the undercoat were also used for the overcoat of Al<sub>2</sub>O<sub>3</sub>.

The roll was heat-treated in the following manner. A retort was constructed of 1020 steel which had the following dimensions: 24 inches ID and 10 feet long. Gas and thermocouple connections were provided at one end of the retort. The roll was placed in the retort and supported on journals at its ends. The retort was then welded closed and leak-tested. The retort was evacuated with a vacuum pump and back-filled with argon twice to remove oxygen from the container. The retort containing the roll was positioned in a gas-fired furnace and pure hydrogen gas was fed to the retort as the temperature was raised in the furnace to 800°C. and held there for a 4-hour soak to effect sealing of the undercoat by reaction/diffusion. The roll and retort were furnace-cooled to room temperature and the retort opened for inspection. The furnace temperature was again raised to 800°C. with the roll exposed to air and held again for a 4-hour soak to form an oxide barrier

on the exposed areas of the undercoat. The roll was then allowed to cool to room temperature whereupon it exhibited a smooth surface of white  $Al_2O_3$ .

The roll was preheated in a clamshell-type glow-bar furnace to a temperature of 300°C. and then installed in a continuous aluminizing line which was capable of aluminizing steel strip at a line speed of approximately 150 feet per minute. This roll was tested in excess of 176 hours, after which it was inspected and found to exhibit no deterioration. As a result of this test the useful life of this roll was estimated to be in excess of 350 hours. An uncoated roll made of 1080 steel has 72 hours of useful life before replacement and thus a 250 to 300 percent improvement in life of a coated roll over an uncoated roll can be expected using the process of this invention.

#### EXAMPLE 6

To determine the effects of a continuous thermal gradient combined with both an oxidizing and molten-metal environment, a steel heater probe made of AISI 1080 steel was prepared for testing in the following manner. The surface of the probe was cleaned with trichloroethylene to remove surface grease and contamination. The surface was mechanically roughened by grit-blasting with 60 mesh  $Al_2O_3$  abrasive. The probe was held in a rotation and traversing mechanism. The rotation speed was 800 rpm, and the traverse rate was 24 inches/minute. A plasma torch fitted with a copper anode was used for spraying the undercoat material. An inert gas shield with argon was used to prevent oxidation of the material during spraying. The undercoat consisted of a mechanical mixture of 96 w/o of an Fe-Cr alloy and 4 w/o of unalloyed Al. The Fe-Cr alloy was 80 w/o Fe and 20 w/o Cr. The thickness of the undercoat was 0.006 inch.

The overcoat, composed of pure  $Al_2O_3$ , was sprayed on top of the undercoat. No surface preparation was required. A plasma arc torch was used with a copper anode as above. The overcoat of  $Al_2O_3$  was deposited to a thickness of 0.0045 inch. The same rotation and traverse speeds as used for the undercoat, were used for the overcoat of  $Al_2O_3$ .

The probe was heat-treated in the following manner. The probe was held vertically on a steel pedestal and loaded in a resistance heated vacuum furnace. The furnace was evacuated to a pressure of  $10^{-5}$  to  $10^{-6}$  torr to effect reaction/diffusion of the undercoat. The probe was furnace-cooled to room temperature and removed.

The surface was smooth and white with no cracks or discoloration. The probe was installed in an aluminizing line and functioned to melt dross and slag at the exit end of the chute which carries the strip. The probe was fitted with a silicon carbide resistance heater to provide heat for melting the slag or dross. The probe lasted in excess of two weeks while an uncoated probe would last only 2 to 3 days. Thus a 450 percent increase in the life of a coated probe over an uncoated probe would be realized by using the process of this invention.

#### EXAMPLE 7

To determine the combined effects of impact loading and a molten metal with a high vapor pressure, a stabilizer or flutter roll, which keeps the steel strip straight and in contact with the sink roll for the purpose of galvanizing the surface of the strip, was prepared and tested.

The surface of a high carbon steel roll which was 8 inches in diameter and 74 inches long was cleaned with N-D-150, a degreasing fluid. The surface was mechanically roughened by grit-blasting with 60 mesh  $Al_2O_3$  abrasive. The roll was positioned in a rotation and traverse mechanism. The rotation speed was 397 rpm, and the traverse speed was 0.41 inch/second. A plasma torch with a copper anode was used for spraying the undercoat material. An inert gas shield with argon was used to protect the molten particles from oxidation during spraying. The undercoat consisted of a mechanical mixture of 96 w/o of an alloy of Fe-Cr and 4 w/o of unalloyed Al. The Fe-Cr alloy was 80 w/o Fe and 20 w/o Cr. The thickness of the deposited undercoat was 0.003 inch.

The overcoat, composed of pure  $Al_2O_3$ , was sprayed on top of the undercoat. No surface preparation was required prior to spraying the  $Al_2O_3$ . The rotation and traverse speeds used were the same as those used for the undercoat. A plasma torch with a copper anode was used, as above, to deposit the  $Al_2O_3$  to a thickness of 0.003 inch.

The roll was heat-treated under the following conditions. A mild steel retort 24 inches ID by 10 feet long was fabricated. Gas and thermocouple connections were provided at one end of the retort. The roll was supported at each end on the journals. The retort was welded closed and leak-tested with a soap solution. The retort was evacuated with a vacuum pump and back-filled with argon twice to remove oxygen from the container. The retort containing the roll was positioned in a gas-fired furnace and pure hydrogen gas was fed to the retort as the temperature was raised in the furnace to 800°C. and held there for a 4-hour soak period. The roll and retort were furnace-cooled to room temperature and the retort opened. The furnace temperature was again raised to 800°C. with the roll exposed to air and held again for a 4-hour soak to oxidize the exposed areas on the undercoat. The roll was allowed to cool to room temperature.

The roll was preheated to about 300°F. and installed in a continuous galvanizing line. This line galvanizes steel sheet at a line speed of approximately 150-200 feet per minute. After 7 days the roll was still functioning and showed no sign of apparent damage.

#### EXAMPLE 8

Two T-shaped cross-sectional area test specimens made of HA-188\*, a cobalt-base superalloy, and each measuring 4 inches long, three-eighths inches wide on its top face, one-sixteenth inch thick and having a three-eighth inch center leg, were first plasma coated on their top faces with a 0.003 to 0.005 inch layer of a mixture of 80 wt/o of an alloy of 75 wt/o Co and 25 w/o Cr, and 20 wt/o of unalloyed Al. An overcoat, 0.002 to 0.003 inches thick of  $MgZrO_2$ , was then plasma deposited onto the first coat on each specimen. The specimens were then heated to 1,079°C. in hydrogen and held at this temperature for 5 hours so as to seal the undercoat by reaction/diffusion.

\* Trademark of Cabot Corporation

Four similar sized specimens were plasma sprayed with a 0.004 to 0.005 inch thick undercoat layer of a synergistic nickel-aluminum powder as in Example 1 and then a 0.003 inch overcoat of  $MgZrO_3$  was plasma deposited thereon.



Two similar sized specimens were plasma sprayed with a 0.004 to 0.005 inch thick undercoat of Stellite 31\* alloy (25.25 wt/o Cr, 10.5 wt/o Ni, 7.5 wt/o W, 0.5 wt/o C, Balance Co) and then a 0.003 inch overcoat of MgZrO<sub>3</sub> was plasma deposited thereon.

\* Trademark of Cabot Corporation

All the specimens were tested in a special oxyacetylene torch flame impingement apparatus to simulate the conditions in a gas turbine burner can. The torch flame was directed to impinge the coated top faces of the T-shaped specimens whereupon the temperature at the coated surfaces increased to 2,700°F. The test was continued for one hour after which the specimens were examined. All the test specimens, except the CoCr+Al undercoated specimens which were prepared in accordance with this invention, had spalled. A metallographic examination of the CoCr+Al undercoated specimens showed the undercoat of each to be slightly oxidized but the coating was intact except at the edges.

What is claimed is:

1. A process for producing a corrosion resistant duplex coated article comprising:

- a. depositing an undercoat of at least two materials, each of which is selected from one of the groups consisting of metals, alloys, and intermetallics, onto an article such that the materials are simultaneously deposited in a substantially unreacted state;
- b. depositing a primary coating selected from at least one of the groups consisting of metals, metal alloys, intermetallics, metal oxides, metal carbides, metal nitrides, metal borides, metal silicides, and cermets, onto the as-deposited undercoat; and
- c. heating said duplex coated articles in a non-contaminating atmosphere at a temperature and for a time period sufficient to cause the substantially unreacted materials in the undercoat layer to react or diffuse together thereby forming a substantially sealed, nonporous undercoat layer.

2. The process of claim 1 wherein the undercoat layer in step (a) is deposited by plasma deposition techniques, and wherein the metals are selected from a group consisting of nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, zirconium, vanadium, hafnium, magnesium, zinc, titanium, antimony, calcium, manganese and palladium; wherein the alloys are selected from a group consisting of the alloys of the above metals, and wherein the intermetallics are selected from a group consisting of the intermetallics of the above metals.

3. The process of claim 1 wherein each of the materials in step (a) is selected from one of the groups consisting of nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, titanium, zirconium, vanadium, hafnium, magnesium, zinc, antimony, calcium, manganese, palladium, nichrome, iron-chromium alloys, iron-chromium intermetallics, cobalt-chromium alloys, cobalt-chromium intermetallics, iron-chromium alloys containing rare earth additions, nickel-chromium alloys containing rare earth additions, cobalt-chromium alloys containing rare earth additions, copper-aluminum alloys and copper-aluminum intermetallics.

4. The process as in claim 3 wherein the material of the article is selected from a group consisting of steel and cast iron; wherein in step (a) one of the materials

is aluminum and the other material is selected from a group consisting of iron-chromium alloys, nickel-chromium alloys and cobalt-chromium alloys; and wherein in step (b) said primary coating is alumina.

5. The process of claim 1 wherein an additional step is added after step (c) as follows:

- d. subjecting the duplex coated article to an oxidizing atmosphere, a carburizing atmosphere, a nitriding atmosphere, a boriding atmosphere, or a siliciding atmosphere for a time period and at a temperature sufficient to react the medium in the atmosphere with segmented areas on the surface of the undercoat that are exposed to the exterior through the porosity of the primary coating thereby providing a layer of the reacted medium on said exposed areas.

6. The process of claim 4 wherein after step (c) the following step is added:

- d. subjecting the duplex coated article to an oxidizing environment for a time period and at a temperature sufficient to oxidize segmented areas on the surface of the undercoat that are exposed to the exterior through the porosity of the primary alumina coating thereby providing an oxidized layer on said exposed areas.

7. The process of claim 5 wherein the medium in the atmosphere is present in a sufficient amount and under a sufficient partial pressure so as to effectively react the medium with one of the materials on the exposed areas of the undercoat surface.

8. The process as in claim 3 wherein in step (a) the two materials are aluminum, and a cobalt-chromium alloy containing rare earth additions; and wherein in step (b) said primary coating is MgZrO<sub>3</sub>.

9. A process for producing a corrosion resistant duplex coated article comprising:

- a. depositing an undercoat of at least two materials, each of which is selected from one of the groups consisting of metals, alloys, and intermetallics, onto an article such that the materials are simultaneously deposited in a substantially unreacted state;
- b. heating said coated article in a non-contaminating atmosphere at a temperature and for a time period sufficient to cause the substantially unreacted materials in the undercoat layer to react or diffuse together thereby forming a substantially sealed, nonporous undercoat layer; and
- c. depositing a primary coating selected from at least one of the groups consisting of metals, metal alloys, intermetallics, metal oxides, metal carbides, metal nitrides, metal borides, metals silicides, and cermets, onto the substantially sealed undercoat layer thereby producing a duplex layer having excellent corrosion-resistant characteristics.

10. The process as in claim 9 wherein each of the materials in step a) is selected from the group consisting of nickel, aluminum, cobalt, iron, chromium, copper, molybdenum, tungsten, niobium, tantalum, titanium, zirconium, vanadium, hafnium, magnesium, zinc, antimony, calcium, manganese, palladium, nickel-chromium, iron-chromium alloys, iron-chromium intermetallics, cobalt-chromium alloys, cobalt-chromium intermetallics, iron-chromium alloys containing rare earth additions, nickel-chromium alloys containing rare earth additions, cobalt-chromium alloys containing rare earth additions, copper-aluminum alloys and copper-aluminum intermetallics.

\* \* \* \* \*



UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,837,894 Dated September 24, 1974

Inventor(s) Robert C. Tucker, Jr.

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

Column 4, line 15; (ZrW) should read -- (ZrN) --

Column 11, line 13; after the word "hours" insert  
-- to 120 hours --

Signed and sealed this 17th day of December 1974.

(SEAL)  
Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents