Current Research Status of Corrosion Resistant Coatings

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Abstract: The recent patents on corrosion resistant coatings were reviewed in this paper. The materials of corrosion resistant components, e.g., metals and alloys, ceramics, polymers as well as composite materials, developed for environmental, economic and other concerns were discussed. In addition, the novel methods for forming the coatings, including the powder floating by vibration and the precursor gas, as well as some widely employed methods in the industrial applications were also included to provide useful information for colleagues.

Keywords: Corrosion resistant, coatings, materials, methods.

INTRODUCTION

The corrosion of materials causes great loss in the industrial applications, especially under some extreme conditions, i.e. the corrosive atmosphere and high temperature. The corrosion resistant coatings have attracted many attentions for many years due to its simplicity and efficiency [1-2]. For example, the cadmium plating has been widely used for corrosion protection of steel workpieces because of its good corrosion resistance and lubricity [1]. However, the environmental protection regulations have restricted the use of cadmium, which is considered to be toxic. Similarly, the chromium-containing materials also need to be carefully handled to avoid the formation of chromate phase; e.g., see Suzuki *et al.* [3], Nagaraj *et al.* [4], Hazel *et al.* [5] and Hawkins [6]. Therefore, there is the need for developing materials to replace the toxic elements in traditional coatings. In this paper, the recent patents on corrosion resistant coating developed for environmental, economic and other concerns will be reviewed, including metals and alloys, ceramics, polymers, as well as composite materials.

In addition, it is often desired to form a film only in a specific region to be exposed to the corrosive environments [7]. Furthermore, there is also the need for forming the coating at locations inside components and at locations normally unreachable by a gas flowing through the components, such as gas flow regulators in microelectronic fabrication [8]. The novel methods for forming the coating in the desired region as well as some conventional application techniques were also reviewed in this paper to provide useful information for colleagues.

MATERIALS OF CORROSION RESISTANT COMPONENTS

(i). Compositions for Corrosion Resistant Concern

Fig. (**1**) shows the distribution of patents on corrosion resistant coatings disclosed from 2005 to 2009. Metals and

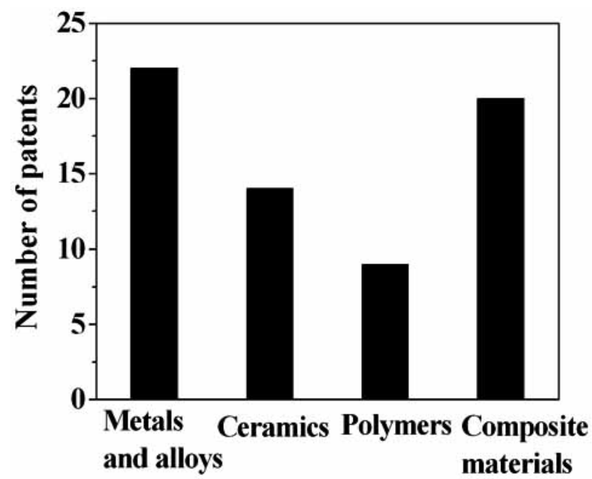

Fig. (1). The distribution of patents on corrosion resistant coatings disclosed from 2005 to 2009.

alloys are most commonly chosen for corrosion resistant concern, especially for metallic or ceramic substrates. A coating of gold was applied to the substrate of the microstructure product (e.g., platinum silicide) and the handler substrate, due to its good corrosion resistance, electrical conductivity and reliability [2]. A Rhenium (Re) based alloy coating was applied to the Ni-based super alloy substrate, as a diffusion barrier layer, to provide the enhanced corrosion resistance for the high temperature components, e.g., a blade for jet engines or gas turbines [9-11]. In addition, a two-layered coating was patented by Creech *et al.* [12], as a diffusion barrier layer, to provide the corrosion resistance for Ni-based alloy components, such as turbine blades and vanes. Such coating includes a first layer comprising an MCrAl(Y,Hf) alloy, where M is selected from Co, Ni, Fe, and a second layer comprising a noble metal, silicon, aluminum and chromium. A coating of stainless steel was utilized to protect the joint bead, between the stainless steel hanger bar and the copper starter sheet, from corrosion to provide an improved electrolytic cathode for use in the refining of copper [13]. An alloy coating comprising at least 60 weight percent (wt %) iron, cobalt and nickel was applied to the base steel member of sprocket wheels, as the corrosion resistant material, to improve the service life and performance characteristics [14]. A corrosion resistant

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coating comprised of Sc, Ti, Cr, Zr, Nb, Mo, Hf, Ta, W, Ni, and Al, and their alloys was patented by Kim *et al.* [15-17] for the water-cooled stator bars clips used in electrical generators to extend the projected lifetime of the clips. Shibata *et al.* [18] patented a coating comprising corrosion resistant metals, such as Ta, Pt and TiW, to protect the electrode wires against corrosion in an ink jet head circuit board.

Ceramics are also favored in the design of corrosion resistant coatings. A protective coating comprised of a metal silicate, such as yttrium silicate, scandium silicate, zirconium silicate, hafnium silicate, or rare earth silicate, was disclosed [19] for a silicon-containing substrates in a corrosive water-containing environment, such as gas turbine engines, heat exchangers and internal combustion engines. A coating of Y_2O_3 was applied to the surface of an Al_2O_3 substrate as the corrosion resistant component in the semiconductor manufacturing equipment, which is exposed to plasma and subjected to relatively rapid corrosion, e.g., shower head, focus ring and shield ring [20]. A corrosion resistant coating of calcium aluminum oxide, e.g., $Ca_{12}Al_{14}O_{33}$ or $Ca_3Al_2O_6$, was developed for a base material made of aluminum nitride by Hattori *et al.* [21], in the manufacture of the semiconductor device and the liquid crystal device. In addition, such material also contains about 10 wt % SiO_2 to maintain the desired corrosion resistance. A coating consisting of zirconia toughened alumina (ZTA) was invented for the metals/alloys substrates, e.g., aluminum, stainless steel and refractory metals, in the semiconductor processing equipment, such as plasma etch chambers, to improve the corrosion resistant of the component and reduce the particle and metallic contamination of the wafer surface [22]. A corrosion resistant coating comprising graphite was developed by Iqbal *et al.* [23, 24] for the bipolar plate of the fuel cell, e.g., aluminum. Such design also includes an electrically conductive coating of graphite emulsion to bond the corrosion resistant coating with the metal plate.

In addition, some polymers also act as corrosion resistant materials due to the impervious nature. For example, a polymeric bushing was employed by diGirolamo *et al.* [25] for isolating the anchor bolt from a treated sill and providing an impervious barrier to prevent the anchor bolt from being corroded due to the treated nature of the seal. An impermeable polymeric coating was patented by Lee *et al.* [26-27] to protect the bipolar plate of the PEM (i.e., Proton Exchange Membrane) fuel cell, e.g., aluminum and its alloys, from corrosion. Such coating comprises polymers, e.g., epoxies, silicones, polyesters, polyphenols, polyamide-imides, polyether-imides and urethanes. A Xylan/Teflon fluorocarbon coating was developed by Thomae [28] for zinc-iron electroplated substrate in automobile applications, such as automotive body sheet steel, underbody parts and under-hood parts, to meet a minimum of 500 salt spray testing hours to white corrosion, and 1500 salt spray testing hours to red corrosion when tested to ASTM B117 standards. Such coating comprises polytetrafluoroethylene and a blend of fluorocarbon lubricants bound by an organic resin and solvent system. Fredericksen *et al.* [29] patented an epoxy coating for the metal strapping material to obtain a dramatic (e.g., ten-fold) increase in the corrosion resistance characteristics, compared with that of commercially available liquid coated strap. A corrosion resistant coating was applied to the surface of aluminum or aluminum alloy by Kramer *et al.* [30], especially for the reflectors with high overall reflection in the visible and infrared wavelength ranges. Such coating comprises a polymer of cross-linked inorganic siloxanes with alcohol groups that are bonded to the silicon with a carbon bond.

Moreover, composite materials have been developed to provide the necessary corrosion resistance in the components. A composite coating was employed by Hazel *et al.* to provide the better corrosion resistance for gas turbine components, such as the turbine blade [4] as well as the turbine disk, shaft and seal [5], compared with nickel-base super alloys at elevated temperature. Such coating comprises from 0 to about 95 % alumina and from about 5 to 100 % non-alumina particulates having an overlay metal alloy, e.g., MCrAlY (M is a nickel or nickel-cobalt alloy), and yttria-stabilized zirconia. Another composite coating, comprising the aluminum-containing metal particulates with a phosphate and/or silica-containing insulating layer and a glass-forming binder component, was patented by Buczek *et al.* [31] to provide the necessary corrosion resistance for the gas turbine components, e.g., the turbine disk, shaft, blade and vane. The insulating layer can be derived from triethyl phosphate, ammonium monohydrogen phosphate, tetraethyl orthosilicate, etc. The binder component comprises glass particulates, frits comprising other inorganic minerals, as well as phosphate binder, e.g., aluminum phosphate, magnesium phosphate and chromium phosphate.

(ii). Compositions for Environmental Concern

Some novel compositions of the corrosion resistant coatings have been developed for environmental concern. For example, a zinc-nickel alloy coating, comprised of about 85 to 95 wt % zinc and about 5 to 15 wt % nickel, was designed to replace cadmium in steels as the corrosion resistant material [1].

The use of hexavalent-chromium, i.e., chromate phase, has been restricted by environment regulations in recent years, in spite of its excellent corrosion resistance. Many efforts have been made on the chromium-containing corrosion resistant materials to avoid the formation of the chromate phase during the manufacture. For example, a chromium-containing coating was invented for steel substrates without containing the toxic chromate phase [3]. Such structure includes a Zn/Ni alloy layer with a Ni content of 6 to 15 wt %, a trivalent chromate layer positioned on top of the Zn/Ni alloy layer, and a resin layer positioned on top of the trivalent chromate layer. A phosphate-containing binder was also employed in the corrosion resistant component developed for gas turbine components [4, 5], including aluminum phosphate, magnesium phosphate, or chromium phosphate to avoid the formation of chromate phase for environmental concern.

Some environmental friendly compositions have also been investigated to replace the hexavalent-chromium as the corrosion resistant materials. A conversion coating prepared using ferrate (VI) as the oxidizing agent was patented by Minevski *et al.* [32] for metal substrates, such as aluminum and aluminum alloys to provide a corrosion-resistant coating on metal surfaces without containing the hexavalent-chromium. The aqueous solution employed for forming the conversion coating comprises ferrate anion (0.0166 % to 1.66 wt %) and other transition metal oxyanion such as permanganate, molybdate, vanadate or tungstate to maintain a pH greater than 13.5. The conversion coatings containing vanadate as the corrosion resistant material for metal substrates, such as aluminum, iron, zinc, magnesium, cadmium, and alloys, also can be found in recent patents, e.g., see Buchheit *et al.* [33] and Dolan *et al.* [34]. The aqueous solution developed by Buchheit *et al.* [33] for forming the conversion coating comprises vanadate salt (10 to 150 mM), and soluble metal anions, e.g., ferricyanide, iron, molybdenum, tungsten, manganese, boron and phosphorous. In addition, Dolan *et al.* [34] disclosed a surface modification by a solution containing fluorometallate before forming the conversion coating.

(iii). Compositions Developed for Economic Concern

Economic concern is another driving force to develop new compositions of corrosion resistant coatings. An indium-containing coating was invented by Hill [35] to provide a cost effective corrosive resistant thermal barrier coating for use in high temperature applications, such as industrial gas turbines and aero-engine parts, compared with the conventional materials, e.g., the expensive scandia for zirconia stabilization and the high volatility of indium in the conventional indium stabilized zirconia. A bushing made of a plastic or polymeric material was disclosed in U.S. Pat. No. 7520105 [25] to provide an economic material for the corrosion resistance of the fasteners, compared with other candidate materials, e.g., corrosion-resistant alloys, impermeable compounds painting, and galvanic coating such as zinc. Brady patented a bilayer coating system, comprising a titanium-based coating and a polymer-based coating, for the metal substrate, e.g., aluminum, magnesium or titanium, in an electrochemical cell [36] to provide the corrosion resistance and electrical conductivity. The titanium-based coating also comprises zirconium, vanadium, niobium, tantalum, gold and platinum. The polymer-based coating comprises a matrix of a polymeric binder, e.g., silicones, polyphenols and urethanes, and electrically conductive particles, such as gold, platinum, nickel, tin, silver, palladium and graphite. Another conductive, corrosion resistant coating for the bi-polar plate in the fuel cell was disclosed by Kriksunov [37], including a binder, e.g., epoxy or silicones, and the highly conductive corrosion-resistant particles, e.g., titanium particles, titanium nitride particles and graphite fiber. Low cost metallic materials, including steel, aluminum and aluminum alloys then can be employed in bi-polar plates with such coating.

(iv). Compositions Developed for Other Concerns

Some other elements have been added to improve the performance of the corrosion resistant components for different applications. A titanium tungsten adhesion coating was employed as the underlying coating for the gold coating [2], to allow the boding process to be operated at an elevated temperature (i.e. >385 °C) while remaining the corrosion resistance of gold. A coating containing a high concentration of Cr, Al and/or Si was applied to the surface of the heat-resistant materials, such as Cr_2O_3, Al_2O_3 or SiO_2, to reduce the mechanical deterioration of the substrate and provide the necessary corrosion resistance [7]. The coating also comprises a refractory metal, a rare-earth element and a platinum group element for improving the diffusion, adhesion and mechanical characteristics of the coating, respectively. The Re content of the Re based alloy coating was controlled to be about 50 to 98 atom % [9-11] to provide the necessary corrosion resistance and thermal shock resistance for high temperature components, e.g., a blade for jet engines or gas turbines, because of its excellent thermal shock resistance.

The design of composite materials is another effective approach to obtain corrosion resistant components with versatile properties, as summarized in Table **1**. For example, a composite corrosion resistant coating was invented [3] to improve the adhesive strength between the metal layer and the resin layer in a steel material, by forming a de-Zn layer as well as a trivalent chromate layer. The de-Zn layer can be accomplished by subjecting a Zn/Ni alloy layer to an aqueous solution of sulfuric acid to eliminate Zn from the Zn/Ni alloy and oxidize the Ni surface to form a passivation coating film layer. The trivalent chromate layer can be formed by an immersion treatment using a sulfuric acid type chromate treatment solution containing only trivalent chromium ions. A corrosion resistant and alkali resistant coating for a metal substrate, e.g., iron, steel and alloys, at the temperature of 10 to 85°C was disclosed by Pawlik *et al.* [38, 39]. Such coating comprises (a) the cured reaction product of one epoxy with a molecular weight of 220 to 4500 and one phosphorus-containing acid; (b) a curing agent, e.g., melamine-based aminoplasts; and (c) the material consisting of elemental silicon. The weight percent of (a), (b) and (c) is 50 to 100, 5 to 25 and 1 to 30, respectively. A wear resistant and corrosion resistant coating on a substrate for high temperature erosion-corrosion environments, such as in boilers, was disclosed by Seitz [40]. Such coating consists of a tubular metallic outer sheath formed of a nickel base alloy (>40 wt %), and a powder inner core comprised of boron carbide (>35 wt %) and chrome carbide, which improves the wear resistance, hardness and bonding characteristics of the coating. In addition, the inner core further comprises tungsten carbide nickel powder, a boride (e.g., chrome boride, nickel boride or iron boride), and an oxide (e.g., aluminum oxide, chrome oxide or zirconium oxide).

Table 1. Properties of Corrosion Resistant Coatings Made of Composite Materials

Properties	References
good adhesion characteristics	[3]
strain tolerance	[4-5]
self-healing characteristics	[33]
heat conductivity	[34]
electrical conductivity	[36-37]
alkali resistance	[38-39]
wear resistance	[14, 40]

Methods of Making the Corrosion Resistant Coatings

Table **2** summarizes some conventional application techniques, e.g., thermal spraying, immersion, welding, screen printing, dip-coating, chemical vapor deposition and physical vapor deposition [4, 5, 13, 15-17, 21, 22, 38-40], which are still widely used in industry to apply the corrosion resistant coatings to the substrates.

On the other hand, some efforts have also been made to eliminate the adverse effects of the conventional application techniques. For example, a method for steel treatment was provided in U.S. Pat. No. 7514153 [1] to reduce the embrittlement of the steel substrate during the conventional processes for plating zinc-nickel alloys as well as the dezincification corrosion. Such method includes activating the steel surface, depositing an activated hydrogen barrier coating on the activated steel surface, plating a zinc-nickel alloy layer on the activated hydrogen barrier coating to form a porous plate, subjecting the zinc-nickel porous plate to an embrittlement-relief baking operation in an inert atmosphere, and sealing the zinc-nickel porous plate with a conversion coat. Recently, Hill patented a novel method for forming the indium-containing coating, without the loss of indium in the traditional deposition process [35]. Such method includes blending Indium oxide with one indate forming oxide, e.g., lanthanum series oxide, magnesium oxide, calcium oxide or yttrium oxide, to form a chemical mixture, heating the mixture to form an indate precursor, blending the indate precursor with zirconia or halfnia to form a co-stabilized mixture, e.g., $Zr_{1-x-y}In_xM_yO_z$, where M is selected from the indate forming oxide group; x is about 0.01 to 0.20; y is about 0.01 to 0.20; and z is about 1.6 to 2.4., to form the coating with desired performances.

Table 2. The Conventional Application Techniques for Making the Coatings

Applications	Techniques	References
gas turbine components	spraying	[4-5]
electrolytic cathode for copper refinement	thermal spraying	[13]
water-cooled stator bars clips used in electrical generators	chemical vapor deposition physical vapor deposition	[15-17]
the semiconductor device and the liquid crystal device	screen printing dip-coating thermal spraying	[21]
the semiconductor processing equipment	thermal spraying sputtering immersion chemical vapor deposition physical vapor deposition	[22]
alkaline-containing environment	spraying Immersion roll coating	[38-39]
high temperature erosion-corrosion environments	thermal spraying spray and fuse welding	[40]

Moreover, it is often desired to selectively form a film only in a specific region to be exposed to the corrosive environments. In addition, the conventional application technique, such as plating process, has restrictions on a combination and composition control of film-forming elements and requires a heat treatment at a high temperature so as to ensure adhesion of the film, although it is theoretically capable of forming a film onto a region allowing an electrolytic solution to enter. The methods to form coating in a desired region of the substrate are thus attractive for researchers [7, 8]. For example, a method for forming a high temperature corrosion resistant coating in desired region of the substrate can be found in the U.S. Pat. No. 7378134 [7], which includes utilizing a floating phenomenon of fine particles induced by vibration, and an electric current heating process to allow vapor of the fine powder generated by the heating to be diffused into the target member from a surface to form a diffusion film layer, and allow the floated fine powder to be attached onto the surface to form a fine-powder film layer on the diffusion film layer. In addition, a corrosion resistant coating was designed to form at desired locations by a gas flowing through the components, such as gas flow regulators in microelectronic fabrication [8]. The process includes placing the precursor gas, e.g., TEOS (tetraethoxysilane), within the interior of the component, heating the component inside the oven to thermally decompose the precursor gas into a gas phase intermediate product and a gas phase organic product, and form a thin corrosion resistant film on the interior metal surface of the component by forming an absorbate on the metal surface during the thermal decomposition, and withdrawing the gas phase organic product from the interior of the component.

CURRENT & FUTURE DEVELOPMENTS

Many patents on the corrosion resistant coatings as well as methods for forming the coatings have been disclosed in recent years. There is still the need for developing new materials with enhanced corrosion resistance while maintaining the inherent properties of the base body. In addition, more information is also needed to form the coatings only on the desired region. Of course, the coatings should be formed on the substrates in an environmental friendly and economic way to make the large-scale manufacture possible.

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