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(54) ELECTROPLATING FORMULATION AND PROCESS FOR PLATING IRON DIRECTLY ONTO ALUMINUM OR ALUMINUM ALLOYS

ELEKTOPLATTIERUNGSFORMULIERUNG UND PROZESS ZUR PLATTIERUNG VON EISEN DIREKT AUF ALUMINIUM ODER ALUMINIUM-LEGIERUNGEN

FORMULATION D'ELECTROPLACAGE ET PROCEDE DE DEPOT DE FER PAR ELECTROPLACAGE DIRECTEMENT SUR DE L'ALUMINIUM OU D'ALLIAGES D'ALUMINIUM

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- **CHEMICAL ABSTRACTS, vol. 119, no. 18, 1 November 1993 (1993-11-01) Columbus, Ohio, US; abstract no. 190774, FUJIWARA, YUTAKA ET AL: "Effects of hydroxycarboxylic acids on the electrodeposition of iron -carbon alloys" XP002110614 & DENKI KAGAKU OYOBI KOGYO BUTSURI KAGAKU (1993), 61(7), 840-2 ,1993,**

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to the plating of aluminum and aluminum alloy substrates, and more particularly to the plating of aluminum and aluminum alloy substrates with iron.

BACKGROUND PRIOR ART

[0002] It is generally known to use aluminum or aluminum alloy substrates as structural members for many applications. The use of aluminum in many applications provides numerous advantages, because it is lightweight, easily handled, and generally inexpensive.

[0003] In various applications, however, it is desirable to coat the aluminum or aluminum alloy substrate with a dissimilar metal that is harder than aluminum. For example, it is known to use an aluminum or aluminum alloy substrate to make internal combustion engines with aluminum pistons wherein the aluminum piston or the cylinder bore is coated with another metal that is harder than aluminum to prevent piston skirt scuffing, galling and subsequent engine seizure.

[0004] One method for depositing iron coatings onto aluminum or aluminum alloy substrates is by electroplating. One such method for electroplating iron onto substrates containing aluminum is disclosed by U.S. Patent No. 5,516,419 issued to Phan et al. (hereinafter "Phan"). In the process disclosed by Phan, however, a bath separate from the electroplating bath is required to activate the aluminum or aluminum alloy substrate. *See Phan,* Column 2, Lines 48-58. Additionally, after the substrate is activated, another separate bath is required to place a transitory protective layer, such as a zinc layer, onto the activated substrate to prevent aluminium oxides from reforming after the substrate has been activated. See Phan, Column 2, Lines 59-67, and Column 3, Lines 1-2. Finally, in Phan, an undercoating or intermediate layer, such as a nickel layer, is plated onto the substrate prior to plating iron onto the intermediate layer in another separate plating bath. See Phan, Column 3, Lines 3-25. The undercoating layer is required to provide a layer to which the subsequently-plated iron layer will adhere. See Phan, Column 3, Lines 16-22. In essence, the iron is not directly plated to the aluminium or aluminium alloy substrate, but is instead plated to an undercoating layer of a different metal which has in turn been plated onto the aluminium or aluminium alloy substrate.

[0005] The use of a method for electroplating as described in Phan has significant shortcomings for high volume commercial production. The use of a separate activation bath, a transitory layer, and a undercoating layer all add to the expense, complexity, and time involved with plating an iron layer onto an aluminium or aluminium alloy substrate. Additionally, the use of these separate steps and separate baths adds the difficulty and expense of disposing of the waste produced in each of these steps and baths.

[0006] US Patent No. 4221639 discloses a method of plating a wall surface of an aluminium alloy cylinder with iron, in which method the wall surface is prepared for electroplating by sequentially degreasing, rinsing, pickling, rinsing, zincating, rinsing, copper striking, and further rinsing. The pickling, zincating and copper striking steps are performed in order to obtain a superior adhesion of a hard iron layer which is electrodeposited from an electoplating bath using a cathode current density which is so high that channels are developed in the iron layer which are of a size to receive lubricant and abrasive dust therein in use. The use of an electroplating bath containing 150-250 g/ℓ of metallic iron and 20-50 g/ℓ of boric acid and have a pH of 0.2 to 0.6 g/ℓ is disclosed.

[0007] Another problem that has existed with iron plating baths is that after use, impurities, such as copper or aluminium, remain in the bath solution and adversely affect further plating processes. When impurity concentration becomes too high, the iron plating process must be stopped so that the bath solution can be cleaned or changed.

[0008] It is desirable to provide a formulation and method for electroplating iron directly onto an aluminium or aluminium alloy substrate without the need of a separate activation bath, a transitory layer, or an undercoating layer.

[0009] It is also desirable to provide for a method and apparatus for purifying an iron plating bath solution to remove impurities from the bath without stopping the plating process to clean or change the bath solution.

SUMMARY OF THE INVENTION

[0010] The electroplating formulation and process of the current invention, unlike the formulations and methods of US 5516419 and US 4221639, employs an iron plating/activating bath which acts as both the chemical activation bath to activate the aluminium or aluminium alloy substrate and acts as the electroplating bath for depositing a hard iron layer directly onto the aluminium or aluminium alloy substrate. In the present invention, no separate activation bath, no transitory layers, and no separate undercoating layers are needed. This formulation and process is very useful for high volume commercial production. The formulation and process reduce the time and expense involved with the electrodeposition of the iron onto aluminium or aluminium alloy substrates. The resulting iron layer has good hardness and adherence to the substrate, and has exceptional wear resistant characteristics.

[0011] According to one aspect of the invention, there is provided an activation/electroplating bath solution comprising:

Fe^{+2} having a concentration ranging from about

0.65 to about 2.5 moles per liter of solution;
at least one sulfamate anion associated with the Fe^{+2} ion;
a reducing agent in an amount sufficient to prevent oxidation of Fe^{+2} to Fe^{+3};
Cl^- in an amount sufficient to promote dissolution of the anode and increase the conductivity of the solution;
a wetting agent in an amount sufficient to prevent pitting of the aluminium electroplated surface;
boric acid in an amount sufficient to increase the hardness of said iron layer; and
ammonium ion in an amount sufficient to increase the hardness of said iron layer;
the bath solution having a pH of less than 3.5, and the bath solution being used for activating an aluminium or aluminium alloy substrate cathode and electroplating an iron layer directly onto an aluminium or aluminium alloy surface of said cathode from an iron containing anode.

[0012] According to another aspect of the present invention, there is provided a method for electroplating an iron layer onto an aluminium or aluminium alloy substrate cathode from an iron containing anode without the use of an undercoating layer, said method comprising the steps of:

providing the activation/electroplating bath solution comprising:

Fe^{+2} having a concentration ranging from about 0.65 to about 2.5 moles per liter of solution;
at least one sulfamate anion associated with the Fe^{+2} ion;
a reducing agent in an amount sufficient to prevent oxidation of Fe^{+2} to Fe^{+3};
Cl^- in an amount sufficient to promote dissolution of the anode and increase the conductivity of the solution;
a wetting agent in an amount sufficient to prevent pitting of the aluminium electroplated surface;
boric acid in an amount sufficient to increase the hardness of said iron layer; and
ammonium ion in an amount sufficient to increase the hardness of said iron layer;
activating said surface of said cathode by immersing said cathode in said solution;
immersing said anode in said solution; and
electroplating said iron layer onto said activated aluminium or aluminium alloy surface of said cathode in said solution.

[0013] One feature and advantage of the current invention is to provide an iron plating formulation and method wherein the iron plating solution acts as both the chemical activation solution for the aluminium or aluminium alloy substrate and acts as the electroplating bath for depositing a hard iron layer directly onto the aluminium or aluminium alloy substrate.

[0014] Another feature and advantage of the current invention is to provide for plating iron directly onto an aluminium or aluminium alloy substrate without the need of a transitory layer to prevent oxidation of the activated surface of the substrate after activation.

[0015] Another feature and advantage of the current invention is to plate iron directly onto an aluminium or aluminium alloy substrate without the need of an undercoating.

[0016] Another feature and advantage of the current invention is to provide an iron coating on an aluminium substrate with the thickness of about 0.25 to about 0.6 mils and a micro-hardness up to about 60 Rockwell C that has exceptional adhesion and wear resistance characteristics.

[0017] Another feature and advantage of the present invention includes providing for removal of impurities that are dissolved in the electroplating bath on a continuous basis without the need to interrupt the electroplating process.

[0018] Other features and advantages of the invention will become apparent to those skilled in the art upon review of the following detailed description and claims.

[0019] Before embodiments in the invention are explained in detail, it is to be understood that the invention is not limited in its application for the details of the composition or concentrations of components set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways. Also, it is understood that the phraseology and terminology used herein are for the purpose of description and should not be regarded as limiting.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0020] The present invention provides an electroplating formulation and process which employs a mixed iron plating bath used to both chemically activate and to electrodeposit a hard iron layer on an aluminum or an aluminum alloy substrate. As used herein, the term 'substrate' means any member or component made of or comprising aluminum or aluminum alloy to which the iron layer will be deposited using the formulation and process of the current invention. Preferably, the substrate is a piston made of aluminum or aluminum alloy that is for use in an internal combustion engine, but other aluminum or aluminum alloy parts, components, or members may be used as the substrate.

[0021] In preparing the substrate for iron plating, the substrate is first cleaned using a non-etching cleaning step. This cleaning step removes particulates, oil, grease, or other matter that may be present on the surface of the substrate as a result of previous machining operations or other handling. Many non-etching methods and compositions generally known may be used in this cleaning step.

[0022] Preferably, the cleaning step involves immersion of the substrate into a cleaning bath solution for a sufficient amount of time for the cleaning solution to remove particulate, oil, grease, or other matter from the substrate. Additionally, the cleaning bath solution is preferably maintained at a temperature of about 140°F (60°C), and the substrate is immersed in the cleaning solution for a sufficient amount of time to allow the part to reach the temperature of the cleaning solution, although this is not critical. Generally, times for immersion of the substrate in the cleaning solution range from about 15 seconds to about 2 minutes. However, immersion times outside of this range are workable.

[0023] Numerous commercially available cleaning solution products are readily available for use in the cleaning step. Preferably, the cleaning solution is an alkaline cleaning solution. One suitable cleaning solution is commercially available from Deveco Corporation under the trademark DEVECO 232.

[0024] After being cleaned in the cleaning step, the substrate is then rinsed in water to remove excess cleaner.

[0025] The substrate is then etched in an etching step. The etching step removes excess silicon that may be present on the surface of the substrate, and provides a mechanical tooth on the surface of the substrate that allows for an increased adhesion between the surface of the substrate and the iron coating, as will be seen below.

[0026] Those skilled in the art will recognize that there are many methods and formulations that may be used to etch the substrate. Preferably, the etching step of the current invention involves immersion of the substrate into an etch bath comprising a suitable etching solution.

[0027] Typical etching solutions include various combinations of sulfuric, hydrochloric, and hydrofluoric acid. Any of the acid etches known to those skilled in the art for removing excess silicon, removing aluminum oxides and providing for a mechanical tooth on the surface of the substrate may be employed as the etching solution. Preferably, an acid containing fluorine is used for the effective removal of excess silicon. One know acid etch which is suitable for use as the etching solution in the current invention comprises about 50% nitric acid, about 10% hydrofluoric acid, and the remainder being water.

[0028] Generally, the substrate is immersed in the etch bath for an amount of time sufficient to provide for the desired etching results. Preferably, the substrate is immersed in the etch bath for about 10 to about 50 seconds, and more preferable for about 20 to about 40 seconds. After removing the substrate from the etched bath, it is rinsed with water to remove any excess etching solution.

[0029] The etching step does remove the aluminum oxides from the surface of the substrate, thereby chemically activating the surface of the substrate. It is at this point where previous formulations and methods, such as the process described in the Phan patent, deposit a transitory protective layer to the surface of the substrate to preserve the activation. For example, in the Phan process, a zinc layer was deposited. Additionally, previous formulations and methods, such as that disclosed in Phan, would then plate an intermediate metal layer, such as nickel, to the surface of the substrate, and then plate iron over the intermediate layer.

[0030] In the current invention, neither the protective transitory layer nor the undercoating layer is needed or used. After the activation step, the substrate is rinsed with water. It is likely that an aluminum oxide layer again forms on the surface of the substrate, thereby deactivating the surface. The activation provided by the etching step need not be maintained in the current invention because, as will be seen below, the electroplating solution of the current invention acts as both an activation and the electroplating solution.

[0031] Now that the substrate has been prepared for plating as described above, the substrate is ready for activation and plating. In the ativation/electroplating process, the substrate is immersed in an activation/electroplating bath. The same bath acts as the activation solution to activate the surface of the substrate and as the iron electroplating solution. The bath includes an aqueous, or a water based, activation/electroplating solution of ferrous ions and other necessary components.

[0032] The activation/electroplating bath includes the following components:

(1) Fe^{+2} having a concentration ranging from about 0.65 to about 2.5 moles per liter of solution;
(2) at least one sulfamate anion associated with the Fe^{+2} ion;
(3) a reducing agent in an amount sufficient to prevent oxidation of Fe^{+2} to Fe^{+3};
(4) Cl^- in an amount sufficient to promote dissolution of the anode and increase the conductivity of the solution; and
(5) a wetting agent in an amount sufficient to prevent pitting of the aluminum electroplated surface by preventing adherence of hydrogen gas bubbles to the substrate surface.

[0033] More preferably, the total Fe^{+2} content of the electroplating bath is from about 1.0 to about 2.15, and most preferably is about 1.8 moles per liter of solution.

[0034] The anion associated with the Fe^{+2} ion is sulfamate, because it is believed that the sulfamic acid that is formed in the bath due to the presence of the sulfamate ion performs, at least partially, the activation function as will be seen below.

[0035] One suitable source for iron and ferrous sulfamate is a product called Barrett SIR which is commercially available from MacDermid, Incorporated.

[0036] The bath also includes a reducing agent to maintain iron in the ferrous state. The reducing agent is needed in an amount sufficient to prevent the oxidation of Fe^{+2} to Fe^{+3}. Suitable reducing agents include those known in the art which do not have a significant detrimental effect upon the activation/electroplating function of the bath.

Preferably, the reducing agent is selected from the group consisting of glycolic acid, ascorbic acid, sodium bisulfite, sodium metabisulfite, sodium hydrasulfite, sodium hypophosphite, hydrazine, boric acid, and mixtures thereof. More preferably, the reducing agent includes glycolic acid, and is employed in a concentration ranging from about 0.01 to about 0.10, more preferably about 0.03 to about 0.05, and most preferably about 0.04 percent by volume of the total solution. One suitable reducing agent is commercially available from MacDermid Incorporated under the name SISR. It is thought that SISR includes from about 0.5 to about 1% glycolic acid, from about 0.1 to about 1% carbon, with the remainder being water.

[0037] Cl^- must also be present in the bath. The Cl^- anion serves three important functions in the bath. First, Cl^- helps to promote the dissolution of the anode. Second, the Cl^- provides for increased conductivity within the bath, thereby increasing the efficiency of the electroplating process. Finally, the Cl^- helps in the formation of the iron crystalline structure such that the iron is in a martensitic form.

[0038] The source for the Cl^- is generally a chloride salt that is added to the bath. Preferably, the source of Cl^- is selected from the group consisting of sodium chloride, potassium chloride, ammonium chloride, calcium chloride, and mixtures thereof. More preferably, the source of Cl- is pure sodium chloride.

[0039] The concentration of Cl- in the bath can range from about 0.17 to about 1.02 moles per liter of solution, and may be between about 0.17 and about 0.34 moles per liter of solution. Preferably the concentration of Cl-ranges from about 0.34 to about 1.00, and most preferably is about 0.68 moles per liter.

[0040] A wetting agent is employed in the activation/electroplating bath solution in an amount sufficient to prevent pitting of the electroplating surface by attachment of hydrogen bubbles during electroplating. This is necessary since hydrogen evolution occurs during the iron deposition on the aluminum cathodes. The wetting agent prevents adherence of hydrogen bubbles on the aluminum cathode that would otherwise cause pitting of the aluminum part or cracking of the iron deposit due to embrittlement.

[0041] Most known wetting agents may be employed in the practice of the present invention. The wetting agent selected should not significantly interfere with the activation or electroplating function of the bath. Preferably, the wetting agent used is selected from the group consisting of sodium lauryl sulfate, polyethylene glycol, and mixtures thereof. Most preferably, the wetting agent used is sodium lauryl sulfate. A suitable wetting agent is commercially available from MacDermid Incorporated under the name SNAP-L.

[0042] The wetting agent generally makes up from about 0.1% to about 0.3% of the total bath by volume. Preferably, the wetting agent makes up about 0.2% of the total bath by volume.

[0043] Additionally, ammonium ion are employed in the bath. The ammonium ion is thought to contribute to the hardness of the electroplate without sacrificing ductility. It is believed that the additional ammonium ion acts as a grain refiner and thereby helps to form the crystalline structure of the iron coating.

[0044] The source of the ammonium ion may be any known source of ammonium that will not have a significant detrimental impact upon the function of the bath. Preferably, the source of ammonium is selected from the group consisting of ammonium sulfamate, ammonium hydroxide, and mixtures thereof. Most preferably, the source of ammonium in ammonium sulfamate.

[0045] The ammonium concentration in the bath may be in the range of about 0.08 to about 0.55 moles per liter. Preferably, the ammonium concentration is from about 0.17 to about 0.40, and most preferably about 0.30 moles per liter.

[0046] Additionally, boric acid is employed in the bath to increase the hardness of the electroplate. As discussed above, boric acid may be used as a reducing agent. However, boric acid also acts to increase the hardness of the electroplate. The concentration of boric acid in the solution may be in the range of about 11 to about 26 grams per liter of the total solution.

Preferably, the boric acid concentration is between about 15 and about 22.5, and more preferably is about 18.7 grams per liter of total solution.

[0047] The iron plating bath may also include appropriate additional agents, such as wetters, brighteners, and stress reducing agents, and other appropriate agents commonly employed in iron plating, to enhance the plating characteristics. A brightener permits the use of higher current densities, which make it possible to plate the part faster. The composition and concentration of such addition agents are well known in the art.

[0048] In the method of the present invention, the activating/plating bath is preferably maintained at a pH of about 1 to about 4, more preferably from about 1.5 to about 3.5, and most preferably at a pH of about 2.75. The pH of the plating solution appreciably influences the structure and mechanical properties of the iron deposit. Accordingly, this pH range provides the best combination of desired structural and mechanical properties of the iron deposit. The pH is adjusted with one of sulfamic acid, sulfuric acid, or ammonium hydroxide, or combinations thereof, as appropriate. As the plating process proceeds, and the bath is operating properly, the pH tends to rise slowly. It is preferable to adjust the rising pH by adding sulfamic acid to the bath to maintain the iron sulfamate characteristics, and maintain the activation characteristics of the bath. On a short term basis, other acids may be used to adjust the pH downwardly, but the use of sulfamic acid is preferred to maintain these preferred characteristics of the bath.

[0049] The activating/plating bath is maintained at a normal bath operating temperature that ranges from about 26.7°C (80°F) to about 76.7°C (170°F). Preferably, the operating temperatures are about 48.9°C (120°F) to about 60°C (140°F), and most preferably about 54.4°C (130°F). The temperature affects the deposition rates and the internal stresses of the iron deposits. Accordingly, the preferred plating temperature ranges provide the best combination of desired deposit rate and reduced internal stresses of the iron deposit.

[0050] The substrate is immersed in the plating bath and the plating bath acts to remove the aluminum oxide from the surface of the substrate and thereby activate the substrate. The substrate therefore has a surface which is aluminum or aluminum alloy. It is believed that the sulfamic acid that is formed in the bath due to the presence of the sulfamate ion performs, at least partially, the activation function.

[0051] The substrate is then electroplated in the same tank and with the same electroplating solution as the activation immediately following activation and directly over the activated substrate. During electroplating, the substrate is made the cathode, and an appropriate iron containing anode is used to complete the circuit.

[0052] In the current invention, any suitable iron containing anode can be employed. Pure iron, and carbon steel cathodes are preferably used. Most preferably, due to cost and availability, the cathode used in the current invention is a carbon steel cathode.

[0053] The iron electroplating bath is agitated, for example, by stirring, by mechanical agitation, by bubbling inert gas such as nitrogen through the bath, by plating parts rotating in the bath, or by ultrasonic agitation. However, agitation using air should be avoided, since this results in excessive oxidation of the Fe(II).

[0054] A current having a current density between about 1.1 to about 13.2 amps/dm^2 (about 10 to about 120 amps per square foot) is applied on the substrate, as cathode. Preferably, the current density is between about 2.2 and about 11 amps/dm^2 (about 20 and about 100), and most preferably is about 8.8 amps/dm^2 (80 amps per square foot). The preferred ranges of current density provide the best combination of fast plating time consistent with good visual appearance of the iron plate.

[0055] The iron is plated directly onto the aluminum or aluminum alloy substrate to a thickness of about 0.005 to about 0.05mm (about 0.0002 to about 0.002 inch). Preferably, the thickness is between about 0.0063 to about 0.0152mm (about 0.000250 to about 0.000600), and more preferably, between about 0.0089 to about 0.01 mm (about 0.00035 to about 0.0004 inch) in thickness so as to achieve high hardness without increasing internal stresses.

[0056] The dwell time needed to obtain the desired thickness is inversely proportional to the current density used. The dwell time can range from about 4 minutes to about 30 minutes depending upon the current density used and the desired thickness. For example, if a thickness of 0.0089 mm (0.00035 inches) is desired, and a current density of about 11 amp/dm^2 (about 100 amps per square foot) is used, a dwell time of about 4 minutes is needed. Likewise, if a thickness of 0.0089 mm (0.00035 inches) is desired, and a current density of about 20 2.2 amp/dm^2 (amps per square foot) is used, a dwell time of about 30 minutes is needed. Preferably, the dwell time is about 6 minutes and 45 seconds at a current density of about 8.8 amps/dm^2 (80 amps per square foot). However, shorter or longer times at higher or lower current densities, respectively, may be employed in the practice of the invention to obtain the desired thicknesses. It is important to note that faster rates of iron deposition result in higher hardness of the electroplate. This increased hardness is important for substrates such as pistons used in the lawn and garden industry, where engines typically operate at high grit conditions in which the piston is subject to considerably more abrasion than would be found in most automotive applications.

[0057] The use of this activation/electroplating formulation and process allows the formation of relatively thick iron layers from about 6.35 to about 15.24 µm (about 0.25 to about 0.6 mils) that have a micro-hardness up to about 60 Rockwell C. Preferably, the micro-hardness is in the range of about 50 to about 60 Rockwell C.

[0058] After electroplating, the part is removed from the activation/electroplating bath and rinsed with cold water to remove excess plating solution.

[0059] The rinse may then be followed by a step wherein a rust inhibiting or protective agent is applied to the iron coated substrate. Conventionally known agents and methods for inhibiting rust and protecting the iron may be used in the current invention.

[0060] Preferably, the rust inhibiting application step includes immersion of the iron coated substrate in a rust inhibitor solution containing rust inhibiting agents immediately after rinsing. Preferably, the rust inhibitor solution contains sodium metasilicate, ethanoamine, alcohols, and a surfactant to prevent flash rusting of the active iron deposited on the substrate. One suitable rust inhibiting solution comprises about 97% water and 3% neutralizing rinse mixture, wherein a suitable neutralizing rinse mixture is commercially available from Broco Products Incorporate of Cleveland, Ohio under the trademark V200NC. The preferred neutralizing rinse mixture provides a completely dry to the touch substrate in addition to the rust protection without the use of another flash plating procedure.

[0061] This preferred rust inhibiting application step is advantageous over the use of oils or other such agents because if such oils are used near the electroplating bath, or while the substrates are still on the electroplating rack, some of the oils may be inadvertently placed into the electroplating bath. Such oils in an electroplating bath may cause operating problems and electroplating defects. Longer term rust protection means such as soluble oils, mineral oils, greases, etc. can be utilized as off line procedures after the iron plated substrate has been removed from the vicinity of the electroplating bath and apparatus.

[0062] The apparatus usable to perform the current invention of electroplating iron directly onto the substrate using the above discussed formulations and process are apparatus that are generally well known in the art for use in electroplating.

[0063] Generally, the activation/electroplating bath is maintained in a tank that is made of or lined with a material that is resistant to all of the chemicals used in the bath. Preferably, the tank is lined with a material such as polyvinyl chloride or polypropylene. The tank must be large enough to accommodate the activation/electroplating bath solution, the substrate to be plated, the anode, and any type of support structure that may be used to support or hold the substrate in the bath. Preferably, the tank for use in the current invention is about 3 407 litres (900 gallons).

[0064] A support structure such as a support rack or tree is preferably use to support the substrate throughout the activation/electrodeposition process. The shapes and sizes of such support racks/trees usable in the current invention are well known in the art. Preferably, the support racks/trees are shaped such that when they are supporting the substrates to be plated, the distance between the center of the substrate being plated and the center line of the anode is about 7 inches.

[0065] The support rack/tree may include current thieves attached thereto. Generally, the function and placement of current thieves are known in the art for use in other electroplating applications, but their use in the electrodeposition of iron, especially the electrodeposition of iron using the current formulation and method, are thought to be new. The form and function of current thieves as know in the art for use in other applications are generally suitable for use in the current invention.

[0066] The substrates to be plated with iron are generally placed upon the plating rack/tree. Without the current thieves, the substrates mounted on the ends of the rack/tree would generally receive higher current densities than the substrates near the middle of the rack/tree. As the electrodeposition proceeds, the substrates receiving the higher current densities receive a higher rate of iron deposition. Therefore, a thicker final coating of iron will be deposited on the substrates near the ends of the rack/tree in comparison to those in the middle of the rack/tree.

[0067] However, a uniform final coating thickness is usually desired among all of the substrates on a given rack/tree. Therefore, the current thieves are used and act to lessen the current densities in the substrates supported on the ends of the rack/tree, thereby substantially equalizing the amount of current running through all of the substrates mounted on a rack/tree. The substantial equalization of the current densities helps to provide a substantially uniform thickness of iron coating among all of the substrates on a single rack/tree. Preferably, the current thieves are steel plates mounted at the edges of the support rack/tree.

[0068] In the electroplating process, metal impurities may be deposited in the bath. Aluminum and copper from the substrate may be dissolved into the electroplating bath and become impurities within the bath. If the aluminum impurities reach a level of about 20 parts per million within the bath, defects begin to be created in the plating process. Additionally, when copper impurities reach a level of about 10 parts per million in the bath, defects begin to be created in the plating process.

[0069] Another aspect of the current invention, however, makes it possible to remove these metals impurities. In one embodiment of the invention, the copper and aluminum impurities are removed from the bath by a precipitation step. In the precipitation step, the pH of the bath is purposefully increased to about 5.5 at which point the aluminum and copper ions precipitate out of solution. The solid aluminum and copper can then be removed from the bath.

[0070] Preferably, however, the aluminum and copper impurities are removed from the bath on a continuous basis by the use of an ion exchange apparatus and method. The ion exchange apparatus includes an ion exchange column that is in fluid communication with the tank containing the activation/electroplating bath. The ion exchange column has a first end and a second end. The first end of the column is interconnected with the tank such that the column is in fluid communication with the tank with a first pipe. The second end of the column is interconnected with the tank such that the column is in fluid communication with the tank with a second pipe. The ion exchange column includes an ion exchange resin contained therein. The ion exchange resin is of a type that will perform ion exchange with the copper and aluminum ions present within the activation/electroplating bath. One suitable ion exchange resin is available from Rohm and Hass Company under the trademark IRC-718.

[0071] As the activation/electroplating bath portion is filtered through the ion exchange column, ion exchange occurs to remove the aluminum and copper ions from the bath. The purified bath is then moved from the opposite end of the ion exchange column and returned to the activation/ electroplating bath tank.

[0072] It is desirable, however, to use the ion exchange method of removing the aluminum of copper from the bath because it is a continuous process and activation/ electroplating of the aluminum or aluminum alloy parts does not need to be interrupted.

[0073] The following example is intended to exemplify one embodiment of the invention and is not to be construed as a limitation thereof.

Example

[0074] In this example, aluminum alloy pistons for use in internal combustion engines were used as the substrate. A layer of iron was coated directly onto the aluminum alloy surface of the pistons using a method and activation/electroplating bath embodying the current invention.

[0075] First, the aluminum alloy pistons were mounted onto a workbar or rack and put through a cleaning step. In the cleaning step, the pistons were immersed in a non-etching alkaline cleaner, Deveco 232 at a 3% concentration at 140°F for a period of 4 minutes to loosen and remove any soils, chips, soluble oils or coolants from previous machining operations. The pistons were then rinsed thoroughly with water in two air agitated counterflow rinses to remove any residual cleaner.

[0076] The pistons were then ready for chemical etching and milling of the surface to provide a mechanical "tooth" for the iron plating. The pistons were submerged in the nitric/hydrofluoric acid mixture for a period of 30 seconds to remove any silica that was present and to roughen the surface until a uniform gray-white matted surface was obtained. The acid utilized in the chemical etching was a mixture of seven volumes of 36° Baume' (52.3% nitric acid) and one volume of 70% Hydrofluoric acid operating at room temperature.

[0077] After chemical etching, the pistons were rinsed twice with water in a counterflow rinsing operation before being placed into an activation/electroplating bath.

[0078] An activation/electroplating bath solution was prepared by incorporating a ferrous sulfamate concentrate product named Barret SIR, a stabilizer named Barrett SISR, a wetting agent named SNAP-L, each of which is commercially available from MacDermid, Incorporated, and ferrous iron, ammonium sulfamate, sodium chloride, and boric acid.

[0079] A suitable bath tank, anodes, and filtration equipment was cleaned and leached as known in the art. The required amount of water was added to to the tank, and an the pH of the water was reduced to about 2.5 by adding acid. The required quantity of Barrett SIR was diluted with water in the cleaned tank. The necessary amount of boric acid was added, and then necessary amount of SISR stabilizer was added. The system was then heated to operating temperature, and the required amount of ammonium sulfamate and sodium chloride was added. Thereafter, SNAP-L was added in the required amount, and the solution was brought to operating level with water. The pH was adjusted, as necessary, to about 2.5. The solution was then dummied at 0.2 to 0.5 with mild agitation for several hours while maintaining the pH between about 2.5 and about 3.0.

[0080] The activation/electroplating bath used in this example had an Fe^{+2} concentration of 74.9 g/l (10 oz/gal) and a pH of 2.75. Glycolic Acid, from the SISR stabilizer, was used as a reducing agent at a concentration of 0.3% by volume. Sodium chloride was used as the source of Cl^- and was added at a concentration of 41.2 g/l (5.5 oz/gal). Sodium lauryl sulfate, from the SNAP-L, was the wetting agent present in the bath in a concentration of about 0.2% by volume. Ammonia sulfamate was used as the source of ammonium, and was present in the solution in a concentration of 33.7 g/l (4.5 oz/gal). Boric acid was present in the solution at a concentration of 18.7 g/l (2.5 oz/gal).

[0081] The pistons were then placed into the plating bath. The surface of the aluminum alloy pistons was activated by the bath. Voltage was applied to the workbar and the pistons were plated at a cathode current density 7.7 amps/dm^2 of (70 amps per square foot) for a period of 6 minutes and 45 seconds at a temperature of 54.4°C (130°F). The pistons were plated with the aid of "current thieves" mounted on the work bar to maximize the uniformity of plating for all the pistons which ranges form 72 to 120 on the workbar.

[0082] During the plating process, the bath pH was maintained at about 2.75 while iron concentration in the bath was maintained at about 74.9 g/l (10 oz/gal). Sulfamic acid was used to maintain pH. The iron concentration was maintained by the annode.

[0083] The concentration of ammonia sulfamate was maintained at about 33.7 g/l (4.5 oz/gal) and the concentration of sodium chloride was maintained at about 41.2 g/l (5.5 oz/gal). The concentration of the glycolic acid was maintained at about 0.3% by volume and the concentration of the boric acid was maintained at about 18.7 g/l (2.5 oz/gal).

[0084] During electroplating, the bath was filtered continuously through 25 µm (25 micron) filters at a rate of three bath turnovers per hour as well as the bath being cleaned of contaminants by an ion exchange process that removes the aluminum and copper dissolved in the bath during electroplating. The ion exchange process utilizes a selective ion exchange resin for removal of the aluminum and copper under the acidic conditions present in the bath. A 1-5% cross-linked strong acid resin is used alternately for removal of the aluminum only. In either case, the ion exchange resin is regenerated by acid stripping of the contaminants with hydrochloric acid followed by removal of ferric iron on the resin with a mixture of sodium bisulfite/sodium hydrosulfite followed by putting the resin back into the sodium form fully with sodium chloride. During extended periods of inactivity, the bath is cleaned by adjustment of the pH to 5.5 with ammonium hydroxide to precipitate the aluminum followed by dummying of the bath to remove the copper and other trace metals that may be present.

[0085] After electroplating, the pistons were removed from the bath and quickly rinsed with water in a 3 stage counterflow rinse operation that removes the residual plating solution from the pistons. The pistons were then immersed in a commercially available neutralizing alkaline cleaner/rust preventer containing sodium metasilicate at 3% concentration at 71.1°C (160°F) for a period of 30 seconds. The pistons were removed from the bath and excess water is allowed to flash dry from the surface of the pistons before removing them from the workbar.

[0086] A number of the pistons that were electroplated in the above method were then subjected to various tests. One of these tests included a microhardness measurement perpendicular to the thickness of the electroplate. The microhardness of the iron plating measured between about 50 and 57 Rockwell C.

[0087] Adhesion tests were also conducted. One adhesion test consisted of slowly heating the electroplated piston to 315°C (600°F) followed by quick immersion into cold) 10°C. (50°F) water. The pistons subjected to this test illustrated no significant loss of adhesion of the iron layer on the aluminum alloy piston even when this test is repeated 20 times in succession on the same piston.

[0088] Another test included endurance testing whereby an electroplated piston was placed in an engine and the engine was operated at rated speed and full load for a period of 500 hours minimum. The plating on the pistons that were plated in the above process withstood the test, and did not wear through, and galling/seizing of the engine did not occur.

[0089] Cold box starting tests of an engine incorporating an iron-plated piston of the current invention were conducted at -28.9°C (-20°F). Additionally, grit tests of an engine incorporating an iron-plated piston of the current invention were also conducted, whereby a measured amount of a particular fineness of grit is added to the engine oil before running at full load. The iron-plated pistons of the current invention did as well as or exceeded the performance of chrome plated pistons in these tests in side by side testing. Peak torque tests and duty cycle tests for various types of driven equipment were also conducted. Generator cycle testing, on-off cycle tests, oil consumption tests, piston scuff tests, and air emissions tests were also conducted to determine the overall effectiveness and viability of the electroplating. In each of these tests, the iron-plated pistons of the current invention exhibited good strength and wear resistance, and did as well as or exceeded the performance of chrome plated pistons.

[0090] Various feature and advantages of the invention are set forth in the following claims.

Claims

1. An activation/electroplating bath solution comprising:

   Fe^{+2} having a concentration ranging from about 0.65 to about 2.5 moles per liter of solution;

   at least one sulfamate anion associated with the Fe^{+2} ion;

   a reducing agent in an amount sufficient to prevent oxidation of Fe^{+2} to Fe^{+3};

   Cl^- in an amount sufficient to promote dissolution of the anode and increase the conductivity of the solution;

   a wetting agent in an amount sufficient to prevent pitting of the aluminum electroplated surface;

   boric acid in an amount sufficient to increase the hardness of said iron layer; and

   ammonium ion in an amount sufficient to increase the hardness of said iron layer;

   the bath solution having a pH of less than 3.5, and the bath solution being used for activating an aluminum or aluminum alloy substrate cathode and electroplating an iron layer directly onto an aluminum or aluminum alloy surface of said cathode from an iron containing anode.

2. The activation/electroplating bath solution of claim 1, wherein the reducing agent is selected from the group consisting of glycolic acid, ascorbic acid, sodium bisulfite, sodium metabisulfite, sodium hydrasulfite, sodium hypophosphite, hydrazine, boric acid, and mixtures thereof.

3. The activation/electroplating bath solution of claim 1, wherein the reducing agent includes glycolic acid having a concentration ranging from about 0.01 to about 0.10 percent by volume of said solution.

4. The activation/electroplating bath solution of claim 1, wherein said Cl^- has a concentration between about 0.165 and about 1.00 moles per liter.

5. The activation/electroplating bath solution of claim 1, wherein said Cl^- has a concentration between about 0.330 and about 1.00 moles per liter.

6. The activation/electroplating bath solution of claim 1, wherein the source of said Cl^- in said solution is selected from the group consisting of sodium chloride, potassium chloride, ammonium chloride, calcium chloride, and mixtures thereof.

7. The activation/electroplating bath solution of claim 1, wherein the wetting agent is selected from the group consisting of sodium lauryl sulfate, polyethylene glycol, and mixtures thereof, and wherein said wetting agent is present in an amount ranging from about 0.1 to about 0.3 percent by volume of the solution.

8. The activation/electroplating bath solution of claim

1, wherein the wetting agent is sodium lauryl sulfate.

9. The activation/electroplating bath solution of claim 1, wherein the wetting agent has a concentration of between about 0.1 to about 0.3 percent by volume of the solution.

10. The activation/electroplating bath solution of claim 1, wherein the concentration of said boric acid is between about 11 and about 26 grams per liter.

11. The activation/electroplating bath solution of claim 1, wherein the concentration of said ammonium ion is between about 0.08 and about 0.55 moles per liter of solution.

12. The activation/electroplating bath solution of claim 1, wherein the source of said ammonium ion in said solution is selected from the group consisting of ammonium sulfamate, ammonium hydroxide, and mixtures thereof.

13. The activation/electroplating bath solution of claim 1, wherein said iron layer has a microhardness of at least about 50 Rockwell C.

14. The activation/electroplating bath solution of claim 1, wherein said iron layer has a microhardness of at least about 55 Rockwell C.

15. The activation/electroplating bath solution of claim 1, wherein the pH of the solution is between about 1 and about 4.

16. The activation/electroplating bath solution of claim 1, wherein the pH of the solution is between about 1.5 and about 3.5.

17. The activation/electroplating bath solution of claim 1, wherein the pH of the solution is between about 1.5 and about 2.5.

18. A method for electroplating an iron layer onto an aluminum or aluminum alloy substrate cathode from an iron containing anode without the use of an undercoating layer, said method comprising the steps of:

providing the activation/electroplating bath solution comprising:

Fe^{+2} having a concentration ranging from about 0.65 to about 2.5 moles per liter of solution;
at least one sulfamate anion associated with the Fe^{+2} ion;
a reducing agent in an amount sufficient to prevent oxidation of Fe^{+2} to Fe^{+3};
Cl^- in an amount sufficient to promote dissolution of the anode and increase the conductivity of the solution;
a wetting agent in an amount sufficient to prevent pitting of the aluminum electroplated surface;
boric acid in an amount sufficient to increase the hardness of said iron layer; and
ammonium ion in an amount sufficient to increase the hardness of said iron layer;

activating said surface of said cathode by immersing said cathode in said solution;
immersing said anode in said solution; and
electroplating said iron layer onto said activated aluminum or aluminum alloy surface of said cathode in said solution.

19. The method of claim 18, wherein said electroplating step includes electroplating at a current density ranging from about 1.1 to about 13.2 amps/dm^2 about 10 to about 120 Amp/ft^2) for a dwell time sufficient to plate said layer of iron onto said surface to a thickness ranging from about 0.005 to about 0.05 mm (about 0.0002 to about 0.002 inch).

20. The method of claim 19, wherein said electroplating step includes electroplating for a dwell time sufficient to plate said layer of iron onto said surface to a thickness ranging from about 0.0089 to about 0.01 mm (about 0.00035 to about 0.0004 inch).

21. The method of claim 19 wherein said electroplating step includes electroplating for a dwell time between about 4 minutes and about 30 minutes.

22. The method of claim 18 wherein said electroplating step includes electroplating such that said iron layer has a microhardness of at least about 50 Rockwell C.

23. The method of claim 18, wherein said electroplating step includes electroplating such that said iron layer has a microhardness of at least about 55 Rockwell C.

24. The method of claim 18, wherein said providing step further includes providing said boric acid in a concentration between about 11 and about 26 grams per liter.

25. The method of claim 18, wherein said providing step further includes providing said ammonium ion in a concentration between about 0.08 and about 0.55 moles per liter.

26. The method of claim 18 whereby said providing step further includes providing a source of said ammonium ion in said solution selected from the group consisting of ammonium sulfamate, ammonium hydroxide, and mixtures thereof.

27. The method of claim 48 whereby said providing step further includes providing the reducing agent selected from the group consisting of glycolic acid, ascorbic acid, sodium bisulfite, sodium metabisulfite, sodium hydrasulfite, sodium hypophosphite, hydrazine, boric acid, and mixtures thereof.

28. The method of claim 27, whereby said providing step includes providing glycolic acid as the reducing agent present in said solution in a concentration between about 0.01 to about 0.10 percent by volume of said solution.

29. The method of claim 19, wherein said providing step further includes providing said Cl^- in a concentration between about 0.165 and 1.00 moles per liter.

30. The method of claim 18, whereby said providing step includes providing a chloride salt as a source of said Cl^- in said solution.

31. The method of claim 30, whereby said providing step includes providing said chloride salt from the group consisting of sodium chloride, potassium chloride, ammonium chloride, calcium chloride, and mixtures thereof.

32. The method of claim 18, wherein said providing step further includes providing said wetting agent from the group consisting of sodium lauryl sulfate, polyethylene glycol, and mixtures thereof.

33. The method of claim 18, wherein said providing step further includes providing said wetting agent in a concentration between about 0.1 to about 0.3 percent by volume of said solution.

34. The method of claim 18, further including, before said activating step, the steps of:

cleaning said cathode; and
etching said cathode to provide a mechanical tooth on the surface of said cathode.

35. The method of claim 18, further including the steps of:

removing the anode from said solution after said electroplating step; and
applying a rust inhibitor to the iron layer.

36. The method of claim 18, further including, before said activating step, the step of mounting said cathode onto a support structure having current thieves attached thereto, and wherein said electroplating step includes electroplating in the presence of said current thieves.

37. The method of claim 18, further including the step of maintaining the pH of said solution between about 1 and about 4 during the electroplating step.

38. The method of claim 37, wherein said maintaining step includes adding sulfamic acid, sulfuric acid, or ammonium hydroxide, as appropriate, to maintain the pH.

39. The method of claim 18, wherein the providing step further includes said bath solution including sulfamic acid.

40. The method of claim 18, further including a step of continuously removing impurities from said solution during the electroplating step by utilizing an ion exchange column in fluid communication with said solution.

41. The method of claim 40, wherein the continuously removing impurities step includes providing the ion exchange column with a selective ion exchange resin for removal of aluminum and copper.

42. The method of claim 41, further including, after said electroplating step, the step of regenerating said ion exchange resin by acid stripping.

43. The method of claim 18, further including, after said electroplating step, the step of precipitating impurities from the solution by increasing the pH of the solution.

44. The method of claim 18, wherein said immersing step further includes providing said anode made of carbon steel.

Patentansprüche

1. Lösung für Aktivierungs-/Elektroplattierungsbad, die aufweist:

Fe^{+2} mit einer Konzentration im Bereich von etwa 0,65 bis etwa 2,5 Mol pro Liter Lösung;
mindestens ein zu dem Fe^{+2}-Ion gehöriges Sulfamat-Anion;
ein Reduktionsmittel in einem ausreichenden Anteil, um die Oxidation von Fe^{+2} zu Fe^{+3} zu verhindern;
Cl^- in einem ausreichenden Anteil, um die Auflösung der Anode zu fördern und die Leitfähigkeit der Lösung zu erhöhen;

ein Benetzungsmittel in einem ausreichenden Anteil, um eine Grübchenbildung der mit elektroplattierten Aluminiumoberfläche zu verhindern;
Borsäure in einem ausreichenden Anteil, um die Härte der Eisenschicht zu erhöhen; und
Ammoniumionen in einem ausreichenden Anteil,, um die Härte der Eisenschicht zu erhöhen;

wobei die Badlösung einen pH-Wert von weniger als 3,5 aufweist und die Badlösung zum Aktivieren einer Substratkathode aus Aluminium oder Aluminiumlegierung und zum Elektroplattieren einer Eisenschicht von einer eisenhaltigen Anode direkt auf die Oberfläche der Kathode aus Aluminium oder Aluminiumlegierung verwendet wird.

2. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Reduktionsmittel aus der Gruppe ausgewählt ist, die aus Glycolsäure, Ascorbinsäure, Natriumbisulfit, Natriummetabisulfit, Natriumhydrosulfit, Natriumhypophosphit, Hydrazin, Borsäure und Gemischen daraus besteht.

3. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Reduktionsmittel Glycolsäure in einem Konzentrationsbereich von etwa 0,01 bis etwa 0,10 Vol.-% der Lösung aufweist.

4. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Cl^- eine Konzentration zwischen etwa 0,165 und etwa 1,00 Mol pro Liter aufweist.

5. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Cl^- eine Konzentration zwischen etwa 0,330 und etwa 1,00 Mol pro Liter aufweist.

6. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Cl^--Quelle in der Lösung aus der Gruppe ausgewählt ist, die aus Natriumchlorid, Kaliumchlorid, Ammoniumchlorid, Calciumchlorid und deren Gemischen besteht.

7. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Benetzungsmittel aus der Gruppe ausgewählt ist, die aus Natriumlaurylsulfat, Polyethylenglycol und deren Gemischen besteht, und wobei das Benetzungsmittel in einem Anteil im Bereich von etwa 0,1 bis etwa 0,3 Vol.-% der Lösung enthalten ist.

8. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Benetzungsmittel Natriumlaurylsulfat ist.

9. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei das Benetzungsmittel eine Konzentration zwischen etwa 0,1 und etwa 0,3 Vol.-% der Lösung aufweist.

10. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Konzentration der Borsäure zwischen etwa 11 und etwa 26 Gramm pro Liter liegt.

11. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Konzentration der Ammoniumionen zwischen etwa 0,08 und etwa 0,55 Mol pro Liter Lösung liegt.

12. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Quelle der Ammoniumionen in der Lösung aus der Gruppe ausgewählt ist, die aus Ammoniumsulfamat, Ammoniumhydroxid und deren Gemischen besteht.

13. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Eisenschicht eine Mikrohärte von mindestens etwa 50 Rockwell C aufweist.

14. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei die Eisenschicht eine Mikrohärte von mindestens etwa 55 Rockwell C aufweist.

15. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei der pH-Wert der Lösung zwischen etwa 1 und etwa 4 liegt.

16. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei der pH-Wert der Lösung zwischen etwa 1,5 und etwa 3,5 liegt.

17. Lösung für Aktivierungs-/Elektroplattierungsbad nach Anspruch 1, wobei der pH-Wert der Lösung zwischen etwa 1,5 und etwa 2,5 liegt.

18. Verfahren zum Elektroplattieren einer Eisenschicht von einer eisenhaltigen Anode auf eine Substratkathode aus Aluminium oder Aluminiumlegierung ohne Verwendung einer Grundierungsschicht, wobei das Verfahren die folgenden Schritte aufweist:

Bereitstellen einer Lösung für ein Aktivierungs-/Elektroplattierungsbad, die aufweist:

Fe^{+2} mit einer Konzentration im Bereich von etwa 0,65 bis etwa 2,5 Mol pro Liter Lösung;
mindestens ein zu dem Fe^{+2}-Ion gehöriges Sulfamat-Anion;
ein Reduktionsmittel in einem ausreichenden Anteil, um die Oxidation von Fe^{+2} zu

Fe^{+3} zu verhindern;

Cl^- in einem ausreichenden Anteil, um die Auflösung der Anode zu fördern und die Leitfähigkeit der Lösung zu erhöhen;
ein Benetzungsmittel in einem ausreichenden Anteil, um eine Grübchenbildung der elektroplattierten Aluminiumoberfläche zu verhindern;
Borsäure in einem ausreichenden Anteil,, um die Härte der Eisenschicht zu erhöhen; und
Ammoniumionen in einem ausreichenden Anteil, um die Härte der Eisenschicht zu erhöhen;
Aktivieren der Oberfläche der Kathode durch Eintauchen der Kathode in die Lösung;
Eintauchen der Anode in die Lösung; und
Elektroplattieren der Eisenschicht auf die aktivierte Oberfläche der Kathode aus Aluminium oder Aluminiumlegierung in der Lösung.

19. Verfahren nach Anspruch 18, wobei der Elektroplattierungsschritt das Elektroplattieren mit einer Stromdichte im Bereich von etwa 1,1 bis etwa 13,2 A/dm^2 (etwa 10 bis etwa 120 $A/Fuß^2$) über eine Verweilzeit aufweist, die ausreicht, um die Oberfläche mit der Eisenschicht bis zu einer Dicke von etwa 0,005 bis etwa 0,05 mm (etwa 0,0002 bis etwa 0,002 Zoll) zu plattieren.

20. Verfahren nach Anspruch 19, wobei der Elektroplattierungsschritt das Elektroplattieren über eine ausreichende Verweilzeit aufweist, um die Oberfläche mit der Eisenschicht bis zu einer Dicke von etwa 0,0089 bis etwa 0,01 mm (etwa 0,00035 bis etwa 0,0004 Zoll) zu plattieren.

21. Verfahren nach Anspruch 19, wobei der Elektroplattierungsschritt das Elektroplattieren über eine Verweilzeit von etwa 4 Minuten bis etwa 30 Minuten aufweist.

22. Verfahren nach Anspruch 18, wobei der Elektroplattierungsschritt ein Elektroplattieren auf eine solche Weise aufweist, daß die Eisenschicht eine Mikrohärte von mindestens etwa 50 Rockwell C aufweist.

23. Verfahren nach Anspruch 18, wobei der Elektroplattierungsschritt ein Elektroplattieren auf eine solche Weise aufweist, daß die Eisenschicht eine Mikrohärte von mindestens etwa 55 Rockwell C aufweist.

24. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen der Borsäure in einer Konzentration zwischen etwa 11 und etwa 26 Gramm pro Liter aufweist.

25. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen von Ammoniumionen in einer Konzentration zwischen etwa 0,08 und etwa 0,55 Mol pro Liter aufweist.

26. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen einer Quelle für die Ammoniumionen in der Lösung aufweist, die aus der Gruppe ausgewählt ist, die aus Ammoniumsulfamat, Ammoniumhydroxid und deren Gemischen besteht.

27. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen des Reduktionsmittels aufweist, das aus der Gruppe ausgewählt ist, die aus Glycolsäure, Ascorbinsäure, Natriumbisulfit, Natriummetabisulfit, Natriumhydrosulfit, Natriumhypophosphit, Hydrazin, Borsäure und Gemischen daraus besteht.

28. Verfahren nach Anspruch 27, wobei der Bereitstellungsschritt ferner das Bereitstellen von Glycolsäure als Reduktionsmittel aufweist, das in der Lösung in einer Konzentration zwischen etwa 0,01 und etwa 0,10 Vol.-% der Lösung enthalten ist.

29. Verfahren nach Anspruch 19, wobei der Bereitstellungsschritt ferner das Bereitstellen des Cl^- in einer Konzentration zwischen etwa 0,165 und 1,00 Mol pro Liter aufweist.

30. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt das Bereitstellen eines Chloridsalzes als Cl^--Quelle in der Lösung aufweist.

31. Verfahren nach Anspruch 30, wobei der Bereitstellungsschritt das Bereitstellen des Chloridsalzes aus der Gruppe aufweist, die aus Natriumchlorid, Kaliumchlorid, Ammoniumchlorid, Calciumchlorid und deren Gemischen besteht.

32. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen des Benetzungsmittels aus der Gruppe aufweist, die aus Natriumlaurylsulfat, Polyethylenglycol und deren Gemischen besteht.

33. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner das Bereitstellen des Benetzungsmittels in einer Konzentration zwischen etwa 0,1 und etwa 0,3 Vol.-% der Lösung aufweist.

34. Verfahren nach Anspruch 18, das ferner vor dem Aktivierungsschritt die folgenden Schritte aufweist:

Reinigen der Kathode; und
Ätzen der Kathode, um eine mechanische Zahnung auf der Oberfläche der Kathode zu erzeugen.

35. Verfahren nach Anspruch 18, das ferner die folgenden Schritte aufweist:

Entfernen der Anode aus der Lösung nach dem Elektroplattierungsschritt; und

Aufbringen eines Rostschutzmittels auf die Eisenschicht.

36. Verfahren nach Anspruch 18, das ferner vor dem Aktivierungsschritt den Schritt zur Montage der Kathode auf einer Trägerstruktur mit daran angebrachten Stromableitern aufweist, und wobei der Elektroplattierungsschritt das Elektroplattieren in Gegenwart der Stromableiter aufweist.

37. Verfahren nach Anspruch 18, das ferner den Schritt zum Halten des pH-Werts der Lösung zwischen etwa 1 und etwa 4 während des Elektroplattierungsschritts aufweist.

38. Verfahren nach Anspruch 37, wobei der Schritt zum Halten des pH-Werts die Zugabe von Sulfaminsäure, Schwefelsäure oder gegebenenfalls Ammoniumhydroxid zum Halten des pH-Werts aufweist.

39. Verfahren nach Anspruch 18, wobei der Bereitstellungsschritt ferner die Badlösung einschließlich der Sulfaminsäure einschließt.

40. Verfahren nach Anspruch 18, das ferner einen Schritt zum kontinuierlichen Entfernen von Verunreinigungen aus der Lösung während des Elektroplattierungsschritts mit Hilfe einer Ionenaustauschersäule aufweist, die in Fluidverbindung mit der Lösung steht.

41. Verfahren nach Anspruch 40, wobei der Schritt zum kontinuierlichen Entfernen von Verunreinigungen das Füllen der Ionenaustauschersäule mit einem selektiven Ionenaustauscherharz zum Entfernen von Aluminium und Kupfer aufweist.

42. Verfahren nach Anspruch 41, das ferner nach dem Elektroplattierungsschritt den Schritt zur Regeneration des Ionenaustauscherharzes durch Säurestripping aufweist.

43. Verfahren nach Anspruch 18, das ferner nach dem Elektroplattierungsschritt den Schritt zum Ausfällen von Verunreinigungen aus der Lösung durch Erhöhen des pH-Werts der Lösung aufweist.

44. Verfahren nach Anspruch 18, wobei der Tauchschritt ferner das Bereitstellen der aus Kohlenstoffstahl bestehenden Anode einschließt.

Revendications

1. Solution de bain d'activation/électroplaquage comprenant:

Fe^{2+} avec une concentration variant d'environ 0,65 à environ 2,5 moles par litre de solution;
au moins un anion de sulfamate associé à l'ion Fe^{2+};
un agent réducteur dans une quantité suffisante pour prévenir l'oxydation de Fe^{2+} en Fe^{3+};
Cl^- dans une quantité suffisante pour favoriser la dissolution de l'anode et augmenter la conductivité de la solution;
un agent mouillant dans une quantité suffisante pour prévenir la formation de piqûres de la surface d'aluminium électroplaquée;
de l'acide borique dans une quantité suffisante pour augmenter la dureté de ladite couche de fer; et
des ions ammoniums dans une quantité suffisante pour augmenter la dureté de ladite couche de fer;
la solution de bain possédant un pH inférieur à 3,5 et la solution de bain étant utilisée pour l'activation d'un substrat de cathode d'aluminium ou d'alliage d'aluminium et pour l'électroplaquage d'une couche de fer directement sur une surface d'aluminium ou d'alliage d'aluminium de ladite cathode à partir d'une anode contenant du fer.

2. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle l'agent réducteur est choisi dans le groupe constitué d'acide glycolique, d'acide ascorbique, de bisulfite de sodium, de métabisulfite de sodium, d'hydrosulfite de sodium, d'hypophosphite de sodium, d'hydrazine, d'acide borique et de mélanges de ceux-ci.

3. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle l'agent réducteur inclut de l'acide glycolique avec une concentration variant d'environ 0,01 à environ 0,10 pourcent en volume de ladite solution.

4. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle lesdits ions Cl^- présentent une concentration comprise entre environ 0,165 et environ 1,00 mole par litre.

5. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle lesdits ions Cl^- présentent une concentration comprise entre environ 0,330 et environ 1,00 mole par litre.

6. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle la source desdits ions Cl^- dans ladite solution est choisie dans le groupe constitué de chlorure de sodium, de chlorure de potassium, de chlorure d'ammonium, de chlorure de calcium et de mélanges de ceux-ci.

7. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle l'agent mouillant est choisi dans le groupe constitué de sulfate de lauryle de sodium, de polyéthylèneglycol et de mélanges de ceux-ci, et dans laquelle ledit agent mouillant est présent dans une quantité variant d'environ 0,1 à environ 0,3 pour-cent en volume de la solution.

8. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle l'agent mouillant est du sulfate de lauryle de sodium.

9. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle l'agent mouillant présente une concentration comprise entre environ 0,1 et environ 0,3 pour-cent en volume de la solution.

10. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle la concentration dudit acide borique est comprise entre environ 11 et environ 26 grammes par litre.

11. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle la concentration desdits ions ammoniums est comprise entre environ 0,08 et environ 0,55 mole par litre de solution.

12. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle la source desdits ions ammoniums dans ladite solution est choisie dans le groupe constitué de sulfamate d'ammonium, d'hydroxyde d'ammonium et de mélanges de ceux-ci.

13. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle ladite couche de fer possède une micro-dureté d'au moins environ 50 Rockwell C.

14. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle ladite couche de fer possède une micro-dureté d'au moins environ 55 Rockwell C.

15. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle le pH de la solution est compris entre environ 1 et environ 4.

16. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle le pH de la solution est compris entre environ 1,5 et environ 3,5.

17. Solution de bain d'activation/électroplaquage suivant la revendication 1, dans laquelle le pH de la solution est compris entre environ 1,5 et environ 2,5.

18. Procédé pour l'électroplaquage d'une couche de fer sur un substrat de cathode d'aluminium ou d'alliage d'aluminium à partir d'une anode contenant du fer sans utilisation d'une couche sous-jacente, ledit procédé comprenant les étapes consistant:

à fournir la solution de bain d'activation/électroplaquage comprenant:

Fe^{2+} avec une concentration variant d'environ 0,65 à environ 2,5 moles par litre de solution;

au moins un anion de sulfamate associé à l'ion Fe^{2+};

un agent réducteur dans une quantité suffisante pour prévenir l'oxydation de Fe^{2+} en Fe^{3+};

Cl^- dans une quantité suffisante pour favoriser la dissolution de l'anode et augmenter la conductivité de la solution;

un agent mouillant dans une quantité suffisante pour prévenir la formation de piqûres de la surface d'aluminium électroplaquée;

de l'acide borique dans une quantité suffisante pour augmenter la dureté de ladite couche de fer; et

des ions ammoniums dans une quantité suffisante pour augmenter la dureté de ladite couche de fer;

à activer ladite surface de ladite cathode en immergeant ladite cathode dans ladite solution;

à immerger ladite anode dans ladite solution; et

à électroplaquer ladite couche de fer sur ladite surface activée d'aluminium ou d'alliage d'aluminium de ladite cathode dans ladite solution.

19. Procédé suivant la revendication 18, dans lequel l'étape d'électroplaquage inclut un électroplaquage à une densité de courant variant d'environ 1,1 à environ 13,2 Amp/dm^2 (environ 10 à environ 120 Amp/ft^2) pendant un temps d'arrêt suffisant pour déposer ladite couche de fer sur ladite surface à une épaisseur variant d'environ 0,005 à environ 0,05 mm (d'environ 0,0002 à environ 0,002 pouce).

20. Procédé suivant la revendication 19, dans lequel ladite étape d'électroplaquage inclut un électroplaquage pendant un temps d'arrêt suffisant pour déposer ladite couche de fer sur ladite surface à une épaisseur variant d'environ 0,0089 à environ 0,01 mm (d'environ 0,00035 à environ 0,0004 pouce).

21. Procédé suivant la revendication 19, dans lequel ladite étape d'électroplaquage inclut un électroplaquage pendant un temps d'arrêt compris entre environ 4 minutes et environ 30 minutes.

22. Procédé suivant la revendication 18, dans lequel ladite étape d'électroplaquage inclut un électroplaquage de sorte que ladite couche de fer possède une micro-dureté d'au moins environ 50 Rockwell C.

23. Procédé suivant la revendication 18, dans lequel ladite étape d'électroplaquage inclut un électroplaquage de sorte que ladite couche de fer possède une micro-dureté d'au moins environ 55 Rockwell C.

24. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut en outre la fourniture dudit acide borique dans une concentration comprise entre environ 11 et environ 26 grammes par litre.

25. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut en outre la fourniture desdits ions ammoniums dans une concentration comprise entre environ 0,08 et environ 0,55 mole par litre.

26. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut en outre la fourniture d'une source desdits ions ammoniums dans ladite solution choisie dans le groupe constitué de sulfamate d'ammonium, d'hydroxyde d'ammonium et de mélanges de ceux-ci.

27. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut en outre la fourniture de l'agent réducteur choisi dans le groupe constitué d'acide glycolique, d'acide ascorbique, de bisulfite de sodium, de métabisulfite de sodium, d'hydrosulfite de sodium, d'hypophosphite de sodium, d'hydrazine, d'acide borique et de mélanges de ceux-ci.

28. Procédé suivant la revendication 27, dans lequel ladite étape de fourniture inclut la fourniture d'acide glycolique en tant qu'agent réducteur présent dans ladite solution dans une concentration comprise entre environ 0,01 et environ 0,10 pour-cent en volume de ladite solution.

29. Procédé suivant la revendication 19, dans lequel ladite étape de fourniture inclut en outre la fourniture desdits ions Cl^- dans une concentration comprise entre environ 0,165 et 1,00 mole par litre.

30. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut la fourniture d'un sel de chlorure en tant que source desdits ions Cl^- dans ladite solution.

31. Procédé suivant la revendication 30, dans lequel ladite étape de fourniture inclut la fourniture dudit sel de chlorure parmi le groupe constitué de chlorure de sodium, de chlorure de potassium, de chlorure d'ammonium, de chlorure de calcium et de mélanges de ceux-ci.

32. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut en outre la fourniture dudit agent mouillant parmi le groupe constitué de sulfate de lauryle de sodium, de polyéthylèneglycol et de mélanges de ceux-ci.

33. Procédé suivant la revendication 18, dans lequel ladite étape de fourniture inclut la fourniture dudit agent mouillant dans une concentration comprise entre environ 0,1 et environ 0,3 pour-cent en volume de ladite solution.

34. Procédé suivant la revendication 18, incluant en outre, avant ladite étape d'activation, les étapes consistant:

à nettoyer ladite cathode; et
à attaquer (graver) ladite cathode pour donner des dents mécaniques sur la surface de ladite cathode.

35. Procédé suivant la revendication 18, incluant en outre les étapes consistant:

à retirer l'anode de ladite solution après ladite étape d'électroplaquage; et

à appliquer un inhibiteur de rouille sur la couche de fer.

36. Procédé suivant la revendication 18, incluant en outre, avant ladite étape d'activation, l'étape consistant à monter ladite cathode sur une structure support avec des écrans voleurs de courant attachés sur celle-ci, et dans lequel ladite étape d'électroplaquage inclut un électroplaquage en présence desdits écrans voleurs de courant.

37. Procédé suivant la revendication 18, incluant en outre l'étape consistant à maintenir le pH de ladite solution entre environ 1 et environ 4 durant l'étape d'électroplaquage.

38. Procédé suivant la revendication 37, dans lequel ladite étape de maintien inclut l'ajout d'acide sulfamique, d'acide sulfurique ou d'hydroxyde d'ammonium, comme c'est approprié, pour maintenir le pH.

39. Procédé suivant la revendication 18, dans lequel l'étape de fourniture inclut en outre ladite solution de bain incluant de l'acide sulfamique.

40. Procédé suivant la revendication 18, incluant en outre une étape consistant à retirer en continu les impuretés provenant de ladite solution durant l'étape d'électroplaquage en utilisant une colonne échangeuse d'ions en communication de fluide avec ladite solution.

41. Procédé suivant la revendication 40, dans lequel l'étape de retrait en continu des impuretés inclut la fourniture d'une colonne échangeuse d'ions avec une résine échangeuse d'ions sélective pour le retrait d'aluminium et de cuivre.

42. Procédé suivant la revendication 41, incluant en outre, après ladite étape d'électroplaquage, l'étape consistant à régénérer ladite résine échangeuse d'ions par une rectification acide.

43. Procédé suivant la revendication 18, incluant en outre, après ladite étape d'électroplaquage, l'étape consistant à précipiter les impuretés à partir de la solution en augmentant le pH de la solution.

44. Procédé suivant la revendication 18, dans lequel ladite étape d'immersion inclut en outre la fourniture de ladite anode constituée d'acier au carbone.