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(54) **Shot material for mechanical plating, and high corrosion resistant coating using the same**

(57) Shot material for mechanical plating is provided, comprising steel core particles clad with an alloy comprising 1 to 5% by weight of aluminum, 3 to 15% by weight of magnesium, preferably 5 to 15% by weight of magnesium, and the balance of zinc and unavoidable impurities. The alloy may contain a total of 1% by weight of impurities. An Fe-Zn alloy layer may be provided between the alloy cladding and the steel core. The shot material may contain 3 to 80% by weight of iron. The preferable average diameter of the shot particles is 100 to 600 μm.

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Description

Field of the Invention

[0001] The present invention relates to a shot material used in mechanical plating for forming a high corrosion resistant coating on a metal material surface, and to a high corrosion resistant coating formed using the shot material.

Description of the Prior Art

[0002] Forming a zinc or zinc alloy coating (referred to hereinbelow as "zinc based coating") on iron-based metal materials is a widely-used method of improving the corrosion resistance of the iron-based metal. Specific technologies for this that are in practical industrial use include hot dipping, phosphate plating, electroplating, and mechanical plating.

[0003] If zinc based coating formed by zinc plating or the like is exposed to the air without first being treated, it can give rise to white rust of the zinc in a relatively short time, expediting deterioration of the coating. This is especially pronounced in an outside environment. To prevent that happening, a treatment such as chromating is used to form a protective coating on the zinc based coating.

[0004] Because a zinc based coating formed by mechanical plating has a layered, flaky structure as if oflike a pie crust, structure, when it is subjected to chromate treatment, the chromate solution can fully permeate the coating, providing a good improvement in the corrosion resistance. For example, in the case of a zinc based coating formed by mechanical plating on which it takes around 24 hours for red rust to form in a salt spray test (herein meaning a test conforming to JIS Z-2371), the use of chromate treatment increases the time until red rust appears to around 3000 hours, providing a dramatic improvement in corrosion resistance.

[0005] Chromate treatment is widely used because it facilitates the formation of a coating that provides good protection at a relatively low cost. However, the solution used for the treatment contains hexavalent chromium, which is toxic. While there are also methods of providing protection using a trivalent chromium coating, polymer chelate coating, silicate-based inorganic coating and the like, the protective effect of such coatings is inferior to that provided by a hexavalent chromate coating. One reason for this is the other coatings do not have the self-repairability exhibited by a hexavalent chromate coating. That is important, because there is a sharp decrease in the corrosion resistance of locations that suffer damage. Another drawback with methods that do not use hexavalent chromium is that the administration of the treatment solution is complicated and can readily give rise to post-treatment variations in characteristics, making the treatment quite costly compared to the hexavalent chromate treatment.

[0006] There have been various studies on ways of improving the corrosion resistance of the zinc based coating itself formed by mechanical plating. JP 55-119101 A (Reference No. 1), JP 56-93801 A (Reference No. 2) and JP 57-110601 A (Reference No. 3) disclose the use of powders of zinc alloy in which aluminum, magnesium and the like are used as alloying elements. Also, in order to improve the durability of such zinc based coatings, it is important to improve the bonding of the coating to the base metal. JP 56-45372 A (Reference No. 4) and JP 62-140768 A (Reference No. 5) teach using, as the shot material, core particles of iron or iron alloy that are clad with zinc or zinc alloy. The idea is that a large bombardment energy can be obtained by impacting the surface of the material to be treated with particles having a hard, heavy iron-based core in the projection treatment of the blasting process, thereby improving the coating adhesion by increasing the cladding pressure.

Object of the Invention

[0007] Thus, as described in the above, the corrosion resistance of zinc based coatings formed by mechanical plating can be greatly improved by chromate treatment. However, as environmental regulations become stronger, the use of toxic hexavalent chromium is being subjected to increasingly rigorous restrictions. At the same time, there is as yet no established alternative treatment method for forming an effective protective coating.

[0008] However, without such treatment, parts that are coated by mechanical plating are limited in terms of corrosion resistance. Specifically, with respect to the methods of Reference Nos. 1 to 3 that use zinc alloy powder to improve corrosion resistance, the time it takes for red rust to arise when the salt spray test is performed is around 500 hours in the case of a simple Zn-Al-Mg alloy composition, and can be increased to no more than 1500 hours or so by adding special elements such as sodium or beryllium or the like. However, for car parts applications it is desirable that red rust does not arise for 1800 hours or more, and 3000 hours or more in the case of car parts and the like used in corrosively salty environments. It is difficult to meet such needs simply by bonding zinc alloy having high corrosion resistance.

[0009] Similarly, the methods of Reference Nos. 4 and 5 that use shot material having a core of iron-based particles, also do not achieve any dramatic improvement in the corrosion resistance.

[0010] In view of the foregoing, the object of the present invention is to provide a zinc based coating formed by mechanical plating that itself has a markedly improved corrosion resistance that does not rely on protective coating formation treatment such as chromate treatment or the like.

Summary of the Invention

[0011] In accordance with the present invention, the above object is attained by shot material for mechanical plating, comprising steel core particles clad with an alloy comprising 1 to 5% by weight of aluminum, 3 to 15% by weight of magnesium, preferably 5 to 15% by weight of magnesium, and the balance of zinc and unavoidable impurities. The unit of "% by weight" regardpertains to the same meaning as those of "% by mass" in the present specification. The alloy may contain a total of up to around 1% by weight of impurities. An Fe-Zn alloying layer may be provided between the alloy cladding and the steel core.

[0012] The shot material may contain 3 to 80% by weight of iron. Preferably, the shot particles have an average diameter of 100 to 600 μm.

[0013] The invention also provides a high corrosion resistant coating having a thickness of 2 to 15 μm formed on a surface of metal material such as steel or the like by projectblasting the above shot material, the high corrosion resistant coating comprising 1 to 5% by weight of aluminum, 3 to 15% by weight of magnesium, up to 20% by weight of iron, and the balance of zinc and unavoidable impurities. The coating may contain a total of up to around 1% by weight of impurities.

[0014] In accordance with the present invention, the corrosion resistance of parts having the coating as formed by mechanical plating is dramatically improved. This makes the invention applicable to various existing parts without the use of chromate treatment, making it possible to reduce the cost of manufacturing parts and to cope with environmental regulations. In particular, by increasing the magnesium content in the zinc based alloy cladding layer constituting the shot material, it is possible to obtain iron-based parts having a very high corrosion resistance, as indicated in the salt spray test by a time for red rust to be produced that exceeds 4000 hours. Moreover, since an adequate effect can be obtained with a coating thickness of 15 μm or less, or an even thinner 2 to 5 μm, high corrosion resistance can be imparted to parts such as bolts, to which hot-dip plating cannot be applied due to the thick, heavy coating weight having thick layer. This makes it possible to use the coating of this invention for outside structures instead of the stainless steel that has had to be used, thereby providing major cost reductions.

Detailed Description of the Invention

[0015] As a result of various studies, the inventors found that a very marked corrosion resistance improvement effect could be obtained when the following two points were combined.

i) Using Zn-Al-Mg system alloy as the material adhered by mechanical plating, and using a magnesium content thereof that is at least 3% by weight, and preferably 5% or more by weight.

ii) Impacting the surface of the subject material to be treated with shot material having steel core particles that incorporates the material adhered by the mechanical plating.

[0016] A marked improvement in corrosion resistance was not observed when just one of the above i) and ii) was used without the other. The present invention utilizes a novel corrosion resistance improvement effect produced by the synergism of i) and ii). At present the mechanism that brings about this synergy has not been fully clarified.

Zn-Al-Mg system alloy adhesion material

[0017] In the coating formed by the mechanical plating, highly intricate corrosion products are produced between the zinc and the aluminum, creating a stable, sealed coating. To utilize this effect to the full, the formed coating preferably contains 1% or more by weight of aluminum. However, if the amount exceeds 5% by weight, it will not be expected to produce an effect corresponding to the amount added. The composition of the alloy cladding around the steel core of the shot material more or less is a reflection of the composition of the coating formed on a part, and as such, the aluminum content in the alloy cladding layer of the shot material is set at 1 to 5% by weight.

[0018] In the coating formed by mechanical plating, magnesium forms oxides and hydroxides. Magnesium oxides or hydroxides have high electrical insulation properties that suppress corrosion current produced when the zinc in the coating corrodes. It also prevents oxygen permeation, thereby exhibiting a protective effect with respect to zinc corrosion. Magnesium has a lower electric potential than zinc, but in a corrosive environment produces stable corrosion products and alleviates the galvanic action of zinc. It is thought that this controls the elution of the zinc in the coating, elevating the corrosion prevention effect. Through detailed studies, the inventors found that these effects of magnesium became apparent when the magnesium content in the coating was 3% or more by weight. A magnesium content of 5% or more by weight is preferable. When there is a high magnesium concentration of 7% or more by weight, in combination with the effect of the above ii) (the impact effect of shot particles with steel cores), the result is a very strong corrosion resistance that exceeds that obtained using chromate treatment. However, magnesium is readily oxidized in the zinc alloy melt, so that an attempt to ensure too high a magnesium content makes it difficult to manufacture the shot material using the molten zinc alloy, as described later. For that reason, the magnesium content has to be kept to not more than 15% by weight. Generally, good results can be obtained using a content that is not more than 12% by weight. Accordingly, the magnesium content is set at 3 to 15% by weight. Preferably, the magnesium content is 5 to 15% by weight, and more preferably 7 to 12% by weight.

[0019] Generally, a coating formed by mechanical plating contains iron from the shot material or parts concerned. Good results can be obtained with an iron content range of up to 20% by weight, such as, for example, from 0.1 to 20% by weight. It is desirable to keep the total content of impurity elements (elements other than zinc, aluminum, magnesium and iron) to not more than 1% by weight.

Shot material

[0020] This invention uses shot particles that have a steel core. That is, the particles are composite particles consisting of steel particles and zinc based alloy. Blasting the surface of the material to be treated with these composite-structure particles provides as good a coating adhesion as those of conventional shot material having an iron core. However, an even more dramatic improvement in corrosion resistance is obtained by using a coating material composition to which is added an Al-Mg composite having a high magnesium content. That is, it brings forth the synergism of i) and ii), which is not something that could be predicted before. It is thought that the impact of the steel-core shot particles strengthens the adhesion bonding of the coating to the base metal and also strengthens the coating itself, increasing the damage resistance of the coating. Also, it is surmised that the sealing effect of the aluminum in the cladding material combines with zinc elution prevention effect provided by elevating the magnesium content, generating the major improvement in the corrosion resistance.

[0021] To adequately manifest the characteristic effect of the invention, the ratio between the steel particle core and the zinc based alloy cladding layer should be controlled so that the content of the iron in the shot material is from 3 to 80% by weight. If the iron content is lower than that, it is difficult to obtain a sufficient impact energy, while a higher content will result in a relatively small amount of cladding material, shortening the life of the shot material during the blasting process of the mechanical plating.

[0022] It is desirable to use steel cores having a hardness in the order of 200 to 700 HV. At least 95% by weight of all shot particles should have a particle diameter that falls within the range 10 to 800 μm, and an average diameter of 100 to 600 μm.

Coating thickness

[0023] The coating formed on the surface of the subject metal material has to be at least 2 μm thick. However, using mechanical plating to form a coating with a heavy coating weight that exceeds 15 μm in thickness is uneconomical. In accordance with the present invention a good corrosion resistance effect can be obtained by controlling the coating thickness to be within the range of about 2 to 15 μm.

Method of manufacturing the shot material

[0024] The shot material of the invention can be manufactured by the steps of preparing a zinc alloy melt having a composition corresponding to the material used to clad the steel core particles, charging the steel core particles into the zinc alloy melt, stirring the mixture, removing it when it cools into a semi-solidified state, crushing and screening. For this, the amount of the zinc alloy melt and the charging amount of the steel particles charged into the melt should be controlled to bring the iron content in the shot particles to within the range of 3 to 80% by weight. When the zinc alloy is adhered around the steel particles by the above process, above, an Fe-Zn alloy layer forms at the interface between the steel particles and the zinc alloy. The Fe-Zn alloy layer is relatively brittle, so when the shot material is impacted on the surface of subject material to be treated in the blasting process, the microparticles of zinc alloy sheared-off finely in the portion of the Fe-Zn alloy layer are pressed onto the surface of the subject material, increasing the uniformity of the coating.

[0025] Commercially available steel shot can be used for the steel particles. As stated in the foregoing, the alloy-clad shot particles should have a diameter within the range 10 to 800 μm. The average particle diameter should be within the range 100 to 600 μm, and may be within the range 100 to 400 μm or 150 to 300 μm. Since the iron content of the shot particles is preferably from about 3 to 80% by weight, the size and quantity of the steel particles used should be set in accordance with those target values.

First Embodiment

Inventive Example 1

[0026] 50 kg of a melt of zinc alloy composed of Zn-3.5% by weight of Al-8.0% by weight of Mg (and less than 1% by weight of impurities) was maintained in a vessel at 570°C for homogenization, following which the burners were switched off and 65 kg of steel shot was chargstirred into the melt. under stirring. The steel shot consisted of commercially available particles having an average diameter of 237 μm and an average hardness of 312 HV. At the point when the melt had cooled to a semi-solidified state, the mixture of zinc alloy and steel shot was taken out from the vessel and transferred to a crusher before full solidification could take place, and crushing was initiated. Crushing was continued until the shot material was obtained comprising separationg into individual particles having nearly spherical surface.

[0027] The shot materials obtained had an average diameter of 218 μm. Based on observation of the cross section of the particles using electron dispersive x-ray spectroscopy (EDS), the steel particles were seen to have cores originating from the steel shot, which were clad by a layer of zinc alloy via an alloy layer formed by the reaction between the steel shot and the melt. Further analysis of the section showed the alloy layer formed by the reaction between the steel shot and the melt to be an Fe-Zn alloy layer, and the zinc alloy cladding layer to have a composition corresponding to the composition of the initial melt. Shot sample composition analysis conducted using the method for the determination of total iron content in iron ore of JIS M-8212-1958 and the potassium permanganate titration method showed the shot material to have an iron content of 49.9% by weight.

[0028] This shot material was used to form a zinc alloy coating on commercial 4T steel bolts, using a mechanical plating apparatus. Shotblasting conditions were as follows. Shotblasting amount: 60 kg/min, shotblasting particle velocity: initial velocity of approximately 51 m/sec, shotblasting duration: 80 minutes. EDS observation related to the section of coated bolts showed the coating to be about 4.4 μm thick. An investigation of the composition showed the coating consisted of approximately 3.3% by weight of aluminum, approximately 7.5% by weight of magnesium, approximately 5.5% by weight of iron, and the balance substantially of zinc. The total amount of other elements (impurities) was less than 1% by weight.

Inventive Example 2

[0029] Shot material was obtained using the same conditions as in Inventive Example 1, except that the melt was composed of Zn-3.5% by weight of Al-6.0% by weight of Mg (and less than 1% by weight of impurities), and was maintained at 535°C. The shot material had an average particle diameter of 217 μm, and had steel cores originating from the steel shot, which were clad by a layer of zinc alloy via an alloy layer formed by the reaction between the steel shot and the melt. Measurements showed the alloy layer formed by the reaction between the steel shot and the melt to be an Fe-Zn alloy layer, and the zinc alloy cladding layer to have a composition corresponding to the composition of the initial melt. The shot material had an iron content of 54.8% by weight.

[0030] The shot material was used to form a zinc alloy coating on commercial 4T steel bolts under the same conditions as Inventive Example 1. The coating thus obtained was about 4.5 μm thick, and consisted of approximately 3.3% by weight of aluminum, approximately 5.6% by weight of magnesium, approximately 6.2% by weight of iron, and the balance substantially of zinc. The total amount of other elements (impurities) was less than 1% by weight.

Comparative Example 1

[0031] Shot material was obtained using the same conditions as in Inventive Example 1, except that a melt of zinc (and less than 1% by weight of impurities) was used, and was maintained at 480°C. The shot material had an average particle diameter of 235 μm, and had steel cores originating from the steel shot, which were clad by a layer of zinc via an alloy layer formed by the reaction between the steel shot and the melt. The shot material had an iron content of 55.7% by weight. The shot material was used to form a zinc alloy coating on commercial 4T steel bolts under the same conditions as Inventive Example 1. The coating thus obtained was about 4.6 μm thick, and in addition to the zinc, contained approximately 13.7% by weight of iron.

Comparative Example 2

[0032] Bolts were produced by using a conventional chromate treatment to form a chromate coating on the coating formed in Comparative Example 1.

Salt spray test

[0033] The bolts obtained by the procedures of the above inventive and comparative examples were subjected to a salt spray test conforming to the method of JIS Z-2371 to investigate the time it took for red rust to form. The results were:

- Inventive Example 1: 5160 hours,
- Inventive Example 2: 1920 hours,
- Comparative Example 1: <24 hours,
- Comparative Example 2 (chromate treatment): 3000 hours.

[0034] In accordance with the present invention, it was possible to impart a high corrosion resistance, as shown by the fact it took over 1800 hours for the salt spray to produce red rust. In particular, coatings having a higher magnesium content (Inventive Example 1) was shown to provide far greater corrosion resistance than that of material subjected to chromate treatment.

Second Embodiment

[0035] Instead of the bolts used in the above inventive and comparative examples of the first embodiment, 0.8 mm cold-rolled steel sheet (SPCC) was used to form a mechanical coating on itsthe surface by using the shot materials obtained in the examples under the same conditions as the examples, and the various properties investigated. Specifically:

Inventive Example 3: Same shot material and conditions as Inventive Example 1.
Inventive Example 4: Same shot material and conditions as Inventive Example 2.
Comparative Example 3: Same shot material and conditions as Comparative Example 1.
Comparative Example 4: Same shot material and conditions as Comparative Example 2 (chromate treatment).

[0036] The following properties of each sample were investigated.

- Adhesiveness of coating: This was evaluated using the bending test according to the adhesiveness of plating test of JIS H-8504 and the grid tape test of JIS K-5400.
- Self-repairability (sacrificial anticorrosion): Using cross-cuts, this was evaluated using the time taken for red rust to be produced by the salt spray test of JIS Z-2371.
- Weatherability: This was evaluated using the time taken for red rust to be produced by the outdoor exposure test (direct exposure test) of JIS Z-2381-1987.

[0037] The results are shown in Table 1.

Table 1

Category	Coating Adhesiveness		Self-repairability (Sacrificial Anticorrosion)	Weatherability (Outdoor Exposure Test)
	Bending Test	Grid Tape Test		
Inventive Example 3	Good	Good	1104 hours	≧6 months
Inventive Example 4	Good	Good	312 hours	≧6 months
Comparative Example 3	Good	Good	< 24 hours	< 1 month
Comparative Example 4 (Chromate treatment)	Good	Good	1080 hours	≧6 months

[0038] As can be seen from Table 1, the inventive examples showed a marked improvement in self-repairability and weatherability while maintaining their good coating adhesiveness. Of particular note is that samples with a higher magnesium content (Inventive Example 3) exhibited the same or better self-repairability than that of materials subjected to chromate treatment.

Claims

1. Shot material for mechanical plating, comprising steel core particles clad with an alloy comprising 1 to 5% by weight of aluminum, 3 to 15% by weight of magnesium, and the balance of zinc and unavoidable impurities.

2. Shot material according to claim 1, wherein the magnesium contents in the alloy are 5 to 15% by weight.

3. The shot material according to claim 1 or 2, wherein there is an Fe-Zn alloy layer between the alloy cladding and the steel core particles.

4. The shot material according to claim 1 or 2, wherein said shot material contains 3 to 80% by weight of iron.

5. The shot material according to claim 1 or 2, wherein the shot particles have an average diameter of 100 to 600 μm.

6. A high corrosion resistant coating having a thickness of 2 to 15 μm formed on a metal material surface by impacting the metal material surface with the shot material according to any of claim 1, said high corrosion resistant coating comprising 1 to 5% by weight of aluminum, 3 to 15% by weight of magnesium, up to 20% by weight of iron, and the balance of zinc and unavoidable impurities.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 55119101 A **[0006]**
- JP 56093801 A **[0006]**
- JP 57110601 A **[0006]**
- JP 56045372 A **[0006]**
- JP 62140768 A **[0006]**