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(54) **Aluminum-zinc alloy composition comprising spangle for hot-dipping steel product, method and product obtainable thereof**

Aluminium-Zinklegierungs-Zusammensetzung mit Paillette zur Schmelztauchbeschichtung von Stahlprodukten sowie zugehöriges Verfahren und hierdurch erhaltenes Produkt

Composition d'un alliage à base d'aluminium et de zinc comprenant des paillettes pour galvaniser des pièces en acier, méthode et produit ainsi obtenu

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(56) References cited:
WO-A-01/27343

- **PATENT ABSTRACTS OF JAPAN vol. 014, no. 377 (C-0748), 15 August 1990 (1990-08-15) & JP 02 138451 A (SUMITOMO METAL IND LTD), 28 May 1990 (1990-05-28)**

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Description

[0001] The present invention is directed to a coating composition, a coated steel product, and a method of making, and in particular, to an aluminum-zinc coating composition employing effective amounts of a particulate compound constituent to enhance the uniformity of the appearance of the unpainted and painted sheet, reduce the visible spangle size, and enhance tension bend rust strain performance.

[0002] The coating of steel components with aluminum-based coating alloys, commonly referred to a hot dip coating, is well known in the prior art. One particular type of coating is trademarked as Galvalume®, which is owned by BIEC International, Inc., and is representative of an aluminum-zinc coating alloy.

[0003] These materials are advantageous as building materials, particularly wall and roof construction due to their corrosion resistance, durability, heat reflection, and paintability. Typically, these materials are manufactured by passing a steel product such as a sheet or plate through a bath of a melted alloy coating composition comprising aluminum, zinc, and silicon. The amount of coating applied to the steel products is controlled by wiping, and then the products are cooled. One characteristic of the coating applied to the steel product is its grain size or spangle facet size.

[0004] U.S. Patent Nos. 3,343,930 to Borzillo et al., 5,049,202 to Willis et al. and 5,789,089 to Maki et al. disclose methods and techniques for the manufacture of steel sheets coated with these aluminum-zinc alloys. The three references are herein incorporated by reference in their entirety.

[0005] European Patent Application No. 0 905270 A2 to Komatsu et al. discloses another coating process utilizing zinc, aluminum, and magnesium. This application is directed at solving the corrosion problems associated with baths containing magnesium as an alloying element. Further, it is disclosed that the undesirable stripe pattern occurring in magnesium-containing baths does not occur in baths without,magnesium.

[0006] United States Patent No. 5,571,566 to Cho discloses another method of manufacturing coated steel sheet using an aluminum-zinc-silicon alloy. The object of the Cho patent is to provide a more efficient production method for manufacturing coated steel sheet. Cho meets this object by uniformly minimizing the size of spangles by introducing a large number of spangle particles into the coating, which limits subsequent growth of the spangles because these particles interfere with their respective growth resulting in a smaller spangle facet size. The seed effect is achieved by using titanium as part of the molten coating composition.

[0007] A similar disclosure with respect to the use of titanium in coating baths to minimize spangle facet size is disclosed in an article entitled "Minimization of Galvalume Spangle facet size By Titanium Addition To Coating Bath", by Cho, presented for the INTERZAC 94 Conference in Canada in 1994. In this article, the author indicates that elements such as titanium, boron, and chromium produce finer spangles in a Galvalume coating, such a disclosure consisted with the disclosure of the Cho patent.

[0008] Notwithstanding the improvements suggested by Cho, presently used coated steel products still have disadvantages. One disadvantage is that, when the coated steel product,is to be painted, a temper rolling is required to flatten the product in preparation for painting. Another problem is cracking when the product is a sheet and is bent. When. this sheet product is bent, the coating can crack, the crack exposing the steel to the environment and premature corrosion. With presently available coated steel sheets, large cracks can form, thereby compromising the corrosion resistance of the sheet product.

[0009] In light of the deficiencies in the prior art, a need has developed to provide an aluminum-zinc coated steel product with reduced and uniform spangle facet size, and improved painted surface appearance.

[0010] Accordingly it is the object of the present invention to provide a method of coating a steel product, an aluminum-zinc steel product coating and a coated steel article providing a reduced and uniform spangle facet size.

[0011] According to the present invention this object is solved by a method according to claim 1. It has been found out, that by making additions of between about 0.0008 to less than 0.001 % by weight, in particular less than 0.00095 % by weight boride particles to the bath a consistent spangle facet size of between about 400 to 500 microns (measured using the mean intercept length method described in ASTM E112) can be obtained. Producers and customers consider such controlled spangle size products superior in visual appearance as compared to conventional spangle aluminum-zinc coated products where boride additions fall outside the specified range.

[0012] The constituent can be prepared in various ways as part of the modification step, e.g., as part of a precursor or master alloy ingot or bath containing principally aluminum, the master alloy then added to an aluminum-zinc bath in the necessary proportions to arrive at a final bath composition suitable for coating and providing the benefits of the invention as a result of the modifier constituent. The constituent can be added to the master alloy as particulate compounds or can be formed in-situ in the master alloy to add to the actual coating bath.

[0013] More particularly, the composition of the coating bath can be modified by: (1) directly adding the particles (as a powder) to the coating bath or a pre-melt pot which feeds the coating bath; (2) adding an ingot than contains the required particles; the ingot may be aluminum with particles, zinc with particles, a zinc-aluminum alloy with particles, etc.; the ingot may be added to a main coating pot or a pre-melt pot; (3) adding molten bath containing the required particles, wherein the liquid may be aluminum with particles, zinc with particles, a zinc-aluminum alloy with particles, etc.; (4) in-situ reaction in

the main pot or pre-melt pot, for example by the reaction of elemental species, such as titanium and boron in an aluminum feed melt, or the reaction of salts on the feed melt pot to produce particles.

[0014] The particle size of the constituent in the coating bath can vary but preferably ranges from about 0.01 and 25 microns.

[0015] The invention also provides a coated steel article employing a coating containing the particulate compound constituent as well as the coating composition as applied to the steel product. The product is preferably a steel sheet or plate for construction purposes.

[0016] The present invention advances the art of hot dipping or coating steel products, particularly plate and sheet products, using an aluminum-zinc molten alloy bath, e.g., a Galvalume bath. According to the invention, the coating bath is modified with particulate compound constituents to reduce the spangle facet size of the coated steel product and create a uniform visible spangle size. The invention allows for the production of an aluminum-zinc alloy coating that has uniform appearance across the width of a shett, along the length of a coil of sheet, and from coil to coil. With the addition of the particulate constituents, improvements may also be realized in the performance of the coated steel product in terms of tension bend rust staining. Tension bend rust staining is a discrete pattern of cosmetic red rust running along the rib of a prepainted, roll formed, building panel caused by cracking of the metallic coating and paint.

[0017] The surface of the coated steel product also yields a painted appearance that is superior to conventional Galvalume product. This is believed to allow for the production of smooth coated steel sheet product without the need for temper rolling. Eliminating the extra processing step of temper rolling also reduces energy consumption, eliminates possible waste streams associated with temper rolling, and simplifies the production process.

[0018] When coating steel products with an aluminum-zinc coating bath, the processing steps of forming the bath to the desired composition and passing the steel product to be coated through the bath are well-known. As a result, a further description of the prior art methods and apparatus to accomplish this conventional coating is not deemed necessary for understanding of the invention.

[0019] The composition of the prior art aluminum-zinc alloy baths is well-known as discussed in the Borzillo et al. and Cho patents, and the Cho publication noted above. Generally, this bath comprises about 55% aluminum, a level of silicon, generally about 1.6% by weight, and the balance zinc. Other variations in the composition are within the scope of the invention as would be conventionally known to those of ordinary skill in the art.

[0020] According to the invention, the aluminum-zinc molten bath comprising about 55% aluminum is modified with a particulate compound constituent to achieve improvements in terms of reduced spangle facet size, improved surface finish, reduction in crack size, and potential improvements in tension bend rust staining. The particulate compound constituent is a boride.

[0021] The particle size of the particulate constituent should range between about 0.01 and about 25 microns.

[0022] The molten bath used to coat this steel product containing the modified aluminum-zinc alloy composition can be prepared in a number of ways. In one method, a master alloy of aluminum is prepared and is modified with the particulate compound constituent boride. This bath is then added to an aluminum-zinc coating bath, the proportions of the two baths calculated to arrive at a target bath composition containing the effective amount of the boride. The modified alloy bath would still track the conventional weight percentages of the aluminum, zinc and silicon for these types of coating baths, e.g., about 55% aluminum, 1-2% silicon, the balance zinc, since the effective amount of the particular compound constituent is a relatively low weight percentage of the overall bath amount. Methods for making master alloys are taught in United States Patent Nos. 5,415,708 to Young et al. and 3,785, 807, both herein incorporated by reference in their entirety.

[0023] Secondly, the master alloy containing the particles could be added to the coating bath in the form of a solid ingot. The ingot may be primarily Al, primarily Zn, or an alloy containing Zn, Al, and/or Si along with the spangle refining particles.

[0024] Alternatively, the particulate compound constituents could be added directly to the aluminum-zinc bath prior to coating a steel product.

[0025] When using aluminum boride as a bath modifier, boron particles are added to an aluminum master alloy to facilitate incorporation of the particles into the melt and improve even distribution of the particles throughout the melt. Alternatively, aluminum boride particles can be added to the aluminum-zinc bath in the appropriate amounts.

[0026] When producing an aluminum master alloy with the particulate compound constituents such as titanium boride, some excess titanium may exist in the bath. This excess may range from 0.01% to 10% relative to the total mass of boron added. In terms of the stoichiometry, titanium additions in excess of one mole of titanium for 2 moles of boron may range from 0.002 to 4.5 excess moles. It is not believed that the excess titanium, whether present through the use of titanium boride or another titanium-containing compound such as titanium carbide or the like, is necessary to obtain the spangle refinement associated with the invention.

[0027] In preparing the alloy bath for coating, the particulate compound constituent can be introduced as a powder or formed in the bath itself. For example, titanium boride powders could be added to an aluminum bath in the appropriate weight percentages. Alternatively, elemental titanium and boron could be added to an aluminum melt and heated at sufficiently high temperatures to form titanium boride particles therein. It is preferred that the compound particles be added to the master alloy

since this processing is much more effective in terms of energy consumption. Similar processing techniques can be employed for the carbides and aluminides.

[0028] It is believed that the presence of titanium and boron in a coating bath alone will not produce the grain refining benefits demonstrated above as compared to adding a compound particulate such as titanium boride. It has been reported that in aluminum casting, the separate addition of titanium and boron to an aluminum melt did not produce titanium boride particles when added at temperatures below 1000°C (1832°F). Instead, the titanium reacted with the aluminum to form $TiAl_3$ particles. Since the coating process is generally conducted at much lower temperatures, i.e., 593°C (1100°F), adding titanium and boron in elemental form to an Al-Zn coating bath would produce similar behavior. In addition, the kinetics of titanium and boron dissolution will be very slow at the low temperatures associated with the coating method. Thus, when forming the titanium boride in the bath itself, it is necessary to go beyond conventional melting parameters to achieve the necessary particulate for use in the invention.

[0029] The inventive coating method produces a coated article, wherein the coating has a coating composition including the added particulate compound constituent described above. The coated product can then be painted as is known in the art,without the need for temper rolling or skin passing.

[0030] A more uniform, consistent spangle size may be produced by adding a small amount of TiB2 grain refiner to the hot-dip coating bath. By making bath additions of between about 0.0008 - 0.0012% by weight boron in the form of boride particles to the bath we are able to produce a consistent spangle facet size of between about 400 to 500 microns (measured using the mean intercept length method described in ASTM E112). Producers and customers consider such controlled spangle size products superior in visual appearance as compared to conventional spangle aluminum-zinc coated products where boride additions fall outside the specified range.

Claims

1. Method of coating a steel product using a molten aluminum-zinc alloy bath comprising about 55% Al and zinc, the improvement comprising modifying the composition of the aluminum-zinc alloy by adding an effective amount of one or more of a particulate compound constituent that produces a coated spangle size on a substrate of between about 400 to 500 microns, said grain refining particulate compound selected from the group consisting of boride compounds in an amount between about 0.0008 to less than 0.001 % by weight, in particular less than 0.00095 % by weight, and having one of titanium and aluminum.

2. The method of claim 1, wherein the particulate compound constitute is one of TiB_2, AlB_2, and AlB_{12}.

3. The method of claim 1 or 2, wherein a particle size of the particulate compound constituent ranges between about 0.01 microns and about 25 microns.

4. The method of any proceeding claim, further comprising the step of making a master alloy bath of aluminum and adding an amount of the particulate compound constituents thereto, and then adding the master alloy bath to an aluminum-zinc coating bath in proportions to attain the effective amount of the particulate compound constituent.

5. The method of any proceeding claim, wherein the particulate compound constituent is the boride compound and the amount of the particulate compound constituent in the alloy bath ranges between about 0.0008 and less than 0.001 % by weight, in particular less than 0.00095 % by weight of boron.

6. The method of any proceeding claim, further comprising painting the coated steel product without subjecting the coated steel product to skin passing.

7. Aluminum-zinc steel product coating composition comprising about 55% Al and zinc capable of producing a coated steel substrate with a coating spangle size between about 400 to 500 microns, the improvement comprising an aluminum-zinc alloy including an effective amount of one or more of a particulate compound constituent selected from the group consisting of boride compounds in an amount between about 0.0008 less than 0.001 % by weight, in particular less than 0.00095 % by weight, and having one of titanium and aluminum.

8. The composition of claim 7, wherein the particulate compound constituent is one of TiB_2, AlB_2, and AlB_{12}.

9. The composition of claim 7 or 8, wherein a particle size of the particulate compound constituent in the coating ranges from between about 0.01 microns and about 25 microns.

10. The composition of any of claims 7 to 9, wherein the particulate compound constituent is the boride compound and the amount of the particulate compound constituent in the alloy bath ranges between about 0.0008 to less than 0.001 % by weight, in particular less than 0.00095 % by weight of boron.

11. Coated steel article comprising a steel substrate and an aluminum-zinc coating thereon according to any of claims 7 to 10.

12. The article of claim 11, further comprising a painted surface on the coated steel product.

Patentansprüche

1. Verfahren für die Beschichtung eines Stahlprodukts, bei dem ein geschmolzenes Aluminium-Zink-Legierungsbad, das ungefähr 55 % Al und Zink enthält, verwendet wird, wobei die Verbesserung umfaßt, dass die Zusammensetzung der Aluminium-Zink-Legierung durch Hinzufügung einer effektiven Menge eines oder mehrerer partikelförmiger Bestandteile modifiziert wird, der eine beschichtete Flitterpartikelgröße auf einem Substrat zwischen ungefähr 400 bis 500 Mikrometer ergibt, wobei die kornverfeinernde Partikelverbindung aus der Gruppe bestehend aus Boridverbindungen in einer Menge zwischen ungefähr 0,0008 bis weniger als 0,001 Gew. %, insbesondere weniger als 0,00095 Gew.% ausgewählt ist, und Titan oder Aluminium aufweist.

2. Verfahren nach Anspruch 1, bei dem der partikelförmige Bestandteil einer von TiB_2, AlB_2 und AlB_{12} ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem die Partikelgröße des partikelförmigen Bestandteils in dem Bereich zwischen ungefähr 0,01 Mikrometer und ungefähr 25 Mikrometer liegt.

4. Verfahren nach einem der vorherigen Ansprüche, das weiterhin den Schritt umfaßt, bei dem ein Vorlegierungsbad aus Aluminium hergestellt und eine Menge der partikelförmigen Bestandteile dazu hinzugefügt wird, und dann das vorlegierungsbad zu einem Aluminium-Zink-Beschichtungsbad in einem Verhältnis hinzugegeben wird, um die effektive Menge an partikelförmigen Bestandteilen zu erhalten.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem der partikelförmige Bestandteil eine Boridverbindung ist und die Menge an partikelförmigem Bestandteil in dem Legierungsbad in dem Bereich zwischen ungefähr 0,0008 und weniger als 0,001 Gew.%, insbesondere weniger als 0,00095 Gew.% Bor liegt.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem weiterhin das beschichtete Stahlprodukt angestrichen wird, ohne dass das beschichtete Stahlprodukt Nachwalzen unterworfen wird.

7. Aluminium- Zink- Stahlproduktbeschichtungs- Zusammensetzung, die ungefähr 55 % Al und Zink beinhaltet und dafür geeignet ist, ein beschichtetes Stahlsubstrat mit einer Beschichtungs-Flitterpartikelgröße zwischen 400 bis 500 Mikrometer zu erzeugen, wobei die Verbesserung eine Aluminium-Zink-Legierung umfasst, die eine effektive Menge eines oder mehrerer partikelförmiger Bestandteile, ausgewählt aus der Gruppe bestehend aus Boridverbindungen in einer Menge zwischen ungefähr 0,0008 und weniger als 0,001 Gew.%, insbesondere weniger als 0,00095 Gew.% beinhaltet und Titan oder Aluminium aufweist.

8. Zusammensetzung nach Anspruch 7, bei dem der partikelförmige Bestandteil einer von TiB_2, AlB_2 und AlB_{12} ist.

9. Zusammensetzung nach Anspruch 7 oder 8, bei dem eine Partikelgröße des partikelförmigen Bestandteils in der Beschichtung in dem Bereich zwischen ungefähr 0,01 Mikrometer und ungefähr 25 Mikrometer liegt.

10. Zusammensetzung nach einem der Ansprüche 7 bis 9, bei dem der partikelförmige Bestandteil die Boridverbindung ist und die Menge des partikelförmigen Bestandteils in dem Legierungsbad in dem Bereich zwischen ungefähr 0,0008 und weniger als 0,001 Gew.%, insbesondere weniger als 0,00095 Gew.% Bor liegt.

11. Beschichteter Stahlartikel umfassend ein Stahlsubstrat und einer darauf angeordneten Aluminium-ZinkBeschichtung gemäß einem der Ansprüche 7 bis 10.

12. Artikel nach Anspruch 11, der weiterhin eine angestrichene Oberfläche auf dem beschichteten Stahlprodukt aufweist.

Revendications

1. Procédé pour recouvrir une pièce en acier en utilisant un bain d'alliage à base d'aluminium et de zinc fondu comprenant environ 55% Al et zinc, l'amélioration comprenant la modification de la composition de l'alliage à base d'aluminium et de zinc en ajoutant une quantité effective de l'un ou plusieurs constituants composés de macroparticules qui produit une grandeur de paillettes de recouvrement sur un substrat entre environ 400 à 500 microns, ledit composé de macroparticules améliorant le grain choisi du groupe consistant en composés de borure dans une quantité entre environ 0,0008 à moins de 0,001 % en poids, en particulier moins de 0,00095 % en poids, et ayant l'un de titane et d'aluminium.

2. Procédé selon la revendication 1, où le constituant composé de macroparticules est l'un de TiB_2, AlB_2, et AlB_{12} .

3. Procédé selon la revendication 1 ou 2, où une gran-

deur de macroparticules du constituant composé de macroparticules est située dans la rangée entre environ 0,01 microns et environ 25 microns.

4. Procédé selon l'une quelconque des revendications antérieures, comprenant de plus l'étape de faire un bain d'alliage intermédiaire à base d'aluminium et en ajoutant-y une quantité des constituants composés de macroparticules, et puis en ajoutant le bain d'alliage intermédiaire à un bain de recouvrement à base d'aluminium et de zinc en proportions pour atteindre la quantité effective du constituant composé de macroparticules.

5. Procédé selon l'une quelconque des revendications antérieures, où le constituant composé de macroparticules est un composé de borure et la quantité du constituant composé de macroparticules dans le bain d'alliage est située dans la rangée entre environ 0,0008 et moins de 0,001% en poids, en particulier moins de 0,00095 % en poids de bore.

6. Procédé selon l'une quelconque des revendications antérieures, comprenant de plus la peinture de la pièce en acier couverte sans soumettre la pièce en acier couverte pour passer la couche de recouvrement.

7. Composition de recouvrement la pièce en acier à base d'aluminium et de zinc comprenant environ 55% Al et zinc capable de produire un substrat en acier couvert avec une grandeur de paillettes de recouvrement entre environ 400 à 500 microns, l'amélioration comprenant un alliage à base d'aluminium et de zinc incluant une quantité effective de l'un ou plusieurs des constituants composés de macroparticules choisis d'un groupe consistant en composés de borure dans une quantité entre environ 0,0008 à moins de 0,001 en poids, en particulier moins de 0,00095 % en poids, et ayant l'un de titane et d'aluminium.

8. Composition selon la revendication 7, où le constituant composé de macroparticules est l'un de TiB_2, AlB_2, et AlB_{12}.

9. Composition selon la revendication 7 ou 8, où une grandeur de macroparticule du constituant composé de macroparticules dans la couche de recouvrement est située dans la rangée entre environ 0,01 microns et environ 25 microns.

10. Composition selon l'une quelconque des revendications 7 à 9, où le constituant composé de macroparticules est le composé de borure et la quantité du constituant composé de macroparticules dans le bain d'alliage est située dans la rangée entre environ 0,008 à moins de 0,001 % en poids, en particulier moins de 0,00095 % en poids de bore.

11. Article en acier couvert comprenant un substrat en acier et une couche de recouvrement à base d'aluminium et de zinc là-dessus selon l'une quelconque des revendications 7 à 10.

12. Article selon la revendication 11, comprenant de plus une surface peinte sur la pièce en acier couverte.