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(54) **POWDER MIXTURE COMPOSITION FOR THERMODIFFUSION GALVANIZATION OF ARTICLES MADE FROM ALUMINIUM ALLOYS, AND METHOD FOR THERMODIFFUSION GALVANIZATION OF ARTICLES MADE FROM ALUMINIUM ALLOYS**

(57) The present invention relates to thermochemical treatment by thermal-diffusion galvanizing of articles made of aluminum alloys. The powdered mixture composition comprises powdered zinc, an inert filler such as silicon, aluminum, iron, calcium oxides with clay and sand impurities, and an activating agent composed of a mixture of components, in % by mass: sodium fluoride 12-15, lithium chloride 20-25, ammonium chloride 10-15, zinc chloride 12-14, potassium chloride to balance, with the following proportion of the composition components, in % by mass:

| | |
|---|---|
| Inert filler | 55 - 60 |
| Activating agent | 3 - 5 |
| Powdered zinc | to balance. |

The process comprises pretreatment of the article surface with shots having the granularity of 0.3-0.4 mm and made of austenitic or austenitic-ferritic steel, loading the articles and a saturating mixture into a container preheated to 100-120°C, loading the container into a furnace preheated to 100-120°C, treating the articles at a temperature of 420-430°C for 1 hour at a container constant rotation rate of 1-2 rpm and at a constant pressure of 1.8-2.2 atm. inside the container, cooling the furnace to 100-120 °C, removing the articles from the container, cooling the articles in water and treating them with ceramic chips together with a passivating solution in a vibration stand, the claimed composition being used as the saturating powdered mixture.

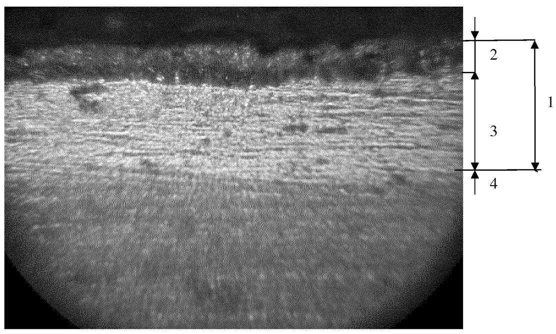


Fig. 1



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## Description

Field of the invention

**[0001]** The present invention relates to a process for thermal-diffusion galvanizing of articles made of aluminum alloys and can find application in all the industries: machine building, automobile manufacture, ship building and aircraft construction, chemical and civil engineering, etc., where pieces, blocks, assemblies of mechanisms and articles made of aluminum alloys work in corrosive media and undergo corrosive damages of various nature.

Background of the invention

**[0002]** Amongst numerous processes for applying protective coatings onto steel and cast iron parts in order to improve their rustproof properties, the thermal-diffusion galvanizing with powdered mixtures holds a particular place.

**[0003]** The main material of the powdered mixtures for thermal-diffusion galvanizing is powdered zinc and an activating agent (such as ammonium chloride).

**[0004]** A number of Russian and foreign papers are known, aimed to mprove powdered mixtures and enabling to improve the quality (rustproof properties, thickness and uniformity) of zing plating on iron-carbon steels and alloys.

**[0005]** It is necessary to point out that heretofore, no success was achieved by any company in the attempts to obtain high-performance rustproof surface layers by thermal-diffusion galvanizing on aluminum alloys. At best, zinc-containing coatings with uneven thickness (5 to 15 $\mu$m) were formed on the article surface, characterized by their high accessible porosity, exceeding 80%. In this case, with its high porosity, the coating practically did not have any adhesion to the underlying material, yet in some places the zinc was only deposited onto the surface without any diffusive saturation of the aluminum alloy.

**[0006]** This fact can be explained by the presence of some original high-strength film of oxide on the surface of articles of aluminum alloys, prohibiting any contact interaction of powdered zinc particles and of zinc gaseous phase being formed at the zinc plating temperature directly with the aluminum alloy surface, which is the main reason of the lack of zinc penetration into the crystal lattice of aluminum alloy. A particular difficulty resides in the fact that after mechanical or chemical elimination of the film of oxide, the same is recreated some seconds later. This procedure is greatly intensified at high temperatures, including during the thermal-diffusion galvanizing.

**[0007]** The above mentioned explains the absence of any scientific publications or substantiated practical recommendations on the subject.

**[0008]** Another important factor restraining works of thermal-diffusion galvanizing of aluminum alloys is based on the theoretical principles of the electrochemical corrosion of metals and alloys having different electrolytic potentials. For example, while analyzing the scale of standard electrolytic potentials of metals [N.D. Tomashov, G.P. Tchernov. Corrosion and rustproof alloys. - M.: Metallurgya, 1973, p.10-11], one can come to the conclusion of unsuitability to provide rust protection of aluminum alloys with zinc coatings. Nevertheless, we have carried out multiple combined studies to demonstrate that the protective coatings formed at the thermal-diffusion galvanizing are characterized by practically equal electrolytic potentials to those of aluminum alloy due to the formation of complex chemical compounds of aluminum with zinc in the same, these compounds showing improved rustproof properties compared to aluminum alloys, perhaps as a result of a stronger effect of the cathodic alloying. Simultaneously, a strong passivating film is formed on the surface that additionally improves the rustproof properties of articles in aluminum alloys.

**[0009]** There are known compositions of powdered mixtures obtained by mixing powdered zinc or zinc dust in amounts of up to 75 % by mass, an inert filler such as alumina in the amount of up to 23 % by mass, and an activating agent such as ammonium chloride in the amount of up to 2 % by mass of the total composition mass. [Thermo-chemical processing of metals and alloys/ Edited by A.S. Liakhovich. - M.: Metallurgya, 1981]. The above given galvanizing composition does not provide the preparation of an impermeable uniform coating with high indices of corrosive resistance.

**[0010]** The document SU 1571103, published on 15.06.1990, discloses a composition for thermal-diffusion galvanizing of steel articles, comprising zinc, aluminum and alumina to which nitrilotrimethylphosphonic acid is added to intensify the process, to improve effectiveness by the increase of the number of cycles of use.

**[0011]** There is a known composition for providing a diffusion coating, comprising a zinc-containing substance, aluminum, ammonium chloride and an inert filler, to which magnesium and carnallite are added to improve the coating corrosive resistance and to reduce generation of gas, and hard zinc is added as a zinc-containing substance [document SU 1521790, published on 15.11.1989].

**[0012]** There is a known composition of a powdered mixture for thermal-diffusion galvanizing, comprising alumina under the form of synthetic corundum or silicon oxide as an inert filler with granularity of no more than 0.2 mm in an amount of 50.0-99.0 % by mass, powdered zinc containing at least 90.0 % by mass of fractions sized up to 0.16 mm in an amount of 0.6 - 40.0 % by mass, and ammonium chloride in an amount of 0.4 - 10 % by mass being used as the activating agent [patent RU 2180018, published on 27.02.2002].

**[0013]** A drawback of the above mentioned galvanizing compositions resides in the possibility to use them only for rust-preventing processing of articles of carbon and low-alloyed steels, including a high-strength steel, of cast iron, of copper. These mixtures cannot be used for rust-preventing processing of articles of aluminum alloys due to the lack of chemical activity of the activating agent and the inert filler used, or to their insufficient chemical activity, the presence of which does not enable to carry out the process of destroying the film of oxide, nor the subsequent protection of the surface of aluminum alloy articles against its formation, in particular under high-temperature processing, which is in the present case a necessary condition for the galvanizing process course.

**[0014]** It is necessary to note that the compositions of powdered mixtures disclosed by the Author's certificates SU 1571103 and SU 1521790, are rather complicated and labor-consuming in manufacture.

**[0015]** There is a known process for thermal-diffusion galvanizing articles of carbon low-alloy steel, including high-resistance steels, as well as of cast iron and of copper, with the use of powdered mixtures composed of powdered zinc and of an inert filler, such as quartz sand [GOST R 51163-96 «Thermal-diffusion zinc coatings on fastening and other small parts»].

**[0016]** There is a known process for thermal-diffusion galvanizing steel wire at a temperature range of 400-600°C, comprising placing the wire into a container followed by loading the same into a furnace. The process is carried out under the conditions of a graded, mostly three-stage temperature lowering within said interval, the container being under some positive pressure. Use is made of three furnaces heated to the respective temperatures $T_1$=540°C, $T_2$=520°C, $T_3$=500°C. The positive pressure of 0.2 - 0.6 atm. is kept inside the container [RU 2195512, published on 27.12.2002].

**[0017]** There is a known process of thermal-diffusion galvanizing [RU 2147046, published on 17.08.1998] that lies in the fact that steel parts and some saturating mixture composed of an inert material and of powdered zinc are loaded into an airtight rotating reactor, heated and kept at a temperature of 390-430°C under an inert atmosphere. Highly dispersed powdered zinc with the fraction size 4-60 $\mu$m is loaded in an amount of 0.10-0.20 kg per 1 $m^2$ of steel parts surface area. An inert carrier is loaded into the reactor in an amount of 40 to 100 % by mass of the parts weight. The inert carrier is used with the fraction size of 60-140 $\mu$m.

**[0018]** It is necessary to note that the economical effect and the waste-free character of this process, while using a standard technology of thermal-diffusion galvanizing, are obtained only as a result of modifying the amount and the fraction size of the powdered zinc and those of the inert filler.

**[0019]** A drawback of these known processes resides in the possibility to use them to provide high-performance zinc diffusion coatings only on articles of steel, cast iron, copper. These processes cannot be used in antirust protection of articles of aluminum alloys since in this case, zinc coatings are formed with uneven thickness, they are not continuous, rough, porous and presenting an inadmissible number of various defects.

**[0020]** The closest composition and process for galvanizing articles of aluminum alloys are disclosed in the China patent No 102002665, published on 03.10.2012. The disclosed composition comprises in % by weight: powdered zinc 14.9 - 84.5, inert powdered metal oxide (mixture of $SiO_2$ and $AlO_3$, in an amount of 14.5 - 84.9), an activating component (ammonium chloride or ammonium nitrate) in an amount of 0.1-0.5 and an auxiliary component ($NH_4NH_2SO_3$) in an amount of 0.1-0.5, the process of galvanizing comprising loading articles of aluminum alloys and said saturating powdered composition into an airtight rotating container, galvanizing at a temperature of 400$\pm$10°C for 60-180 minutes, cooling to ambient temperature and passivating.

**[0021]** A drawback of this composition lies in the fact that it uses, at different percentages, a powdered mixture composition with the traditionally used, for thermal-diffusion galvanizing iron-carbon steels and alloys, cast iron and copper, such components as the activating agent (ammonium chloride) and the inert filler (silicon oxide or alumina), see, for example, the patent [RU 2180018, 2012].

**[0022]** However, the only use of the mentioned components in the activating agent and the inert filler composition, without their determined percentage and ratio, does not provide for the necessary chemical activity of the powdered mixture to carry out the process of zinc saturation for the aluminum alloy surface in the galvanizing process.

**[0023]** It is necessary to note that introducing the additional component $NH_4NH_2SO_3$ into the powdered mixture increases very little the powdered mixture activity but mainly serves to increase the number of its reuses thanks to a lower nodulizing process, to its reduced purification required and to the provided prevention of its eventual inflammation.

**[0024]** This process comprises conventional galvanizing operations that cannot provide for high-performance coatings on articles of aluminum alloys, such as: placing prepared aluminum alloy articles into an airtight steel container, heating the same to a temperature of 400 $\pm$10 °C for 60-180 minutes and cooling to ambient temperature.

Summary of the invention

**[0025]** It is an object of the present invention to provide a powdered mixture composition for thermo-diffusion galvanizing articles of aluminum alloys, and a process for thermal-diffusion galvanizing articles of aluminum alloys, in order to obtain a high-performance rustproof diffusion zinc coating on articles of a wide range of aluminum alloys and to lower the process cost due to a lower cost of the powdered mixture, i.e. reducing the amount of costly components such as powdered zinc and the activating agent.

**[0026]** It is necessary to note that the process of the present invention can be used as well for thermal-diffusion galvanizing steel, cast iron and copper articles in order to improve their corrosion resistance.

**[0027]** The technical result of the present invention application resides in the fact that using this powdered mixture for thermal-diffusion galvanizing and the process for thermal-diffusion galvanizing mainly for articles of aluminum alloys enable to obtain diffusion zinc coatings, with even thickness (60-65 μm), that are continuous, faultless, rustproof (the corrosion resistance in a chamber containing a neutral salt fog is not less than 720 hours) on articles of a wide range of aluminum alloys, provides for a lower cost of the process due to a lower cost of the used powdered mixture, as a result of reducing the amount of costly components such as powdered zinc and the activating agent.

**[0028]** Said technical result is obtained by the use of a powdered mixture composition for thermal-diffusion galvanizing articles of aluminum alloys, comprising powdered zinc, an inert filler and an activating agent composed of a mixture of the following components, in % by mass: sodium fluoride 12-15, lithium chloride 20-25, ammonium chloride 10-15, zinc chloride 12-14, potassium chloride to balance, with the following component ratio, in % by mass:

| | |
|---|---|
| Inert filler | 55-60 |
| Activating agent | 3-5 |
| Powdered zinc | to balance. |

**[0029]** As the powdered zinc, the PTsR-1 powder is used (powdered zinc obtained by pulverizing molten zinc with an inert gas), produced on an industrial scale and having the composition as follows, in % by mass: fractions smaller than 63 μm, at least 50%; fractions of 63-160 μm, not more than 40.0; fractions bigger than 160 μm, not more than 10.0. The metal zinc content is at least 98 % by mass according to the norm GOST 12601-76.

**[0030]** The PTsR-1 powdered zinc according to GOST 12601-76 is widely used for thermal-diffusion galvanizing iron-carbon steels and alloys, cast iron and copper in the composition of powdered mixtures comprising, when necessary, various activating agents and inert fillers.

**[0031]** As the inert filler, use is made of a high-strength, porous, high-melting material of organogenic origin composed of silicon, aluminum, iron, calcium oxides as well as of clay and sand impurities, such as diatomite, opoka, tripolite and others, with the density of 0.7 to 1.0 g/cm$^3$, that are an adsorbent, a catalyst and ballast. In this case, at least 80 % by mass of inert filler are used with the fraction size of 0.8 to 1.2 mm, and up to 20.0 % by mass of inert filler can be used with the fraction size lower than 0.8 mm.

**[0032]** Multiple studies showed that the inert filler according to the present invention, compared to known inert fillers, such as alumina (synthetic corundum) or silicon oxide used in the closest prior art are characterized by increased adsorbing and catalytic properties, which enables to significantly intensify the process of zinc saturation for the crystal lattice of aluminum alloys. Adsorbing capacity of the inert filler is provided due to its low density and high porosity. Just at such a density, it is possible to provide the needed saturation of the inert filler with zinc from the gaseous and solid phases. The high strength and selected particle size enable the reliable disintegration of the oxide film on the surface of aluminum alloys as well as a double effect during the thermal-diffusion galvanizing, such as: the thermo-chemical one (saturation of the aluminum alloy surface from the gaseous phase) and the mechanical one from the solid phase (at the direct contact of the powdered zinc and of the inert filler with the aluminum alloy surface).

**[0033]** As the activating agent, use is made of a mixture composed of the following components, in % by mass: sodium fluoride NaF 12-15, lithium chloride LiCl 20-25, ammonium chloride $NH_4Cl$ 12-15, zinc chloride $ZnCl_2$ 12-14, potassium chloride KCl to balance.

**[0034]** The selection of activating agent components and their percentage are provided with the multiple experiments carried out in thermal-diffusion galvanizing aluminum alloys in order to obtain high-performance, maximum-thickness rustproof coatings: potassium chloride KCl and sodium fluoride NaF increase the thermal-diffusion activity of zinc, enable dissolving aluminum and zinc oxides; lithium chloride LiCl promotes the diffusion process acceleration thanks to the increased thermodynamic activity of zinc, increases the density and the corrosion resistance of zinc coatings, dissolves aluminum and zinc oxides; ammonium chloride $NH_4Cl$ promotes formation of a protective atmosphere in the furnace, promotes the galvanizing reaction acceleration due to the active mixing of reacting materials, to the density increase of the zinc coating; zinc chloride $ZnCl_2$ promotes the zinc diffusion process acceleration due to the increase of its thermodynamic activity, to the dissolution of aluminum and zinc oxides, to the reduction of zinc.

**[0035]** The content of chemically active components in the activating agent provides for reliable protection of the aluminum alloy surface against the formation of an oxide film at galvanizing high temperatures, enabling by the fact, together with the inert filler of the present invention, the formation of high-performance, rustproof zinc coatings.

**[0036]** At a higher content of inert filler and of activating agent, due to an insufficient content of powdered zinc, no necessary thickness of the diffusion zinc layer is formed, and consequently no required corrosion resistance of the zinc coating is provided.

**[0037]** The technical result of the present invention is provided by a process of thermal-diffusion galvanizing articles of aluminum alloys, comprising pretreatment of the surface of the articles with shots of austenitic or austenitic-ferritic steels, having the fineness of 0.3-0.4 mm, loading the articles and the saturating powdered mixture into a container previously heated to 100-120°C, placing the container into a furnace previously heated to 100-120°C, treating the articles at the temperature of 420-430°C for 1 hour at a container constant rotation rate of 1-2 rpm and at a constant pressure inside the container of 1.8-2.2 atm., cooling the furnace to 100-120 °C, removing the articles from the container, cooling the articles in water and treating them in a vibration stand with ceramic chips together with a passivating solution until the deposited powdered zinc layer is completely eliminated from the article surface, the potential difference between the aluminum alloy surface and the obtained diffusion zinc layer being determined by the condition:

$$\Delta \varphi = \varphi_{Al} - \varphi_{Zn} \rightarrow 0,$$

where $\Delta \varphi$ is the difference of electrolytic potentials (in Volts), $\varphi_{Al}$ is the electrolytic potential of the aluminum alloy, $\varphi_{Zn}$ is the electrolytic potential of the diffusion zinc layer, and as the saturating powdered mixture, a composition is used, comprising powdered zinc, an inert filler and an activating agent composed of a mixture of the following components, in % by mass: sodium fluoride 12-15, lithium chloride 20-25, ammonium chloride 10-15, zinc chloride 12-14, potassium chloride to balance, with the following component ratio, in % by mass:

| | |
|---|---|
| Inert filler | 55-60 |
| Activating agent | 3-5 |
| Powdered zinc | to balance. |

**[0038]** The constant pressure inside the container is created by active gaseous substances escaping from the saturated powdered mixture on heating.

**[0039]** The treatment of the articles in the vibration stand with ceramic chips together with the passivating solution is performed until the deposited powdered zinc layer is completely eliminated from the surface of the article.

**[0040]** The need for a preliminary treatment of the surface of aluminum alloy articles with shots of austenitic or austenitic-ferritic steels, having the fineness of 0.3-0.4 mm is conditioned by several factors. The use of shots having the fineness of 0.3-0.4 mm enables to destroy the high-strength oxide film on the articles of aluminum alloys and to form a film of oxide of austenitic or austenitic-ferritic steel that is easily disintegrated under the effect of the powdered mixture and of the active gaseous substances (volatile chemical compositions) released from the same under heating during the thermal-diffusion galvanizing. And, what is the most important, the use of the poured powdered mixture and of the active gaseous substances (volatile chemical compositions) released by the same under heating does not allow the oxide film to get rebuilt on the surface of aluminum alloy articles during the thermal-diffusion galvanizing process.

**[0041]** The use of shots having the fineness less than 0.3 mm does not enable to destroy the film of oxide on the surface of aluminum alloy articles due to the insufficiency of its mass and of the impact energy. Using shots with the fineness exceeding 0.4 mm substantially increases the surface roughness of the processed articles of aluminum alloys.

**[0042]** The need to load the articles of aluminum alloys and the saturating powdered mixture into the container previously heated to the temperature of 100-120°C is conditioned by the fact that the saturating powdered mixture is characterized by its high water-absorbing capacity. The preliminary heating of the container to said temperature enables to considerably decrease the moisture concentration in the same and, hence, in the saturated powdered mixture as well. It is necessary to note that at a higher moisture content in the saturated powdered mixture (at a temperature in the container lower than 100°C), the latter becomes lumpy, and consequently, during the thermal-diffusion galvanizing, no full contact of the saturating powdered mixture with the surface of aluminum alloy articles is provided, which will deteriorate the zinc coating quality. Preliminary heating of the container to a temperature above 120°C is not expedient from the point of view of economy or technology.

**[0043]** The need to place the container into a furnace preheated to 100-120°C is determined by the need to avoid any cooling of the container and, therefore, any possibility of moisture increase in the saturating powdered mixture. At a temperature below 100°C, the container can be cooled and, as a consequence, the moisture content in the container and in the saturating powdered mixture can increase, which leads to nodulizing of the same, and, therefore, no full contact of the saturating powdered mixture with the surface of aluminum alloy articles will be provided, which is accompanied by some decrease of the zinc coating quality.

**[0044]** Preliminary heating of the furnace to a temperature above 120°C is not expedient from the point of view of economy or technology.

**[0045]** The need to carry out the thermal-diffusion galvanizing process at a constant pressure inside the container of 1.8-2.2 atm. developed by the active gaseous substances (volatile chemical compositions) released by the saturating powdered mixture under heating is due to the fact that such a pressure allows to increase the zinc adsorption and the concentration of the active atoms of the same on the surface of aluminum alloy articles. At a pressure below 1.8 atm., no activity of the diffusion process is observed. At a pressure above 1.2 atm., the saturating mixture is nodulized, sintered and adheres to the surface of the articles of aluminum alloys, therefore, it leads to a lower quality of the zinc coating.

**[0046]** The need to cool the furnace with the processed articles of aluminum alloys to 100-120°C after finishing the thermal-diffusion galvanizing process, to remove the articles from the container and to cool them in water is conditioned by the need to clean the treated article surfaces to eliminate the residues of saturating powdered mixture adhered to the same. A lower temperature in the furnace before cooling the articles in water does not provide for a high-performance cleaning. A higher temperature in the furnace before the cooling leads to the deformation of the articles and to eventual modification of their original sizes.

**[0047]** The need to process the articles of aluminum alloys with ceramic chips together with the passivating solution in a vibration stand to provide complete elimination of the deposited zinc layer from the surface of the processed articles until fulfillment of the condition:

$\Delta\varphi = \varphi_{Al}\text{-}\varphi_{Zn} \rightarrow 0$, where $\Delta\varphi$ is the electrolytic potential (B) difference, $\varphi_{Al}$ is the electrolytic potential of the aluminum alloy (B), $\varphi_{Zn}$ is the electrolytic potential of the duffusion zinc layer (B), can be explained as follows: during the thermal-diffusion galvanizing articles of aluminum alloys, a zinc coating is formed on its surface, composed of a layer of powdered zinc deposited on the article surface and of a diffusion zinc layer, see Fig. 1. During the process of treating aluminum alloy articles with ceramic chips (in contrast to the treatment with, for example, steel or cast iron shots), no new chemical compounds are formed on their surfaces, able to modify the phase composition of the diffusion layer surface, or to deteriorate the rustproof properties of the same. The passivating solution additionally improves the rustproof properties of the diffusion layer.

**[0048]** It is necessary to note that the layer of powdered zinc deposited on the surface of aluminum alloy articles is characterized by an important potential difference compared to that of the aluminum alloy, as well as to the diffusion zinc layer. In this case, many combined studies have established that the deposited zinc layer is characterized by a higher positive value of the electrolytic potential compared to the electrolytic potential of the diffusion zinc layer and of aluminum alloy, therefore, it represents an oxidant with respect to the latter, which may have a negative effect on the rustproof properties of the article. The diffusion zinc layers formed at the thermal-diffusion galvanizing are characterized by their electrolytic potential that is practically the same as that of the aluminum alloy, it is probably due to the formation in these layers of complex chemical compounds of aluminum with zinc, characterized by higher rustproof properties compared to the aluminum alloy, therefore, the following condition is fulfilled: $\Delta\varphi = \varphi_{Al\text{-}}\ \varphi_{Zn} \rightarrow 0$.

**[0049]** At the same time, on the surface of the diffusion zinc layer, a corrosion-resisting strong film is formed due to the treatment of the article by the passivating solution.

**[0050]** It is necessary to note that precisely such needed operations of the present invention as the pretreatment of the surface of the aluminum alloy articles with shots (namely of austenitic or austenitic-ferritic steel), developing constant pressure of 1.8-2.2 atm. inside the container by the active gaseous substances released from the saturating powdered mixture under heating, as well as the subsequent treatment with ceramic chips in a vibration stand until the complete elimination of deposited powdered zinc from the surface of the articles, provide, together with the powdered mixture composition of the present invention, the formation of high-performance rustproof zinc coatings.

**[0051]** The investigations to assess the quality of the coating were carried out with prismatic specimens made of aluminum alloy AMg6 (GOST4784-74). The corrosion-resistance test was carried out in a chamber containing a neutral salt fog (norm GOST 9.308-85 "Metallic plating and nonmetallic coatings. Methods of accelerated corrosion tests").

**[0052]** The zinc coating thickness was determined by a metallographic method on cross-sectional micro section specimens with the use of the MMR-4 microscope, the micro section specimen etching being carried out in a 1% hydrofluoric acid solution.

**[0053]** The process of thermal-diffusion galvanizing was carried out as follows. Articles made of aluminum alloy AMg6 (GOST4784-74) were previously treated with shots having the fineness of 0.3-0.4 mm, made of the austenitic steel 12X18H10T until the strong oxide film of the aluminum oxide was completely removed and an oxide film of austenitic steel was formed. The articles and the saturating powdered mixture were loaded into a container previously heated to the temperature of 100-120°C. Use was made of the saturating powdered mixture of the above disclosed composition, able to release, at the temperature of galvanizing, active gaseous substances (volatile chemical compounds). The container was sealed and loaded into a furnace previously heated to 100-120°C.The thermal-diffusion galvanizing process was carried out at the temperature of 420-430°C for 1 hour at B constant rotation rate of 1-2 rpm of the container. The thermal-diffusion galvanizing was carried out at a constant pressure inside the container of 1.8-2.2 atm., developed by the saturating gaseous substances (volatile chemical compounds) released by the powdered mixture under heating. After cooling the furnace to the temperature of 100-120°C, the container was removed from the furnace, the articles were taken off the container and cooled down in water to eliminate the saturating powdered mixture adhered to the surface.

**[0054]** Later on the specimens are treated in a vibration stand with ceramic chips together with the passivating solution to provide for complete elimination of the deposited zinc layer from their surface until fulfillment of the condition:

$$\Delta \varphi = \varphi_{Al} - \varphi_{Zn} \rightarrow 0,$$

where

$\Delta\varphi$ is an electrolytic potential difference in Volts (V),

$\varphi_{Al}$ is an electrolytic potential of the aluminum alloy in Volts (V),

$\varphi_{Zn}$ is an electrolytic potential of the diffusion zinc layer in Volts (V).

Brief description of the drawings

**[0055]**

Fig. 1 shows the general view of the zinc coating obtained while implementing the process of the present invention. The zinc coating is shown as dark and light areas (denoted by1); the deposited zinc layer (denoted by 2); the diffusion layer is given as a light area (denoted by 3); the aluminum alloy AMg6 (denoted by 4).

Fig. 2 illustrates the temperature parameters of the process of the present invention for thermo-diffusion galvanizing articles of aluminum alloys.

1 - Loading the articles and the saturating powdered mixture into a container (100-120°C).

2 - Loading the container into a furnace (100 - 120°C)

3 - Heating of the furnace with the container to a given temperature.

4 - Hold-time at the given temperature (420-430°C).

5 - Cooling with the furnace to 100-120°C.

6 - Unloading the container and removal of the articles (100-120°C).

7 - Cooling the articles in water at T= 100-120°C.

Fig. 3 shows the technological operations while carrying out the thermal-diffusion galvanizing articles of aluminum alloys. 1 represents shot-blasting of an article, 2 represents loading the article and the saturating powdered mixture into a container, 3 represents loading the container into a furnace and carrying out the thermal-diffusion galvanizing; 4 represents removal of the container from the furnace, 5 represents the removal of the container from the furnace, 6 represents cooling the article in water, 7 represents treatment of the articles by chips with a passivating solution.

Examples of embodiments of the invention

Example 1 (comparative)

**[0056]** The specimens made of aluminum alloy AMg6 (GOST4784-74) are pretreated with shots having the fineness of less than 0.3 mm and made of austenitic steel, 12X18H10T grade.

**[0057]** The specimens and the saturating powdered mixture are loaded into a container preheated to the temperature of 100-120°C. Use is made of a saturating powdered mixture composed of powdered zinc, an activating agent and an inert filler, at their ratio as follows, in % by mass:

| | |
|---|---|
| Inert filler | 55-60 |
| Activating agent | 3-5 |

(continued)

| | |
|---|---|
| Powdered zinc | to balance, |

able to release, under heating to the temperature of galvanizing, active gaseous substances (volatile chemical compounds).

**[0058]** The container is sealed and loaded into a furnace previously heated to 100-120°C.

**[0059]** The thermal-diffusion galvanizing process is carried out at the temperature of 420-430°C for 1 hour at a container constant rotation rate of 1-2 rpm.

**[0060]** The thermal-diffusion galvanizing is carried out at a constant pressure inside the container of 1.8-2.2 atm., developed by the saturating gaseous substances (volatile chemical compounds) released by the saturating powdered mixture under heating.

**[0061]** After cooling the furnace to the temperature of 100-120°C, the container is removed from the furnace, the articles are taken off the container and cooled down in water to eliminate the saturating powdered mixture adhered to the surface.

**[0062]** After that, the specimens are treated in a vibration stand with ceramic chips together with a passivating solution to completely remove a deposited powdered zinc layer until the following condition is fulfilled: $\Delta\varphi = \varphi_{Al-} \varphi_{Zn} \rightarrow 0$, where
$\Delta\varphi$ is a difference of electrolytic potentials (B),
$\varphi_{Al}$- is the electrolytic potential of the aluminum alloy (B),
$\varphi_{Zn}$ - is the electrolytic potential of the diffusion zinc layer (B).

**[0063]** The characteristics of the coating obtained are given in Table 1.

Example 2 (comparative)

**[0064]** The specimens made of aluminum alloy AMg6 (norm GOST4784-74), are pretreated with shots having the fineness above 0.4 mm and made of austenitic steel, 12X18H10T grade.

**[0065]** Loading the specimens and the saturating powdered mixture into the container is carried out like in Example 1. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 1. The thermal-diffusion galvanizing temperature is similar to that of Example 1. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 1. The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 1. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution is similar to that of Example 1. The characteristics of the coating obtained are given in Table 1.

Example 3 (The best embodiment of the invention)

**[0066]** The specimens made of aluminum alloy AMg6 (GOST4784-74) are pretreated with shots having the fineness of 0.3-0.4 mm and made of austenitic steel, 12X18H10T grade, until the strong oxide film of aluminum alloy is completely eliminated and an oxide film of austenitic steel is formed.

**[0067]** The specimens and the saturating powdered mixture are loaded into a container preheated to the temperature of 100-120°C. Use is made of a saturating powdered mixture composed of powdered zinc, an activating agent and an inert filler, at their ratio as follows, in % by mass:

| | |
|---|---|
| Inert filler | 55-60 |
| Activating agent | 3-5 |
| Powdered zinc | to balance, |

able to release, under heating to the temperature of galvanizing, active gaseous substances (volatile chemical compounds).

**[0068]** The container is sealed and loaded into a furnace previously heated to 100-120°C.

**[0069]** The thermal-diffusion galvanizing process is carried out at the temperature of 420-430°C for 1 hour at a container constant rotation rate of 1-2 rpm.

**[0070]** The thermal-diffusion galvanizing is carried out at a constant pressure inside the container of 1.8-2.2 atm., developed by the saturating gaseous substances (volatile chemical compounds) released by the saturating powdered mixture under heating.

**[0071]** After cooling the furnace to the temperature of 100-120°C, the container is removed from the furnace, the articles are taken off the container and cooled down in water to eliminate the saturating powdered mixture adhered to the surface.

**[0072]** After that, the specimens are treated in a vibration stand with ceramic chips together with a passivating solution to completely remove from their surface the deposited powdered zinc layer until the following condition is fulfilled: $\Delta\varphi = \varphi_{Al} - \varphi_{Zn} \rightarrow 0$.

**[0073]** The characteristics of the coating obtained are given in Table 1.

Example 4 (comparative)

**[0074]** The shot-blasting of the specimens is similar to that of Example 3. The specimens and the saturating powdered mixture are loaded into a container preheated to a temperature below 100°C. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 1. The temperature of the furnace prior to the container loading is similar to that of Example 1. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution is similar to that of Example 1. The characteristics of the coating obtained are given in Table 1. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0075]** The thermal-diffusion galvanizing temperature is similar to that of Example 3. The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 2.

Example 5 (comparative)

**[0076]** The shot-blasting of the specimens is similar to that of Example 3. The specimens and the saturating powdered mixture are loaded into a container preheated to a temperature above 120°C. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The temperature of the furnace at the container loading is similar to that of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0077]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 2.

Example 6 (comparative)

**[0078]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. Use is made of the saturating powdered mixture composed of powdered zinc, an activating agent and an inert filler, at the component ratio as follows, in % by mass:

| | |
|---|---|
| Inert filler | 17-22 |
| Activating agent | 6-8 |
| Powdered zinc | to balance. |

**[0079]** The temperature of the furnace at the container loading is similar to that of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0080]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 2.

Example 7 (comparative)

**[0081]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. Use is made of the saturating powdered mixture composed of powdered zinc, an activating agent and an inert filler, at the component ratio as follows, in % by mass:

| | |
|---|---|
| Inert filler | above 60 |
| Activating agent | above 5 |
| Powdered zinc | to balance. |

**[0082]** The temperature of the furnace at the container loading is similar to that of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0083]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips together with a passivating solution after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 3.

Example 8 (comparative)

**[0084]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature below 100°C. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0085]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 4.

Example 9 (comparative)

**[0086]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature above 120°C. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3.

**[0087]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 4.

Example 10 (comparative)

**[0088]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The thermal-diffusion galvanizing is carried out at a pressure lower than 1.8 atm., developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating.

**[0089]** The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 5.

Example 11 (comparative)

**[0090]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The thermal-diffusion galvanizing is carried out at a pressure of 2.2 atm., developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating. The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 5.

Example 12 (comparative)

**[0091]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3. The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 6.

Example 13 (comparative)

**[0092]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature of Example 3. The thermal-diffusion galvanizing temperature is similar to that of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3. The temperature of the furnace prior to cooling the specimens in water is higher than 120°C. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing is similar to that of Example 3. The characteristics of the coating obtained are given in Table 6.

Example 14 (comparative)

**[0093]** The shot-blasting of the specimens is similar to that of Example 3. The temperature of the container while loading the specimens and the saturating powdered mixture is similar to that of Example 3. The quality and quantity compositions of the saturating powdered mixture are similar to those of Example 3. The container is loaded into the furnace at a temperature of Example 3. The pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating is similar to that of Example 3. The temperature of the furnace prior to cooling the specimens in water is similar to that of Example 3. The treatment of the specimens in the vibration stand with ceramic chips after the thermal-diffusion galvanizing was carried out until the deposited powdered zinc was partially removed from their surface. The characteristics of the coating obtained are given in Table 7.

Example 15 (comparative, according to the China patent No 102002665 of 03.10.2012)

**[0094]** The specimens made of aluminum alloy AMg6 (GOST4784-74) and previously degreased are loaded into a container. The preparation of the powdered mixture, its composition, the component ratio in % by mass, the component fraction size and the regimes of thermal-diffusion galvanizing were carried out in accordance with the process of the China patent No 102002665, 03.10.2012.

**[0095]** The characteristics of the zinc coating obtained are given in Table 8.

**[0096]** Thus, the powdered mixture composition and the process for thermal-diffusion galvanizing of the present invention enable to carry out thermal-diffusion galvanizing of aluminum alloy articles, to increase the efficiency of the process due to the use of a less expensive saturating powdered mixture, in particular, to a lower content in the same of expensive components, namely the powdered zinc (Table 1, Example 3).

**[0097]** However, as shown by multiple experiments and as one can see from Table 1 (examples 1, 2), Table 2 (examples 4, 5), Table 3 (examples 6, 7), Table 4 (examples 8 and 9), Table 5 (examples 10 and 11), Table 6 (examples 12 and 13), Table 7 (example 14), Table 8 (Example 15), even a minor change of the process of thermal-diffusion galvanizing articles of aluminum alloys, in particular the fineness of shots (Table 1, examples 1 and 2), the container temperature while loading the specimens and the saturating powdered mixture (Table 2, examples 4 and 5), the quantity composition of the saturating powdered mixture (Table 3, examples 6 and 7), the temperature in the furnace at the container loading (Table 4, examples 8 and 9), the pressure inside the container, developed by the active gaseous substances (volatile chemical compounds) released from the saturated powdered mixture under heating (Table 5, examples 10 and 11), the temperature of cooling the furnace prior to cooling the specimens in water (Table 6, Examples 12 and 13) does not provide for the necessary technical result.

**[0098]** As one can see from the data given in Table 8 (example 15), the closest process to that of the present invention does not enable to resolve the task of the present invention nor to achieve the necessary technical result, therefore, it cannot be used for anticorrosive protection of articles of aluminum alloys.

**[0099]** The process of the present invention enables to carry out thermal-diffusion galvanizing articles of aluminum alloys, to increase the efficiency of the process due to a lower cost of the saturating powdered mixture, in particular, to a lower content in the same of expensive components, such as powdered zinc and the activating agent.

Table 1

| Effect of the dispersity of shots of austenitic steel in the shot-blasting of articles of aluminum alloys on the quality of the diffused zinc layer | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Dispersity of shots, mm | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 1 (comparative) | below 0.3 | 15-25 | no damages observed | no damages observed | corrosion spots, selective corrosion | Nonuniform in thickness, continuous, with defects |
| 2 | Example 2 (comparative) | above 0.4 | - | - | - | - | Tests are inexpedient to carry out due to a high roughness of the article surface |
| | Example 3 (of the invention) | 0.3-0.4 | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

Table 2

| Effect of the container temperature on the quality of the diffusion zinc layer while loading the aluminum alloy specimens and the saturating powdered mixture | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Temperature in the container, °C | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 4 (comparative) | below 100 | 15-25 | no damages observed | no damages observed | corrosion spots, selective corrosion | Nonuniform in thickness, continuous, with defects |
| 2 | Example 5 (comparative) | above 120 | 60-65 | no damages observed | no damages observed | no damages observed | Economically and technologically unsuitable |
| 3 | Example 3 (of the invention) | 100-120 | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

Table 3

| Effect of the ratio of saturating powered mixture components on the quality of the diffusion zinc layer | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| No | Examples | Ratio of the powdered mixture components, % by mass | | | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | Inert filler | Activating agent | Powdered zinc | | 120 | 240 | 720 | |
| 1 | Example 6 (comparative) | 17-22 | 6-8 | to balance | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, continuous, without defects economically disadvantageous |
| 2 | Example 7 (comparative) | above 60 | below 3 | to balance | 15-25 | no damages observed | no damages observed | corrosion spots, selective corrosion | Uniform in thickness, continuous |
| 3 | Example 3 (of the invention) | 55-60 | 3-5 | to balance | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

Table 4

| Effect of the temperature in the furnace on the quality of the diffusion zinc layer at loading of the container with specimens together with the saturating powdered mixture into the same | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Temperature of the furnace, °C | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 8 (comparative) | below 100 | 15-25 | no damages observed | no damages observed | corrosion spots, selective corrosion | Nonuniform in thickness, continuous, with defects |
| 2 | Example 9 (comparative) | above 120 | 60-65 | no damages observed | no damages observed | no damages observed | Economically and technologically unsuitable |
| 3 | Example 3 (of the invention) | 100-120 | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

Table 5

| Effect of the change in the pressure of active gaseous substances (volatile chemical compounds) released from the saturating powdered mixture under heating on the quality of the diffusion zinc layer | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Pressure in the container, atm. | Thickness of μm the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 10 (comparative) | Below 1.8 | 15-25 | no damages observed | no damages observed | corrosion spots, selective corrosion | Nonuniform in thickness, continuous, with defects |
| 2 | Example 11 (comparative) | above 2.2 | 15-60 | no damages observed | no damages observed | corrosion spots, selective corrosion | Nonuniform in thickness, continuous, with defects |
| 3 | Example 3 (of the invention) | 1.8-2.2 | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

Table 6

| Effect of the furnace temperature prior to cooling of specimens in water after the thermal-diffusion galvanizing on the quality of the diffusion zinc layer | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Temperature in the furnace, °C | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 12 (comparative) | below 100 | 60-65 | no damages observed | no damages observed | no damages observed | Residues of saturating powdered mixture on the surface |
| 2 | Example 13 (comparative) | above 120 | 60-65 | no damages observed | no damages observed | no damages observed | Change of the initial size and warping of articles |
| 3 | Example 3 (of the invention) | 100-120 | 60-65 | no damages observed | no damages observed | no damages observed | No residues of saturating powdered mixture, no changes of the initial size or warping |

Table 7

| Effect of the deposited powdered zinc layer at the treated specimens on the quality of the diffusion zinc layer | | | | | | | |
|---|---|---|---|---|---|---|---|
| No | Examples | Thickness of the deposited powdered zinc layer, μm | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | | 120 | 240 | 720 | |
| 1 | Example 14 (comparative) | 20-22 | 60-65 | no damages observed | no damages observed | corrosion spots, selective corrosion | Lower rustproof properties |
| 2 | Example 3 (of the invention) | nonexistent | 60-65 | no damages observed | no damages observed | no damages observed | High rustproof properties |

Table 8

| Effect of the methods of thermal-diffusion galvanizing on the quality of the diffusion zinc layer | | | | | | |
|---|---|---|---|---|---|---|
| No | Examples | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | 120 | 240 | 720 | |
| 1 | Example 15 (comparative, according to patent No102002665) | 5-15 | corrosion spots, selective corrosion | Increase of corrosion damages | Continuous corrosion | Nonuniform in thickness, rough, porous, with defects |

(continued)

| Effect of the methods of thermal-diffusion galvanizing on the quality of the diffusion zinc layer | | | | | | |
|---|---|---|---|---|---|---|
| No | Examples | Thickness of the diffusion zinc layer, μm | Test time, hrs (presence of corrosive damages) | | | Remark |
| | | | 120 | 240 | 720 | |
| 2 | Example 3 (of the invention) | 60-65 | no damages observed | no damages observed | no damages observed | Uniform in thickness, smooth, no porosity, without defects |

**[0100]** Note: corrosion damages of the aluminum alloy AMg6 without zinc coating were observed after 12 hours of tests in a chamber containing neutral salt fog.

## Claims

1. Powdered mixture composition for thermal-diffusion galvanizing articles of aluminum alloys, comprising powdered zinc, an inert filler and an activating agent where, as the activating agent, use is made of a mixture of the following components, in % by mass: sodium fluoride 12-15, lithium chloride 20-25, ammonium chloride 10-15, zinc chloride 12-14, potassium chloride to balance, with the following component ratio, in % by mass:

| | |
|---|---|
| Inert filler | 55-60 |
| Activating agent | 3-5 |
| Powdered zinc | to balance. |

2. Composition of claim 1, wherein, as the inert filler, use is made of oxides: silicon, aluminum, iron, calcium with impurities of clay and sand.

3. Composition of claim 1, wherein, as the inert filler, use is made preferably of diatomite, opoka, tripolite with the granularity of not more than 1.2 mm and with the density of 0.7-1.0 g/cm$^3$.

4. Composition of claim 1, wherein at least 80% by mass of inert filler is used with the granularity of 0.8-1.2 mm, and up to 20% of inert filler is used with the granularity smaller than 0.8 mm.

5. Process of thermal-diffusion galvanizing articles of aluminum alloys, wherein it comprises pretreatment of the article surface with shots having the granularity of 0.3-0.4 mm and made of austenitic or austenitic-ferritic steel, loading the articles and a saturating mixture into a container preheated to 100-120°C, loading the container into a furnace preheated to 100-120°C, treating the articles at a temperature of 420-430°C for 1 hour at a container constant rotation rate of 1-2 rpm and at a constant pressure of 1.8-2.2 atm. inside the container, cooling the furnace to 100-120 °C, removing the articles from the container, cooling the articles in water and treating them with ceramic chips together with a passivating solution in a vibration stand, the composition of claim 1 being used as the saturating powdered mixture.

6. Process of claim 5, wherein the constant pressure inside the container is developed by active gaseous substances released from the saturating powdered mixture under heating.

7. Process of claim 5, wherein the treatment with ceramic chips and the passivating solution is carried out until the following condition is fulfilled:

$$\Delta \varphi = \varphi_{Al} - \varphi_{Zn} \rightarrow 0,$$

where $\Delta \varphi$ is the difference of electrolytic potentials, $\varphi_{Al}$ is the electrolytic potential of the aluminum alloy, $\varphi_{Zn}$ is the electrolytic potential of the diffusion zinc layer.

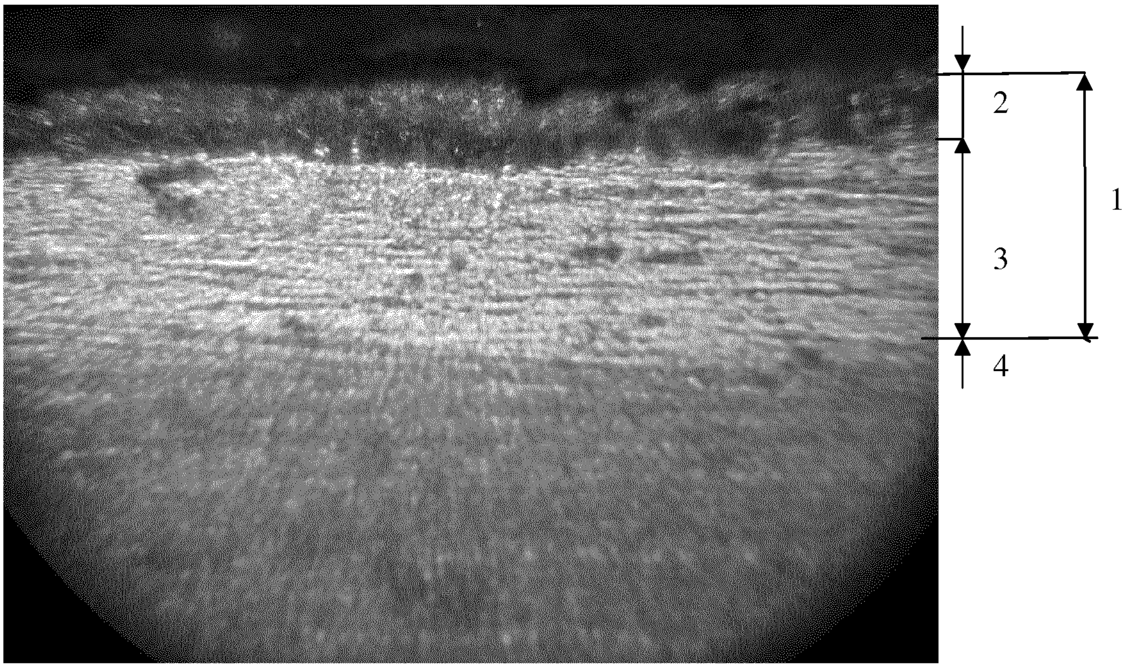


Fig. 1

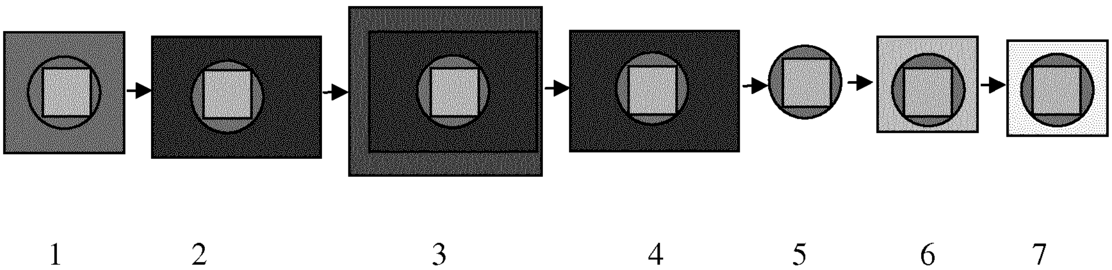


Fig. 3

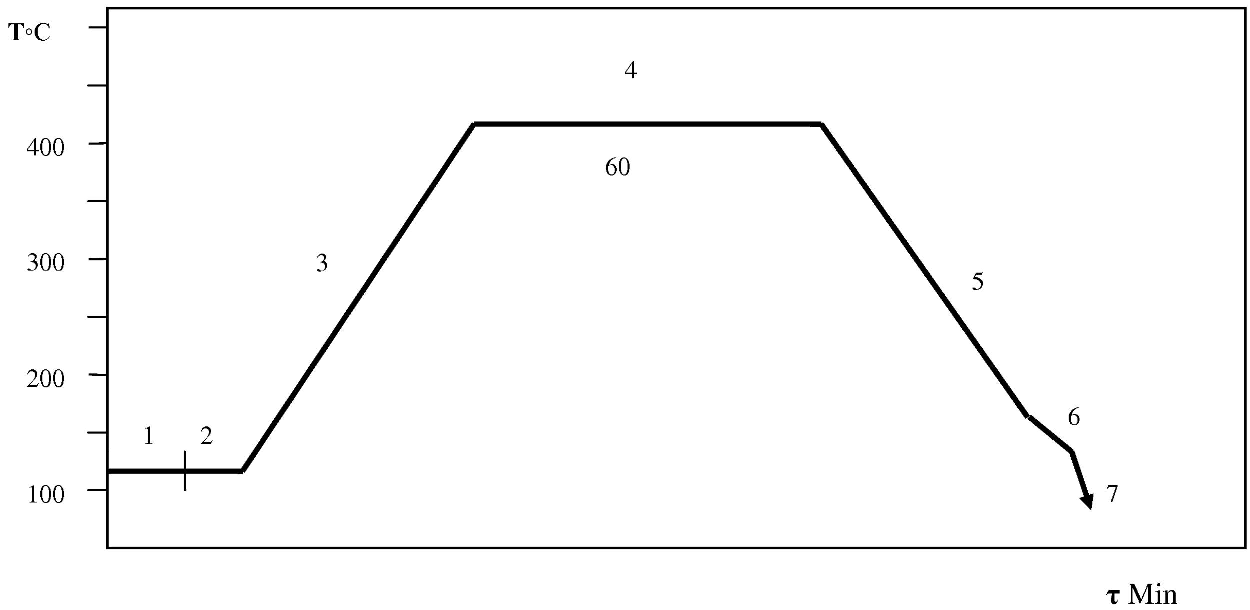


Fig.. 2

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2013/000696

A. CLASSIFICATION OF SUBJECT MATTER

***C23C 10/36*** *(2006.01)*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 10/00, 10/28, 10/34, 10/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Espacenet, PAJ, PatSearch (RUPTO internal), RUPTO, USPTO, Patentscope

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | CN 102002665 A (UNIV BEIJING SCIENCE & TECH) 06.04.2011, abstract | 1-7 |
| A | RU 2451109 C1 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "MZVA") 20.05.2012, abstract | 1-7 |
| A | CN 101191189 A (TIANJIN HANLONG ZINC PLATING S) 04.06.2008, abstract | 1-7 |
| A | UA 75728 C2 (GURMAN VLADIMIR GRIGOREVICH et al.) 15.05.2006, abstract | 1-7 |

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 31 March 2014 (31.03.2014) | 03. April 2014 (03.04.2014) |

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- RU 2195512 **[0016]**
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