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(71) Applicant: **Marcegaglia Ravenna S.p.A.**
46040 Gazoldo degli Ippoliti (MN) (IT)

(72) Inventor: **FERRAIUOLO, Alessandro**
48123 Ravenna (IT)

(74) Representative: **Botti & Ferrari S.p.A.**
Via Cappellini, 11
20124 Milano (IT)

(54) COATING METHOD FOR COATING METAL COMPONENTS WITH METAL POWDER ALLOYS

(57) A coating method for coating metal components with metal powder alloys, comprising: applying a primary layer of liquid metal coating onto a metal component; applying a metal powder onto the primary layer, the primary layer being in an at least partially liquid state; cooling the metal component at a cooling rate to solidify the metal powder onto the primary layer, obtaining an alloy coating. The metal powder is composed of particles which are electrically charged and sprayed onto the primary layer. An average distance D between particles impacting against the primary layer is controlled to be equal to or greater than a calculated value.

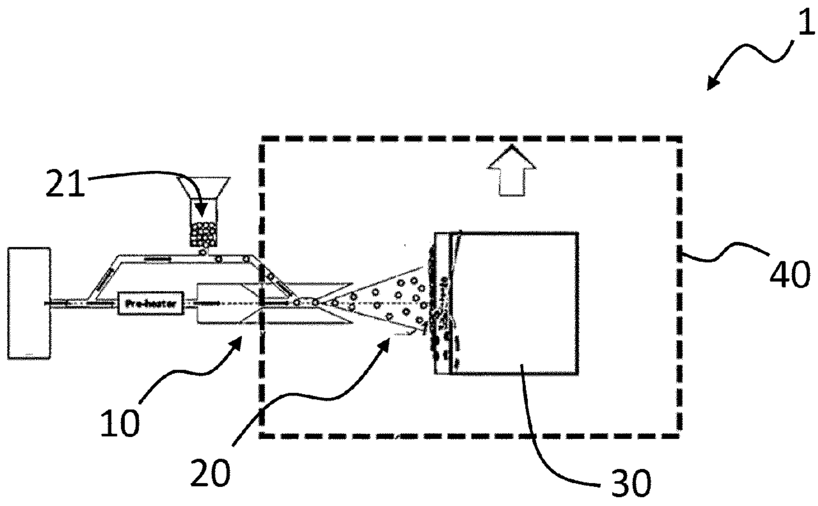

FIG. 1

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Description

Technical field

[0001] The present invention relates to a coating method for coating metal components with metal powder alloys.

[0002] The invention finds a preferred application in the industry of metal surface coatings, for example in relation to the manufacture of rolled steel, and the following description is made with reference to this field of application with the only aim of simplifying the exposition thereof.

Prior art

[0003] Document CN112680685A relates to a method for manufacturing steel bars with a high-corrosion-resistance coating, wherein, after applying a layer of pure zinc in the liquid state, the metal powder is sprayed onto the steel bar surface and the metal powder is melted onto the surface of the zinc liquid to form an alloy plating layer.

[0004] Document KR960009191B1 relates to processes for spraying fine aluminium powder with a granulometry which is less than 5 Pm onto the surface of a galvanised steel sheet, just before the solidification of the molten zinc.

[0005] Document JPS5970753A relates to the manufacture of corrosion-resistant sheet steels, wherein a zinc-alloy plating layer is formed on the steel coil and another metal powder is sprayed to spread the powder into the galvanised layer before the zinc solidification.

[0006] Document JP04160142A relates to a hot-galvanised steel sheet having an excellent corrosion resistance wherein non-metal inorganic particles are sprayed onto the zinc surface of the steel sheet in the molten state.

[0007] Document JP2004107695A relates to a corrosion-resistant hot-galvanised steel, obtained by incorporating a particulate compound from 0,001 to 10% by weight with a particle diameter of ≤0,9 pm composed of one or more types of metals, dispersing the compound in the plating bath by hot dip immersion or directly spraying the particles along with a gas, so that they are precipitated into the plated layer.

[0008] Document JP4725023B2 relates to a method for manufacturing an alloy steel sheet with coating by hot dip immersion.

Summary of the invention

[0009] An object of the present invention is to remedy drawbacks of the prior art.

[0010] A particular object of the present invention is to provide an innovative coating method for coating metal components with metal powder alloys.

[0011] A further particular object of the present invention is to better determine the parameters which are useful to the process for coating metal components with metal powder alloys.

[0012] A further particular object of the present invention is to effectively and promptly exploit the possibilities conferred by apparatuses for coating metal components with metal powder alloys.

[0013] These and other objects are achieved by a coating method for coating metal components with metal powder alloys according to the features of the appended claims which form an integral part of the present description.

[0014] An idea underlying the present invention is to provide a coating method for coating metal components with metal powder alloys.

[0015] Applying a primary layer of liquid metal coating onto a metal component is provided.

[0016] Applying a metal powder onto the primary layer is provided, the primary layer being in an at least partially liquid state.

[0017] Cooling the metal component at a cooling rate to solidify the metal powder onto the primary layer is provided, obtaining an alloy coating.

[0018] The metal powder is composed of particles which are electrically charged and sprayed onto the primary layer.

[0019] An average distance *D* between particles impacting against the primary layer is controlled to be equal to or greater than a value calculated according to the following relationship:

$$D \geq \alpha \, \frac{c(T_f - T_i) + Q_L^{PW}}{Q_L} \, \frac{d^2}{h}$$

wherein α is a parameter comprised between 0.6 and 1.2,
wherein *c* is the specific heat of the metal powder,

wherein T_f is the melting temperature of the metal powder,
wherein T_i is an initial temperature of the metal powder before the application onto the primary layer,
wherein Q_L^{PW} is the latent melting heat of the metal powder,
wherein Q_L is the latent heat of the primary layer of liquid metal coating,
wherein *d* is the average diameter of the particles of the metal powder,
wherein *h* is the thickness of the primary layer of liquid metal coating.

[0020] Advantageously, the present invention allows to determine in a process for coating metal components with metal powder alloys, a minimum spacing between the particles for an optimal coating.

[0021] Advantageously, the present invention allows to effectively determine an average distance *D* between particles impacting against the primary layer.

[0022] Advantageously, the average distance *D* between particles impacting against the primary layer is controllable, among others, by a suitable application of electrical quantities such as electric charge of the particles of the metal powder and, possibly, the potential difference between a device for spraying the electrically charged particles and a substrate of the metal component.

[0023] The present invention allows enhanced coatings to be obtained for a wide range of metal substrates. These coatings are characterized by improved properties, particularly a better corrosion resistance, or also by advantageous functional properties as antibacterial, as hot-forging solution having in particular better resistance to high-temperature oxidation, as well as better heat resistance.

[0024] Moreover, the present invention allows to obtain combinations of phases which are close to the centres of the respective phase diagrams, also referred to as "high-entropy systems", especially in the case of quaternary, quinary and higher-order systems. The method of the present invention thus represents a considerable improvement for manufacturing coated metal components.

[0025] Further features and advantages will be more apparent from the following detailed description of preferred non-limiting embodiments of the present invention, and from the dependent claims which outline preferred and particularly advantageous embodiments of the invention.

Brief description of the drawings

[0026] The invention is illustrated with reference to the following figures, given by way of non-limiting examples, in which:

- Figure 1 exemplifies an embodiment of an apparatus for coating metal components with metal powder alloys.
- Figures 2A and 2B exemplify further embodiments of apparatuses for coating metal components with metal powder alloys.
- Figure 3 exemplifies a preferred embodiment of a device for applying metal powder onto a flat metal component.
- Figures 4A and 4B exemplify particles impacting against a primary layer of liquid metal coating of a metal component.
- Figures 5A, 5B and 5C exemplify particles of a coating of a metal component.
- Figures 6A and 6B illustrate variations in the Gibbs free energy by varying temperature, for particular phases.
- Figures 7A and 7B illustrate entropy variations by varying temperature, for particular phases.

[0027] In the several figures, identical elements will be identified by identical reference numbers.

Detailed description

[0028] The present invention provides a two-step process, or method.

[0029] The method provides a first step of applying, onto a metal component, a primary layer of liquid metal coating (for example Zn) with a thickness which can preferably vary between 1 micron and 5.0 mm.

[0030] The primary coating layer can comprise elements or alloys, for example but not exclusively: Zn, Zn-Al, Zn-Al-Mg, Al, Al-Si, Sn and alloys thereof.

[0031] The method provides a second step, wherein a metal powder is sprayed onto the primary coating, when the primary coating is still liquid or partially liquid, i.e. in a pasty state.

[0032] The metal powder which comes in contact with the primary coating heats and dissolves very rapidly. This second step aims at obtaining a specific metallurgical modification of the coating in terms of formation of new microstructural precipitating phases during solidification in the following controlled cooling at ambient temperature.

[0033] The chemical composition of the metal powder can provide different alloy systems, for example but not exclusively: Zn-Al-Mg, Al-Si or Al and alloys thereof, Zn-Al-Cu or 70Mg-Al-Zn-Cu or Zn-Al-Mg-Cu-Ag-Si.

[0034] In general, the metal powder comprises at least one metal element also comprised in the composition of the primary layer. Moreover, preferably, the metal powder further comprises low-melting metal elements, configured to decrease a melting temperature of the metal powder compared to a second melting temperature of the primary layer, which is higher.

[0035] The phases which form after the second step depend on the chemical composition of the powder and on the controlled cooling rate of the coating.

[0036] Based on these parameters it is possible to obtain a phase which is thermodynamically stable or even metastable with totally new or highly improved functional properties.

[0037] It is thus possible to design the metallurgical phases through thermodynamic calculations and obtain them by acting on process parameters, such as alloy and cooling rate.

[0038] The present invention also relates to coatings with special properties, referred to as "High Entropy Coatings" composed of metallurgical phases obtained when the powders are characterized by three or more elements in an almost equal atomic percent. These "High Entropy Coatings" phases are characterized by an exceptional thermodynamic stability and by resulting high-corrosion-resistance properties.

[0039] The phases which can be developed by the present invention could be metastable and therefore far from the thermodynamic equilibrium. For designing the operating conditions to be adopted in terms of chemical composition of the powder, to assess the cooling rate after spraying the powder, the following differential equation can be adopted:

$$\mu \frac{d^2\xi}{dt^2} + \beta \frac{d\xi}{dt} - F = 0$$

wherein ξ is the thermodynamic function describing the kinetics of formation of a phase (for example the mass fraction of a phase).

[0040] Moreover, μ is, in particular, a specific inertial parameter of the chemical reaction being concerned, i.e. the effective molar mass μ of the phase which is to be selected. In detail $\mu = m\ \sigma$ wherein m is the molar mass of the considered phase and σ is the cross section that is the probability (comprised between 0 and 1) that the chemical reaction of formation of the considered phase actually occurs.

[0041] Parameter β represents the energy dissipation associated with the internal process described by the function ξ. In the particular case of an isothermal transformation, at the absolute temperature T expressed in [K], the following relationship applies $\beta = \tau T \frac{dS_i}{d\xi}$ wherein dS_i is the internal entropy variation corresponding to an incremental variation $d\xi$ of the internal process; parameter τ is a process characteristic constant comprised between 0.6-1.2. The above-quoted formulation of parameter β can be also used in the more general case of non-isothermal transformation, assuming that the system behaves following a series of isotherms at different temperatures (Sheil's additivity principle). Parameter β is particularly relevant since it significantly depends on the cooling rate. Finally, $F = -dG/d\xi$ is the generalized thermodynamic force for the formation of the phase being concerned and it is calculated as a variation in the Gibbs free energy G of the considered system by varying ξ. The value of σ, τ, β and F can be empirically estimated by laboratory tests and/or calculated by thermodynamic models based on literature data.

[0042] By way of example, an approximate solution of the above-quoted differential equation, setting the change of the variable $v(t) = \frac{d\xi}{dt}$, is as follows

$$v(t) = v_o * exp\left(-\frac{\beta}{\mu}t\right) + \frac{F}{\beta}\left[1 - \exp\left(-\frac{\beta}{\mu}t\right)\right]$$

wherein v_o is the transformation velocity at time t=0. Assuming that $v_o = 0$ at time t=0, the velocity of formation of a specific phase takes the final form:

$$v(t) = \frac{F}{\beta}\left[1 - \exp\left(-\frac{\beta}{\mu}t\right)\right]$$

[0043] From this equation it emerges that the velocity of formation of a phase depends on two factors:

First factor: $\frac{\beta}{\mu}$ is the effective viscosity due to the energy dissipation caused by the generation of entropy for the formation of a phase of effective molar mass μ.

Second factor: $\frac{F}{\beta}$ is the effective driving force which is available for the formation of a phase of effective molar mass μ.

[0044] The above-quoted equation is used to calculate the optimal cooling condition to be set for the process in order to obtain the required metallurgical phase.

[0045] The formation of a phase 1 characterized by effective parameters β_1/μ_1 and F_1/β_1 can be kinetically favoured compared to another phase characterized by different effective parameters β_2/μ_2 and $F_2\,/\beta_2$ by acting on the cooling rate of the metal substrate after applying the metal powder. In particular, if a suitable cooling rate is used, phase 1 will form preferentially compared to phase 2 if and only if the cooling rate of phase 1 is greater than the cooling rate of phase 2, i.e. $v_1 > v_2$.

[0046] A method for calculating the cooling rate is described in detail in Example 4 quoted below.

[0047] As already mentioned, the method of the present invention relates to a coating on a metal substrate and it consists in a two-step process wherein the first step consists in applying a primary layer of liquid metal coating onto the metal substrate (steel, aluminium and other metals or alloys) for example through a hot dip immersion process or other similar process. The second step consists in spraying a metal powder onto the primary coating, when this coating is still at least partially liquid.

[0048] The powder melting times are very short and the phenomenon occurs for the heat transfer between the liquid primary coating and a metal powder which heats and melts. This involves a local and considerable modification of the chemical composition of the primary coating. During the following cooling up to ambient temperature the formation of new metallurgical phases during solidification can be induced by suitably controlling the cooling rate, according to techniques which are known per se in the metallurgical sector.

[0049] The present invention allows to obtain a specific metallurgical modification in the coating in terms of additional microstructural phases being formed.

[0050] The method provides in particular:

1) Metallurgical design of the chemical composition of the metal powders in order to obtain, after the melting and solubilization in the primary liquid metal coating, appropriate thermodynamically stable or metastable metallurgical phases, during the controlled cooling of the metal component.

2) Technology for spraying the metal powders onto the primary layer of at least partially liquid metal. The parameters of the spraying process include the size of the particles, the spacing of the particles at time of impact, the temperature of the powder, the temperature of the first coating layer, the electrostatic charge of the powder, the electrostatic field between the nozzles and the steel component. The powders can be pre-heated at a specific temperature comprised between the ambient temperature and the melting temperature of the first layer of liquid metal.

[0051] As it will be clear below, an important parameter is represented by the spacing of the particles at time of impact, which defines an average distance between particles impacting against the primary layer.

[0052] Concerning the second step, the technology of the preferred spraying nozzles for the second step uses a combination of two physical factors: a mechanical impact due to the kinetic energy of the metal particles, and an electrostatic charge of the particles and an implementation of an electrostatic field in the area between the nozzles and the metal component to be coated.

[0053] Example 1: assuming a primary layer in Zn, the manufacture of a high-corrosion-resistance coating can be obtained by spraying a powder, with an average size d = 20 microns, with the following chemical composition, by percentage weight: Al 5.0-12.0; Mg 0.1-12.0 and optionally Si+Ag+Cu 0.01-15, with a balanced Zn and inevitable impurities. Considering that the used process parameters are:
α = 0.9, the specific heat of the metal powder C = 0,79 J/(mol °C), the melting temperature of the metal powder T_f = 340°C, the initial temperature of the metal powder T_i = 20°C, the latent melting heat of the metal powder $Q_L^{PW} = 323\ \mathrm{J/mol}$, the latent heat of the primary layer of liquid metal coating Q_L = *114J/g,* the thickness of the primary layer of zinc coating *h* = 10 microns, an impact distance of the particles of 30 microns was set by acting on the electrostatic charge parameters of the powder applying a negative potential of - 100 kV to the electrode which is present at the outlet of the powder spraying nozzle.

[0054] Example 2: To obtain a coating of high-entropy alloys an Al-Si allow with 10% by weight of Si is considered as a primary layer coating. The metal powder is designed with a composition 70%Mg-20%Zn-10%Al. The result is a coating composed of a solid solution with excellent corrosion resistance properties and an optimal attitude to hot forging.

[0055] Example 3: To obtain a coating which is suited to hot forging a primary coating of Al and a metal powder Al-20%Si were considered. The melting temperature of this powder is 576°C, which is thus suited to melting in the aluminium primary coating.

[0056] Example 4: By way of example a primary coating of Zn and a powder of Zn-Al-Mg are considered, being such as to form, after melting the powder, a solution with a chemical composition 84Zn-10Al-8Mg. The two phases which can form are a eutectic mixture composed of Zn and Mg2Zn1 1 (Phase 1) or alternatively Zn and MgZn2 (Phase 2) respectively. If Phase 2 is to prevail on Phase 1 it is necessary to assess the corresponding velocities of formation of the two phases and determine the cooling rate condition so as to have $v_2 > v_1$. With the aid of commercial software it is possible to graphically or numerically calculate the values of the parameters $\frac{\beta_1}{\mu_1}, \frac{F_1}{\beta_1}$ and $\frac{\beta_2}{\mu_2}, \frac{F_2}{\beta_2}$. In this case it appears that by applying a cooling rate of 50°C/s phase 1 is characterized by $\beta_1 = 2.5 \left[\frac{\mathrm{J}}{\mathrm{mol}}\,\mathrm{s}\right], F_1 = 50 \left[\frac{\mathrm{J}}{\mathrm{mol}}\right] e\; \mu_1 = 763 \left[\frac{\mathrm{g}}{\mathrm{mol}}\right]$, and phase 2 is characterized by the parameters $\beta_2 = 3 \left[\frac{\mathrm{J}}{\mathrm{mol}}\,\mathrm{s}\right], F_2 = 48 \left[\frac{\mathrm{J}}{\mathrm{mol}}\right] e\; \mu_2 = 113 \left[\frac{\mathrm{g}}{\mathrm{mol}}\right]$ whereby, from the above-described cooling rate equation, it is obtained that $v_1 = 0.1$ [s $^{-1}$] and $v_2 = 0.3$ [s $^{-1}$].

[0057] In relation to said Example 4, Figure 6A illustrates the variation in the Gibbs free energy G of phase 1 (Mg2Zn1 1) of the system by varying temperature, while Figure 6B illustrates the variation in the Gibbs free energy G of phase 2 (MgZn2) of the system by varying temperature.

[0058] Always in relation to said Example 4, Figure 7A illustrates the entropy variation linked to the formation of phase 1 (Mg2Zn11) of the system by varying temperature, while Figure 7B illustrates the entropy variation linked to the formation of phase 2 (MgZn2) of the system by varying temperature.

[0059] It is thus possible to calculate the value of the coefficient β (energy dissipation coefficient linked to the entropy variation dS_i) and of F (generalized thermodynamic force for the formation of the phase calculated as a variation in the Gibbs free energy *G* of the system) to obtain an indication of the *driving force* which is available for the formation of the respective phase.

[0060] Considering instead Figures 1, 2A and 2B, they exemplify embodiments of apparatuses for coating metal components with metal powder alloys.

[0061] The architecture of the apparatus 1 comprises one or more nozzles 10 for spraying metal powder 20 onto a component 30 such as a strip or coil. The nozzles 10 are preferably mounted on a support frame 11 allowing to modify the distance of the nozzle 10 from the substrate. The typical distance between the nozzle 10 and the substrate is comprised between 10 and 200 mm.

[0062] A plurality of nozzles 10, as shown in Figures 2A and 2B, allow to cover the greatest width of the strip 30.

[0063] As it can be noted in Figures 2A and 2B, each nozzle 10 has a spraying width which depends on the distance between the strip 30 and the nozzle 10. To perfectly cover the strip 30 without any powder loss on the edges, the whole frame 11 supporting the nozzles 10 can rotate in the way illustrated in Figure 2B.

[0064] The nozzles 10 are preferably connected to a tank 21 for storing and fluidizing the metal powder 20 during the spraying operations.

[0065] The apparatus 1 further provides a system for the electrostatic charge of the metal powder by an appropriate electrode located in the outlet section of the nozzle and set at high voltage (not represented).

[0066] The apparatus 1 further provides an electronic control unit for controlling the process, in terms of mass flow of the powder 20 and distribution of the electrostatic field in the space between the nozzles 10 and the strip 30.

[0067] The apparatus 1 further provides a cooling system for controlling the coating solidification velocity.

[0068] Preferably, the spraying elements are closed inside a vacuum chamber 40 to avoid the leakage of powder 20 in the environment.

[0069] Figure 3 exemplifies a preferred embodiment of a device 10' for applying metal powder onto a flat metal component.

[0070] The device 10', which is similar to a group of nozzles 10 previously described in Figures 2A or 2B, provides a cylindrical chamber 12 with an elongated slot 13 which allows to distribute, through an air knife, the metal particles (already electrostatically charged) carried by the carrier gas, to spray the metal powder onto the primary layer.

[0071] Preferably, the particles are electrically charged by an electrode with a negative potential comprised between - 100 kV and - 60 kV.

[0072] Preferably, the average velocity of the particles impacting against the material being processed is comprised between 0.01 and 50.0 m/s, more preferably comprised between 0.1 and 1.0 m/s; this velocity regulates the penetration of the particles and affects the surface quality of the final product. The pression of the carrier gas is used to regulate the average velocity.

[0073] The powder temperature, controlled by suitably heating the carrier gas (air or nitrogen) is preferably comprised between 20°C and 300°C, more preferably comprised between 25°C and 200°C.

[0074] The electrostatic charge of the metal powder allows a uniform repulsion of the particles to be obtained; this effect is regulated by the potential difference between different metal particles in suspension in the *carrier gas*, and the optimal value is typically comprised between +/- 30 mV and +/-100 mV. In this range of potential difference the powder dispersion is defined as stabilized.

[0075] In particular, the average spacing of the impacting particles controls the uniformity of the microstructure and the melting time of the powder.

[0076] The spacing can be controlled by the electrostatic charge of the particles already indicated and a specific distribution of the electric field in the area between the nozzle 10 or 10' and the metal component 30 to be coated. The electric field is applied between the spraying device or nozzle 10 or 10' for the electrically charged particles and a substrate of the metal component. Preferably the electric field is comprised between 0.1 and 1.0 kV/cm.

[0077] Moreover, the respective dimensions of the primary metal layer and the average size of the powder particles considerably affect the characteristic melting time of the powder which must be preferably in the order of microseconds.

[0078] What is schematized in Figure 4A exemplifies an optimal distribution of particles compared to the characteristic dimensions of the particles and substrate; on the contrary, the configuration schematized in Figure 4B, wherein the particles are partially overlapped, is to be considered as non-optimal.

[0079] It is thus clear that the spacing of the particles affects the melting time, the correct ratio between the primary layer and the metal powder, for a spatial homogeneity of the microstructure and also to prevent voids/pores from appearing.

[0080] The present invention allows to calculate a minimum spacing of the particles as an average distance D between particles impacting against the primary layer according to the following relationship:

$$D \geq \alpha \, \frac{c(T_f - T_i) + Q_L^{PW}}{Q_L} \, \frac{d^2}{h}$$

wherein α is a parameter comprised between 0.6 and 1.2,
wherein c is the specific heat of the metal powder,
wherein T_f is the melting temperature of the metal powder,
wherein T_i is an initial temperature of the metal powder before the application onto the primary layer,
wherein Q_L^{PW} is the latent melting heat of the metal powder,
wherein Q_L is the latent heat of the primary layer of liquid metal coating,
wherein d is the average diameter of the particles of the metal powder,
wherein h is the thickness of the primary layer of liquid metal coating.

[0081] In particular, the value α can be empirically estimated by laboratory tests and/or calculated by thermodynamic models based on literature data.

[0082] The average distance i.e. the minimum spacing of the particles is controlled to be equal to or greater than the so-calculated value, wherein said distance can be controlled by suitably operating on the electrostatic charge of the metal powder and on the distribution of the electric field.

[0083] Once the suitable average distance D to be maintained is determined, the process parameters which allow the calculated value to be met, can be promptly identified.

[0084] By way of example, a good distribution of the metal powder particles is represented in Figure 5A, a worse distribution is represented in Figure 5B while a poor and ineffective distribution is represented in Figure 5C.

Industrial applicability

[0085] The present invention is applicable to several industrial sectors, such as: automotive, Oil & Gas, sheet metals, tubes, structural elements and the like.

[0086] The obtainable metal components can be exposed to severe corrosive conditions, be manufactured by hot forging and/or reduce the proliferation of antibacterial-resistant microorganisms.

[0087] Considering the here-quoted description, the person skilled in the art will be allowed to device further modifications and alternatives, in order to meet contingent and specific requirements.

[0088] It is evident that, where there are no technical incompatibilities which are apparent to the person skilled in the art, the configurations of specific elements described with reference to some embodiments can be used in other here-described embodiments.

[0089] Moreover, technical features of one or more here-described embodiments can be incorporated in other here-described embodiments, if there are no technical incompatibilities which are apparent to the person skilled in the art.

[0090] The here-described embodiments are hence to be considered as illustrative and non-limiting examples of the invention.

Claims

1. Coating method for coating metal components with metal powder alloys, comprising:

   - applying a primary layer of liquid metal coating onto a metal component;
   - applying a metal powder onto said primary layer, said primary layer being in an at least partially liquid state;
   - cooling said metal component at a cooling rate to solidify said metal powder on said primary layer, obtaining an alloy coating;

   wherein said metal powder is composed of particles which are electrically charged and sprayed onto said primary layer,
   wherein an average distance D between particles impacting against said primary layer is controlled to be equal to or greater than a value calculated according to the following relationship:

$$D \geq \alpha \frac{c(T_f - T_i) + Q_L^{PW}}{Q_L} \frac{d^2}{h}$$

   wherein α is a parameter comprised between 0.6 and 1.2,
   wherein *c* is the specific heat of said metal powder,
   wherein T_f is the melting temperature of said metal powder,
   wherein T_i is an initial temperature of said metal powder before said application onto said primary layer,
   wherein Q_L^{PW} is the latent melting heat of said metal powder,
   wherein Q_L is the latent heat of said primary layer of liquid metal coating,
   wherein d is the average diameter of said particles of said metal powder,
   wherein h is the thickness of said primary layer of liquid metal coating.

2. Coating method according to claim 1, wherein said initial temperature T_i of said metal powder is comprised between 20°C and 300°C, preferably controlled by heating a *carrier gas* for spraying onto said primary layer of said electrically charged particles.

3. Coating method according to claim 1 or 2, wherein said cooling rate is calculated to obtain metallurgical phases by solving or approximating the following differential equation:

$$\mu \frac{d^2\xi}{dt^2} + \beta \frac{d\xi}{dt} - F = 0$$

   wherein ξ is a thermodynamic function describing the kinetics of formation of a phase,
   wherein μ is the effective molar mass of the phase according to the equation $\mu = m\,\sigma$ wherein m is the molar mass of the considered phase and σ is the cross section comprised between 0 and 1,

wherein parameter β represents the energy dissipation associated with the internal process described by said thermodynamic function ξ according to the relationship $\beta = \tau\, T \frac{dS_i}{d\xi}$ wherein T is the absolute temperature, dS_i is the internal entropy variation corresponding to an incremental variation $d\xi$ of the internal process, wherein τ is a process characteristic constant comprised between 0.6-1.2,
and wherein $F = -dG/d\xi$ is calculated as a variation in the Gibbs free energy G of the considered system by varying ξ.

4. Coating method according to any one of claims 1 to 3, wherein said metal powder comprises at least one metal element also comprised in said primary layer.

5. Coating method according to claim 4, wherein said metal powder further comprises low-melting metal elements configured to decrease said melting temperature T_f of said metal powder compared to a second melting temperature of said primary layer.

6. Coating method according to claim 4 or 5, wherein said primary layer comprises at least Zn and/or Al.

7. Coating method according to claim 6, wherein said metal powder comprises at least Zn-Al-Mg for high-corrosion-resistance applications.

8. Coating method according to claim 6, wherein said metal powder comprises at least Zn-Al-Cu for antibacterial surface applications.

9. Coating method according to claim 6, wherein said metal powder comprises at least 70Mg-Al-Zn-Cu high-entropy alloys for high-corrosion-resistance applications and antibacterial surface applications.

10. Coating method according to claim 4 or 5, wherein said primary layer comprises at least Al and wherein said metal powder comprises at least Al-Si for hot forging applications.

11. Coating method according to claim 4 or 5, wherein said primary layer comprises at least Sn.

12. Coating method according to any one of claims 1 to 11, wherein said metal component is a coil processed on a continuous line.

13. Coating method according to any one of claims 1 to 12, wherein said parameter α is further predetermined based on a deposition efficiency previously assessed for said metal powder.

14. Coating method according to any one of claims 1 to 13, wherein an average velocity of said particles impacting against said primary layer is comprised between 0.01 and 50.0 m/s, preferably comprised between 0.1 and 1.0 m/s, and wherein said particles are electrically charged by an electrode with a negative potential comprised between - 100 kV and - 60 kV.

15. Coating method according to any one of claims 1 to 14, further comprising applying an electric field between a device for spraying said electrically charged particles and a substrate of said metal component, said electric field being preferably comprised between 0.1 and 1.0 kV/cm.

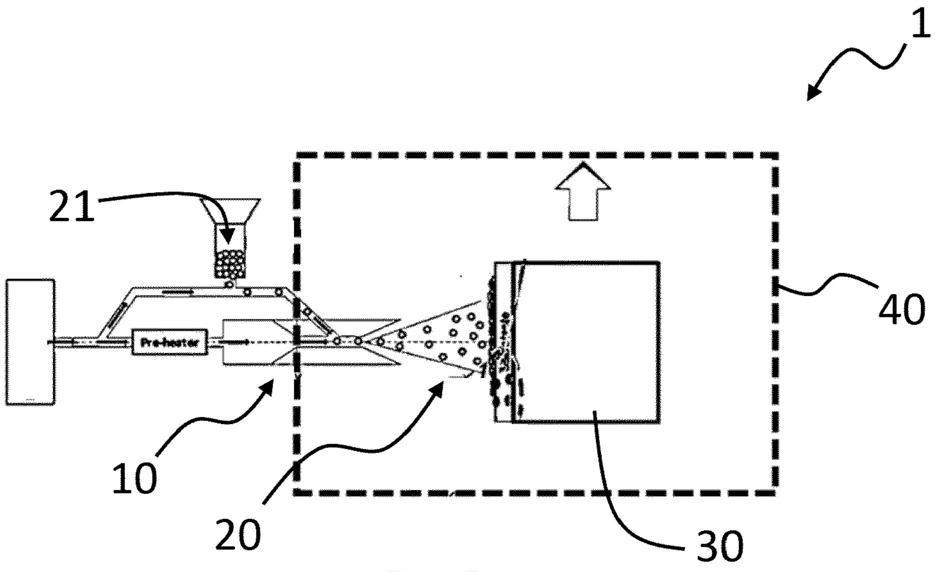

FIG. 1

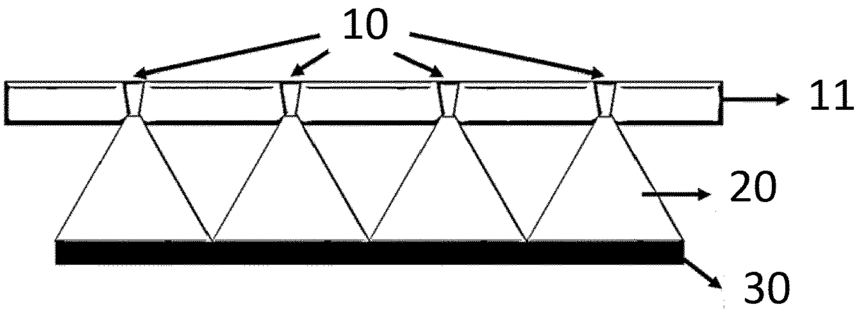

FIG. 2A

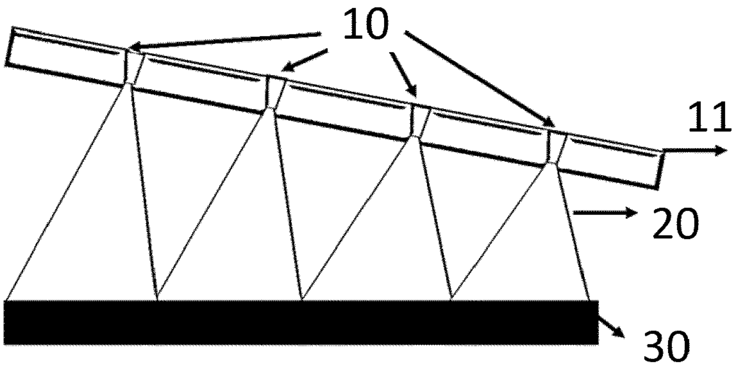

FIG. 2B

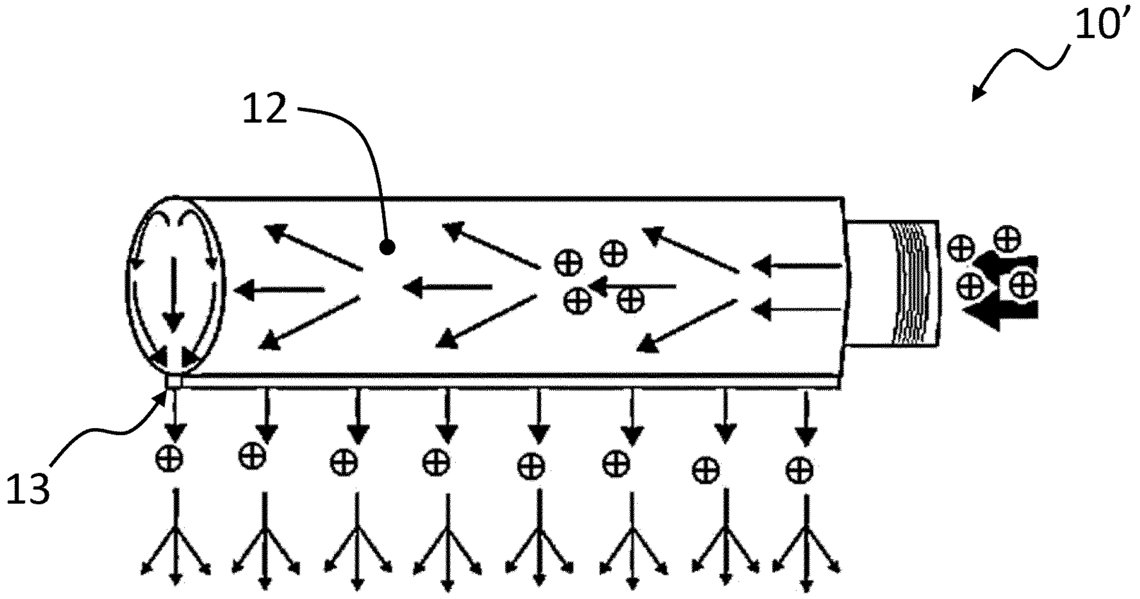

FIG. 3

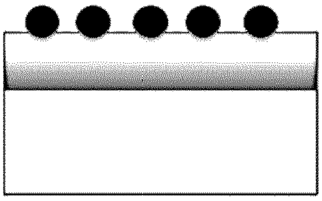

FIG. 4A

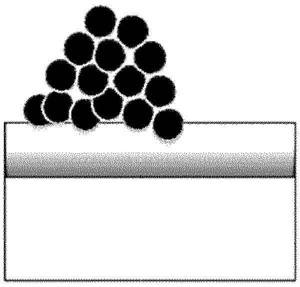

FIG. 4B

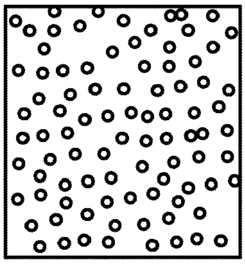

FIG. 5A

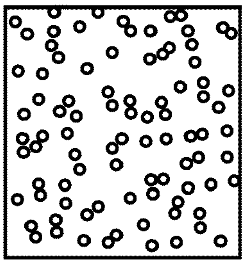

FIG. 5B

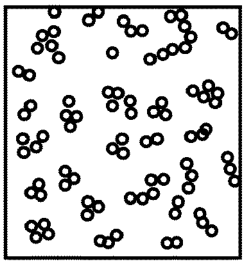

FIG. 5C

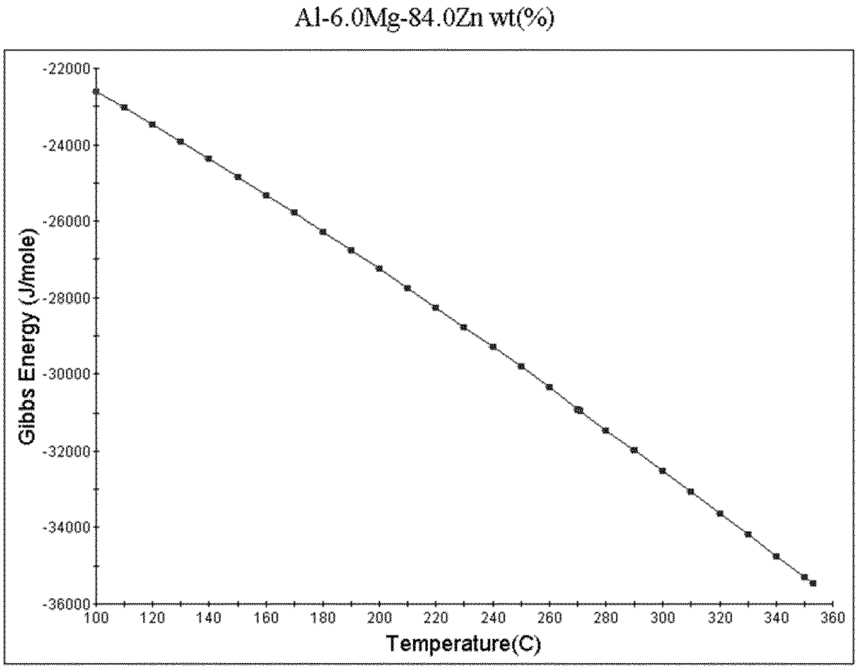
Al-6.0Mg-84.0Zn wt(%)
Gibbs Energy (J/mole)
-22000
-24000
-26000
-28000
-30000
-32000
-34000
-36000
100
120
140
160
180
200
220
240
260
280
300
320
340
360
Temperature(C)

FIG. 6A

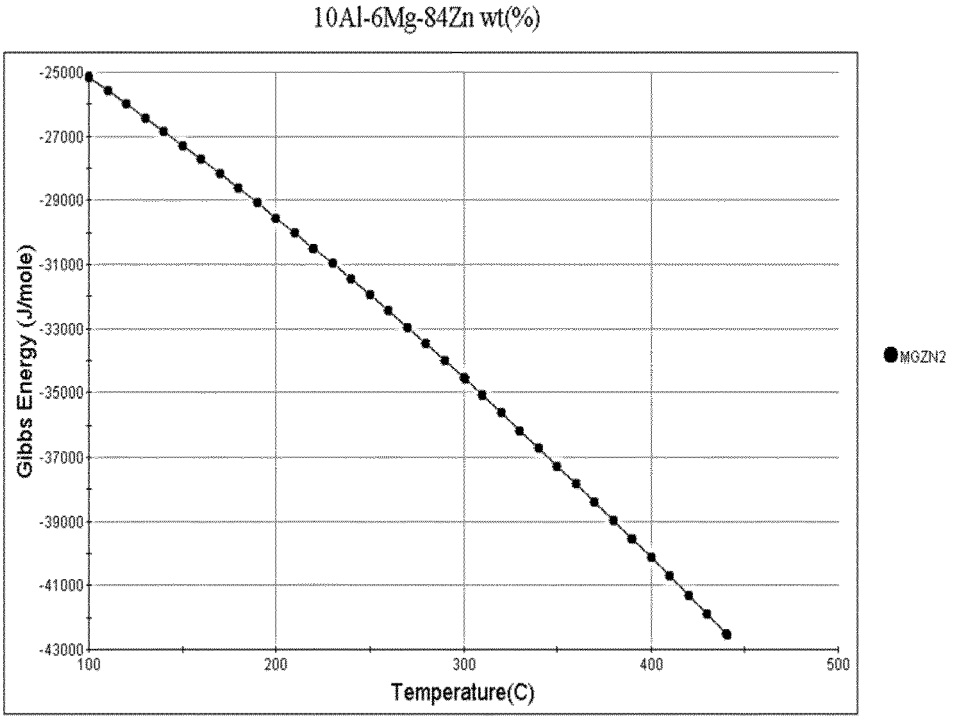
10Al-6Mg-84Zn wt(%)
Gibbs Energy (J/mole)
-25000
-27000
-29000
-31000
-33000
-35000
-37000
-39000
-41000
-43000
100
200
300
400
500
Temperature(C)
MGZN2

FIG. 6B

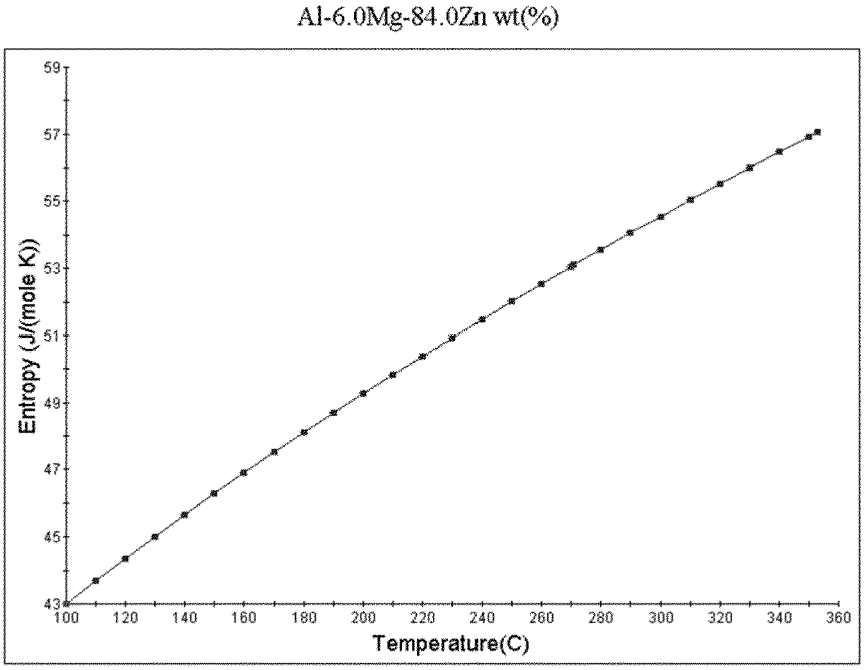
Al-6.0Mg-84.0Zn wt(%)
Entropy (J/(mole K))
59
57
55
53
51
49
47
45
43
100
120
140
160
180
200
220
240
260
280
300
320
340
360
Temperature(C)

FIG. 7A

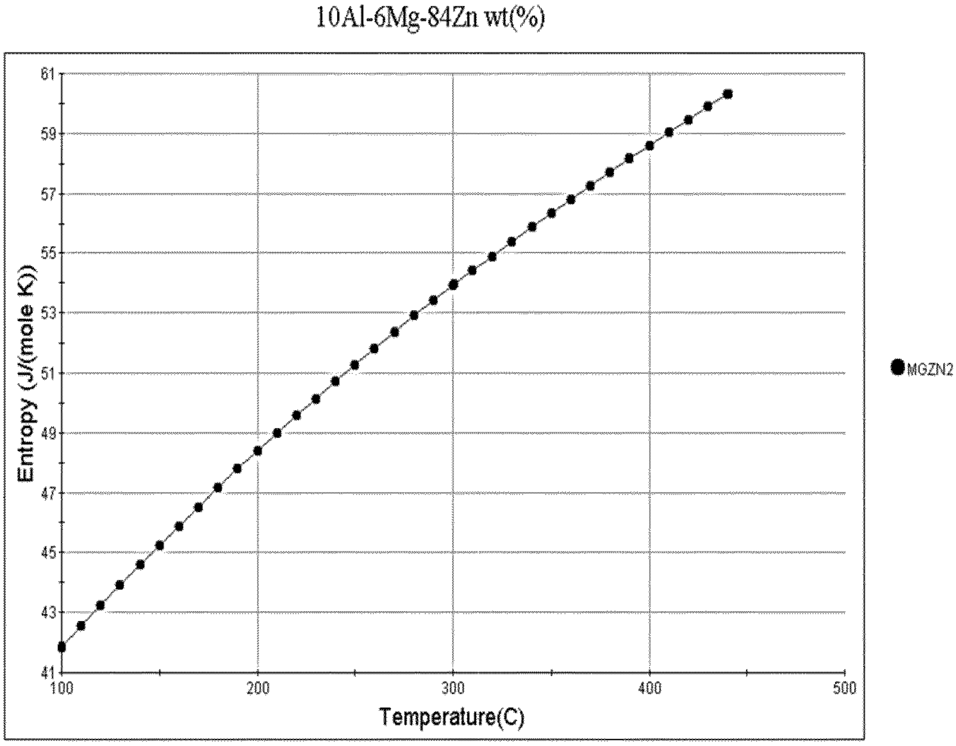
10Al-6Mg-84Zn wt(%)
Entropy (J/(mole K))
61
59
57
55
53
51
49
47
45
43
41
100
200
300
400
500
Temperature(C)
MGZN2

FIG. 7B

Europäisches Patentamt
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EUROPEAN SEARCH REPORT

Application Number
EP 24 16 8982

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 1 109 505 A (GKN SOMERSET WIRE LTD) 10 April 1968 (1968-04-10) * claims 1-9 * -----	1-15	INV. C23C2/06 C23C2/12 C23C2/26 C23C2/28 C23C24/00 C23C24/02 C23C24/04 C23C24/08 C23C24/10 C23C26/00
X	WO 2011/030443 A1 (NAKAMURA HEIHACHI [JP]) 17 March 2011 (2011-03-17) * claims 5, 6, 8; figure 1 * -----	1-15	
A,D	CN 112 680 685 A (NEW METALLURGY HI TECH GROUP CO LTD) 20 April 2021 (2021-04-20) * claims 1-10 * -----	1,2,7	

TECHNICAL FIELDS SEARCHED (IPC)
C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	17 April 2024	Chalaftris, Georgios

CATEGORY OF CITED DOCUMENTS

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L : document cited for other reasons
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& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 24 16 8982

17-04-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1109505 A	10-04-1968	NONE	
WO 2011030443 A1	17-03-2011	NONE	
CN 112680685 A	20-04-2021	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- CN 112680685 A **[0003]**
- KR 960009191 B1 **[0004]**
- JP 04160142 A **[0006]**
- JP 2004107695 A **[0007]**
- JP 4725023 B **[0008]**