(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 471 174 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.12.2024 Bulletin 2024/49

(21) Application number: **24179433.8**

(22) Date of filing: **31.05.2024**

(51) International Patent Classification (IPC):
C23C 10/32 *(2006.01)* ***C23C 10/52*** *(2006.01)*
C23C 10/54 *(2006.01)* ***C23C 10/56*** *(2006.01)*
C23C 10/58 *(2006.01)* ***C23C 10/60*** *(2006.01)*
C23C 30/00 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C23C 10/32; C23C 10/52; C23C 10/54; C23C 10/56; C23C 10/58; C23C 10/60; C23C 30/00

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **31.05.2023 IT 202300011172**

(71) Applicant: **Rina Consulting - Centro Sviluppo Materiali S.p.A.**
00129 Roma (IT)

(72) Inventors:
- **Valle, Roberta**
  00129 Rina Consulting - Centro Sviluppo Materiali S.p.A., Via di Castel Romano 100-102 (IT)
- **Meduri, Angelo**
  00129 Rina Consulting - Centro Sviluppo Materiali S.p.A., Via di Castel Romano 100-102 (IT)
- **Fortunato, Marco**
  00129 Rina Consulting - Centro Sviluppo Materiali S.p.A., Via di Castel Romano 100-102 (IT)
- **Donato, Demetrio Massimiliano**
  00129 Rina Consulting - Centro Sviluppo Materiali S.p.A., Via di Castel Romano 100-102 (IT)

(74) Representative: **Pace Napoleone, Maria et al**
De Simone & Partners S.r.l.
Via Vincenzo Bellini, 20
00198 Roma (IT)

(54) CORROSION RESISTANT COATING

(57) The present invention relates to an aluminium-based coating applied to steel components by means of a "pack cementation" diffusion process to confer anti-corrosion properties and to the process for obtaining said coating.

Description

FIELD OF THE INVENTION

[0001] The present invention relates to an aluminium-based coating applied to steel components, preferably to chromium-molybdenum carbon, by means of Pack Cementation diffusion process to impart anti-corrosion properties. The main intended application is that of biomass boilers, but such a coated material can also be applied in other fields where corrosion resistance plays an important role.

BACKGROUND ART

[0002] Biomass (co)combustion causes degradation phenomena in steel pipes normally applied in coal-fired boilers (SA210 Type A1, SA213 Type T2, T11, T22, T91, 304H and 347H). This results in unplanned outages and increased maintenance expenses in the power generation sector, which cost billions of dollars per year.

[0003] The most promising solutions to avoid these phenomena include: changes in operating conditions, use of advanced materials, use of integrated solutions. Changes in operating conditions are a way to limit corrosion risks, keeping boiler conditions well below those used with clean coal fuels. The disadvantage is that they limit the conversion efficiency. The second solution is the use of advanced materials for boilers, even other than steel. The use of such materials implies a radical change in the field (the boilers currently in use should all be replaced to implement new boilers with these new materials); these are expensive materials; their use requires an international approval process of long duration (due to the strict need for certification of the new materials for the relative application). The third solution is the application of protective coatings on the steel components of existing boilers. This integrated solution ensures an efficient, economical and workable application in the short term (since the basic materials have already known performance). Diffusive coatings are the most suitable for protecting steel components.

[0004] Diffusive processes are thermochemical treatments which enrich a surface layer of the substrate with an element (or a combination of elements) capable of forming a protective layer. A great advantage of diffusion coating treatments is that they are low cost and have easy handling methods, potentially applicable on an industrial scale. The coating process involves exposure to high temperatures. Since the temperature of the heat treatment rarely exceeds 1 100°C, which can be performed in traditional furnaces, the equipment and coating plants do not require large capital investments. Diffusion coatings can be obtained with different methods, such as Pack Cementation and Chemical Vapour Deposition (CVD), but the basic process consists of the same three main steps:

- generating vapours (e.g., vapours containing Al, Cr, Si, B);
- transporting the vapours on the surface of the component to be coated;
- reacting the vapours with the substrate alloy, followed by associated diffusion processes within the alloy.

[0005] Diffusion coatings have a well-established and successful history in coating metal parts. Aluminium-based diffusive coatings are among the most promising and offer good resistance to exposure to high temperatures.

[0006] The properties of the diffusive coatings depend largely on the microstructure and chemical composition of the substrate steel. Therefore, no coating can exist which provides the same performance for all types of steel. Instead, optimal integrated coating/substrate systems must be developed.

[0007] Among the different boiler steels, Cr-Mo Carbon steels and in particular grade K11562 (13CrMo4-5, 1.7335) and K21590 10CrMo9-10 (1.7380) [standard ASTM A213 and DIN EN10216-2] were chosen to be tested. This material is commonly used in boilers. The Cr-Mo steel family (i.e., 12Cr1MoV, 15Mo3, 9CrMo3, and 10CrMo9-10) readily corrodes under high-temperature oxidizing conditions. Therefore, the coating of these substrates is of utmost importance if they are to be used in such environments.

[0008] Regarding the state of the patent art, for example, US3948687 discloses mixtures based on chromic acid and phosphoric acid for obtaining coatings which increase the resistance of steels to particular atmospheric conditions; however, this document does not concern anti-corrosion applications. Furthermore, EP0946784 discloses a method for obtaining diffusive coatings obtained from packs comprising chromium and ferrochrome in combination with ammonium halide and aluminium oxide. In this case, aluminium is used as an oxide, as an inert filler in the composition of the pack.

[0009] The literature lacks a diffusive anti-corrosion aluminium coating on carbon steels, in particular Cr/Mo carbon, such as K11562 (13CrMo4-5, 1.7335), which are used in applications such as boilers. Therefore, the object of the present invention is to eliminate or at least reduce the problems related to the prior art by providing a mixture adapted to obtain an anti-corrosion aluminium diffusion coating and a process for producing said coating on the surface of a steel substrate.

SUMMARY OF THE INVENTION

[0010] An object of the invention is therefore a corrosion-resistant diffusion coating for steel elements, characterized in that said diffusion coating is obtained from a pulverized mixture comprising:

- a metal alloy of Chromium and Aluminium;

- an activator salt, preferably selected from NH_4Cl, NH_4F, in percentage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy; and
- optionally a further activator salt ZrF_4 in percentage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy;

and wherein said mixture comprises between 90-99% of metal alloy.

[0011] Preferably in said pulverized mixture the metal alloy of Chromium and Aluminium contains 65-75% by weight of Cr and 25-35% by weight of Al, preferably said alloy is a Cr 70% and Al 30% alloy.

[0012] Preferably in said pulverized mixture the content of each activator salt in the mixture is comprised between 0.001-0.30% with respect to the percentage content of Aluminium in the alloy, preferably the content of activator salt in said pulverized mixture is about 0.003% with respect to the percentage content of Aluminium in the alloy; preferably the total content of activator salt in said pulverized mixture is comprised between 0.001-0.30% with respect to the percentage content of Aluminium in the alloy, preferably the total content of activator salt in said pulverized mixture is about 0.003% with respect to the percentage content of Aluminium in the alloy.

[0013] Preferably, in the mixture the Chromium and Aluminium metal alloy has a particle size comprised between -10 +4 mm and the activator salt has a particle size comprised between -1 +0.25 mm.

[0014] Preferably the diffusion coating object of the invention is obtained from the pulverized mixture as defined above, where said mixture, prior to diffusion, is dried at a temperature comprised between 50°C and 100°C for times comprised between 1 h and 2 h.

[0015] Preferably, the diffusion coating object of the invention has a thickness comprised between 40 μm and 300 μm.

[0016] A further object of the invention is the diffusion process to obtain a diffusion coating on steel elements where said steel elements are placed inside a reactor and reacted with the mixture as defined above and wherein said process sequentially comprises the following steps:

a) heating step until reaching the final temperature comprised between 900-1100°C, preferably between 900-1010°C, by

- heating ramp comprised between 400-550 °C/h, preferably between 420-500 °C/h; and
- under inert gas flow, preferably Argon or Nitrogen flow, comprised between 0.2-0.3 Nl/min, preferably 0.25 Nl/min;

b) maintenance step where the final temperature reached in step a) is maintained for a time interval comprised between 2 - 10 h, preferably between 2-8 h, preferably for 6 h, and under inert gas flow, preferably Argon or Nitrogen flow, comprised between 0.2-0.3 Nl/min, preferably 0.25 Nl/min;

c) cooling step until reaching room temperature, by

- cooling ramp comprised between 200-700 °C/h, preferably between 250-600 °C/h; and
- under inert gas flow, preferably Argon or Nitrogen flow, comprised between 4-6 Nl/min, preferably 5 Nl/min.

[0017] Optionally said diffusion process further comprises a heat treatment step in which the diffusion-coated steel element obtained at the end of step c) is heat-treated in an inert atmosphere in a temperature range comprised between 650-750°C and a time range comprised between 0.5-3 h.

[0018] Optionally said process comprises, before step a), a step of drying the mixture at a temperature comprised between 50°C and 100°C for times comprised between 1 h and 2 h; preferably the mixture is dried at a temperature of 80°C for times of 1.5 h.

[0019] In a preferred embodiment, the diffusion process is carried out at a pressure comprised between 1020 mbar and 1060 mbar.

[0020] Preferably, the mixture has a particle size for the chromium/aluminium alloy of 2 mm and for the activator salt a particle size of 0.20 mm, the diffusion process is carried out at a pressure of 1040 mbar.

[0021] Preferably the steel elements are placed inside the reactor above the mixture, preferably said steel elements are carbon steel elements, preferably Chromium-Molybdenum carbon. Preferably, said diffusion coating has a thickness comprised between 40 μm and 300 μm.

[0022] A further object of the invention is a steel element comprising the diffusion coating object of the invention, preferably said steel element is selected from Chromium-Molybdenum Carbon steels.

[0023] A further object of the invention is the use of the diffusion coating disclosed above or obtained by the diffusion process disclosed above or the use of the steel element comprising the diffusion coating object of the invention in biomass boilers.

[0024] A further object of the invention relates is a mixture comprising:

- a pulverized Chromium and Aluminium metal alloy, preferably containing 65-75% by weight of Cr and 25-35% by weight of Al, preferably said alloy is a Cr 70% Al 30% alloy;
- an activator salt, preferably selected from NH_4Cl, NH_4F, in percentage by weight comprised between 0.001-5%, preferably between 0.001-0.30% with respect to the percentage content of Al in said alloy, and
- optionally a further activator salt ZrF_4 in percentage by weight comprised between 0.001-5% with respect

to the percentage content of Al in said alloy.

and wherein said mixture comprises between 90-99% of metal alloy.

[0025] Preferably said mixture comprises:

- a pulverized Chromium and Aluminium metal alloy containing 65-75% by weight of Cr and 25-35% by weight of Al, preferably said alloy is a Cr 70% Al 30% alloy;
- an activator salt selected from NH_4Cl, NH_4F, in percentage by weight comprised between 0.001-0.30% with respect to the percentage content of Al in said alloy, and
- optionally a further activator salt ZrF_4 in percentage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy, and wherein said mixture comprises between 90-99% of metal alloy.

[0026] Preferably the coating object of the invention is used for carbon steel elements, preferably Carbon Cr-Mo and in particular grade K11562 (13CrMo4-5, 1.7335) and K21590 10CrMo9-10 (1.7380) [standard ASTM A213 and DIN EN10216-2].

[0027] These and other aspects of the present invention will become more apparent by reading the following description of some preferred embodiments disclosed, and in consideration of the following figures:

Figure 1. Optical microscope analysis (after chemical attack with Nital **ASTM E407**) of: (left) Example 1; (right) Example 6.

Figure 2. Optical microscope analysis (after chemical attack with Nital **ASTM E407**) of: (left) Example 6 before exposure; (centre) Example 6 after exposure to corrosive environment; (right) K11562 (13CrMo4-5, 1.7335) after exposure to corrosive environment. Marker 2500 μm.

Figure 3. SEM-EDS analysis after exposure to the corrosive environment of Example 6.

Figure 4. Optical microscope analysis (after chemical attack with Nital) of Example 7: (left) before and (right) after post-deposition heat treatment.

Figure 5. Optical microscope analysis of Example 8 at various magnifications.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention provides an anti-corrosion coating on metallic materials in accordance with the claims. The present invention relates to an aluminium diffusion coating obtained by means of a pack cementing process having the following parameters:

- a source of aluminium, e.g., Cr(70)Al(30) alloy pellet;
- an activator, e.g., NH4C, NH4F in the range 0.001-5% by weight with respect to the nominal Al content, preferably about 0.003% by weight (thus in the case of Cr(70)Al(30) pellets about 0.001% by weight with respect to the alloy), a possible further activator salt containing ZrF_4 in a percentage by weight comprised between 0.001-5% with respect to the percentage of Al content in said alloy;
- inert atmosphere (nitrogen or argon);
- heating ramp speed in the range 400-600 °C/h, preferably 500 °C/h;
- stasis temperature comprised between 850 and 1050°C, preferably 950°C;
- stasis temperature time comprised between 2 and 10 h, preferably 6 h;
- cooling ramp rate in the range 200-800 °C/h, preferably 600 °C/h;
- a possible post-deposition heat treatment in an inert environment with stasis temperature comprised between 650-750 °C, preferably 700 °C, and a time interval between 0.5-3 h, preferably 2 h.

[0029] In the pack cementation procedure, the surface of the components to be treated is first cleaned to remove oxides and contaminants. The areas of the component to be protected from the deposition process are suitably masked. The components are then placed in a mixture (pack) placed inside a reactor, sealed or semi-sealed, consisting of an aluminium source such as a Cr and Al alloy, and an activator salt, and any salt containing a reactive element (e.g., ZrF_4). The reactor is then placed inside a furnace and heated under an inert atmosphere. In the above-the-pack mode, the components to be coated are positioned above the mixture inside a reactor. The vapours generated inside the pack reach both the external and internal surfaces of the components to be coated, managing to coat the internal passages as well.

[0030] The term mixture or pack, as used herein indifferently, refers to a composition comprising at least the aluminium source and the activator salt, according to the invention.

[0031] In the examples reported herein, the mixture used was, prior to diffusion, dried at a temperature of about 80°C for times of about 1.5 h. Furthermore, the mixture has a particle size for the chromium/aluminium alloy of 7 mm and for the activator salt an average particle size of 0.50 mm. Preferably in the diffusion process the pressure varies over time and on average the process is carried out at a pressure of 1050 mbar.

[0032] Now, the present invention will be disclosed by means of the following non-limiting examples

EXAMPLES

Example 1.

[0033] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) of NH_4F was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 950 °C with a ramp-up of 500 °C/h and with a flow of Ar 0.25 Nl/min. The system was maintained at 950°C and with the same argon flow for 6 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of Ar 5.0 Nl/min. The obtained coating has an average thickness of 85 μm.

Example 2.

[0034] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4Cl (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 904 °C with a ramp-up of 500 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 904°C and with the same argon flow for 3 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of N_2 5.0 Nl/min. The obtained coating has an average thickness of 70 μm.

Example 3.

[0035] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4F (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 904 °C with a ramp-up of 500 °C/h and with a flow of Ar 0.25 Nl/min. The system was maintained at 904°C and with the same argon flow for 8 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of Ar 5.0 Nl/min. The obtained coating has an average thickness of 95 μm.

Example 4.

[0036] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4F (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 1009 °C with a ramp-up of 500 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 1009°C and with the same argon flow for 3 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of N_2 5.0 Nl/min. The obtained coating has an average thickness of 210 μm.

Example 5

[0037] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4F (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 1009 °C with a ramp-up of 500 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 1009°C and with the same argon flow for 8 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of N_2 5.0 Nl/min. The obtained coating has an average thickness of 250 μm. **Figure 2** and **Figure 3** show how the presence of the coating protects the degradation of the steel in a corrosive environment. After exposure, the diffusive aluminium-based coating remained intact and protected the steel.

Example 6

[0038] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4F (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K11562 (13CrMo4-5, 1.7335) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 950 °C with a ramp-up of 420 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 950°C and with the same argon flow for 6 h. After that, the system was cooled to room temperature with a ramp-down of 250 °C/h and with N_2 flow 5.0 Nl/min. The obtained coating has an average thickness of 165 μm.

Example 7

[0039] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets and 1.00 g of NH_4F (0.0033% by weight with respect to aluminium; 0.001% by weight with respect to alloy) was placed in a semi-sealed container, in Inconel, with diameter 200 mm and height 35 mm (volume about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K21590 10CrMo9-10 (1.7380) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 950 °C with a ramp-up of 420 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 950°C and with the same argon flow for 6 h. After that, the system was cooled to room temperature with a ramp-down of 250 °C/h and with flow of N_2 5.0 Nl/min. Finally, the system was subjected to a post-deposition heat treatment in an inert environment at 700 °C for 2 h. The obtained coating has an average thickness of 90 μm. **Figure 4** illustrates the further positive effect on the microstructure of this coating after post-deposition heat treatment.

Example 8

[0040] A pack consisting of 1,000.00 g of Cr(70)Al(30) alloy pellets, 1.00 g of NH_4F (0.0033% by weight with respect to the aluminium; 0.001% by weight with respect to the alloy) and 1.64 g of ZrF_4 (0.0055% by weight with respect to the aluminium; 0.0016% by weight with respect to the alloy) was placed in a semi-sealed container, in Inconel, with a diameter of 200 mm and a height of 35 mm (volume of about 1.1 litres). An Inconel grid is positioned above the pack and the steel specimens K21590 10CrMo9-10 (1.7380) were positioned on this grid in the above-the-pack mode. The container was then covered and placed inside the Pack Cementation apparatus, where it was brought to a temperature of 1009 °C with a ramp-up of 500 °C/h and with a flow of N_2 0.25 Nl/min. The system was maintained at 1009°C and with the same argon flow for 3 h. After that, the system was cooled to room temperature with a ramp-down of 600 °C/h and with flow of N_2 5.0 Nl/min. Finally, the system was subjected to a post-deposition heat treatment in an inert environment at 700 °C for 2 h. The obtained coating has an average thickness of 95 μm. **Figure 5** shows the positive features of this coating obtained in the presence of activator salt with Zr inside the pack.

[0041] Figure 1 compares Example 1 with Example 6, the main difference of which is the temperature ramp (500 °C/h up and 600 °C/h down for Example 1; 420 °C/h up and 250 °C/h down for Example 6), which therefore shows how the final thickness of the coating is influenced by the temperature ramp: a faster ramp (as in the case of Example 1) leads to a coating of thickness 85 μm; a slower ramp (as in the case of Example 6) leads to a coating of thickness 165 μm.

[0042] Figure 2 and Figure 3 show images of samples after exposure in a corrosive environment (consisting of CO_2, SO_2, O_2, H_2O, HCl, N_2), at temperatures above 500 °C for about 800 h.

[0043] In particular, Figure 2 compares three samples, a coated sample before the exposure (on the left); the same coated sample after the exposure (in the middle) and a coated uncoated sample (on the right) after such exposure: it can be noticed how the uncoated sample is very degraded as a result of corrosion, while the coated sample maintains its original shape and it is possible to see a layer of coating surrounding the entire section. Figure 3 shows an enlargement of this last section of the coated sample, showing how the thickness of the aluminized sample remains intact, adhered and uniform. The absence of cracks or corrosion points is also further evidence that the underlying steel has been preserved from corrosion phenomena. The SEM-EDS analysis shows that the aluminized layer is still active and has an aluminium concentration such as to allow it to be used for a long time under the same corrosion conditions (while the uncoated sample is already sufficiently degraded to be considered for replacement). In conclusion, the presence of the coating protects the degradation of the steel in a corrosive environment.

[0044] Figure 4 illustrates the effect of the post-deposition heat treatment on the microstructure.

[0045] Figure 5 shows the coating in the presence of activator salt with Zr inside the pack.

[0046] Furthermore, during the course of the present invention the samples were exposed to a corrosive environment (consisting, for example, of CO_2, SO_2, O_2, H_2O, HCl, N_2), at temperatures above 500 °C.

Claims

1. Corrosion-resistant diffusion coating for steel elements, **characterized in that** said diffusion coating is obtained from a pulverized mixture comprising:

   - a Cr and Al metal alloy containing 65-75% by weight Cr and 25-35% by weight Al;
   - an activator salt selected from NH_4Cl and NH_4F, in a percentage by weight comprised between 0.001-0.30% with respect to the percentage content of Al in said alloy; and
   - optionally a further activator salt ZrF_4 in percentage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy;

   and wherein said mixture comprises between 90-99% of metal alloy.

2. Corrosion-resistant diffusion coating according to claim 1, wherein said metal alloy is a Cr 70% and Al 30% alloy.

3. Corrosion-resistant diffusion coating according to any one of the preceding claims, wherein the activator salt content in the mixture is about 0.003% of the percentage Al content in the alloy.

4. Corrosion-resistant diffusion coating according to any one of the preceding claims, wherein in the mixture the metal alloy of Cr and Al has a particle size comprised between -10 +4 mm and the activator salt has a particle size comprised between -1 +0.25 mm.

5. Corrosion-resistant diffusion coating according to any one of the preceding claims, wherein prior to diffusion, the mixture is dried at a temperature comprised between 50°C and 100°C for times comprised between 1 h and 2 h.

6. Corrosion-resistant diffusion coating according to any one of the preceding claims, having a thickness comprised between 40 μm and 300 μm.

7. Process for obtaining a diffusion coating on steel elements, wherein said steel elements are placed inside a reactor and reacted with the mixture according to any one of claims 1 to 4, optionally dried at a temperature comprised between 50°C and 100°C for times between 1 h and 2 h, and wherein said process sequentially comprises the following steps:

a) heating step until reaching the final temperature comprised between 900-1100°C, preferably between 900-1010°C, by

- heating ramp comprised between 400-550 °C/h, preferably between 420-500 °C/h; and
- under inert gas flow, preferably Argon or Nitrogen flow, comprised between 0.2-0.3 Nl/min, preferably 0.25 Nl/min;

b) maintenance step where the final temperature reached in step a) is maintained for a time interval comprised between 2 - 10 h, preferably between 2-8 h, preferably for 6 h, and under inert gas flow, preferably Argon or Nitrogen flow, comprised between 0.2-0.3 Nl/min, preferably 0.25 Nl/min;

c) cooling step until reaching room temperature, by

- cooling ramp comprised between 200-700 °C/h, preferably between 250-600 °C/h; and
- under inert gas flow, preferably Argon or Nitrogen flow, comprised between 4-6 Nl/min, preferably 5 Nl/min; and optionally

d) a heat treatment step in which the diffusion-coated steel element obtained at the end of step c) is heat-treated in an inert atmosphere in a temperature range comprised between 650-750°C and a time range comprised between 0.5-3 h.

8. Process according to claim 7, wherein the diffusion process is carried out at a pressure comprised between 1020 mbar and 1060 mbar.

9. Process according to claim 7 or 8, wherein the steel elements are placed inside the reactor above the mixture according to any one of claims 1 to 4, preferably said steel elements are carbon steel elements, preferably Chromium-Molybdenum carbon.

10. Process according to claims 7 to 9, wherein said diffusion coating has a thickness comprised between 40 μm and 300 μm.

11. Steel element comprising the coating according to any one of claims 1 to 6, preferably said steel element is selected from Chromium-Molybdenum Carbon steels.

12. Use of the diffusion coating according to any one of claims 1 to 6 or obtained by the process according to any one of claims 7 to 10 or use of the steel element according to claim 11 in biomass boilers.

13. Mixture comprising:

- a pulverized Chromium and Aluminium metal alloy, preferably containing 65-75% by weight of Cr and 25-35% by weight of Al, preferably said alloy is a Cr 70% Al 30% alloy;
- an activator salt, preferably selected from NH_4Cl, NH_4F, in percentage by weight comprised between 0.001-5%, preferably between 0.001-0.30% with respect to the percentage content of Al in said alloy, and
- optionally a further activator salt ZrF_4 in percentage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy, and wherein said mixture comprises between 90-99% of metal alloy.

14. The mixture according to claim 13 comprising:

- a pulverized Chromium and Aluminium metal alloy containing 65-75% by weight of Cr and 25-35% by weight of Al, preferably said alloy is a Cr 70% Al 30% alloy;
- an activator salt selected from NH_4Cl, NH_4F, in percentage by weight comprised between 0.001-0.30% with respect to the percentage content of Al in said alloy, and
- optionally a further activator salt ZrF_4 in per-

centage by weight comprised between 0.001-5% with respect to the percentage content of Al in said alloy, and wherein said mixture comprises between 90-99% of metal alloy.

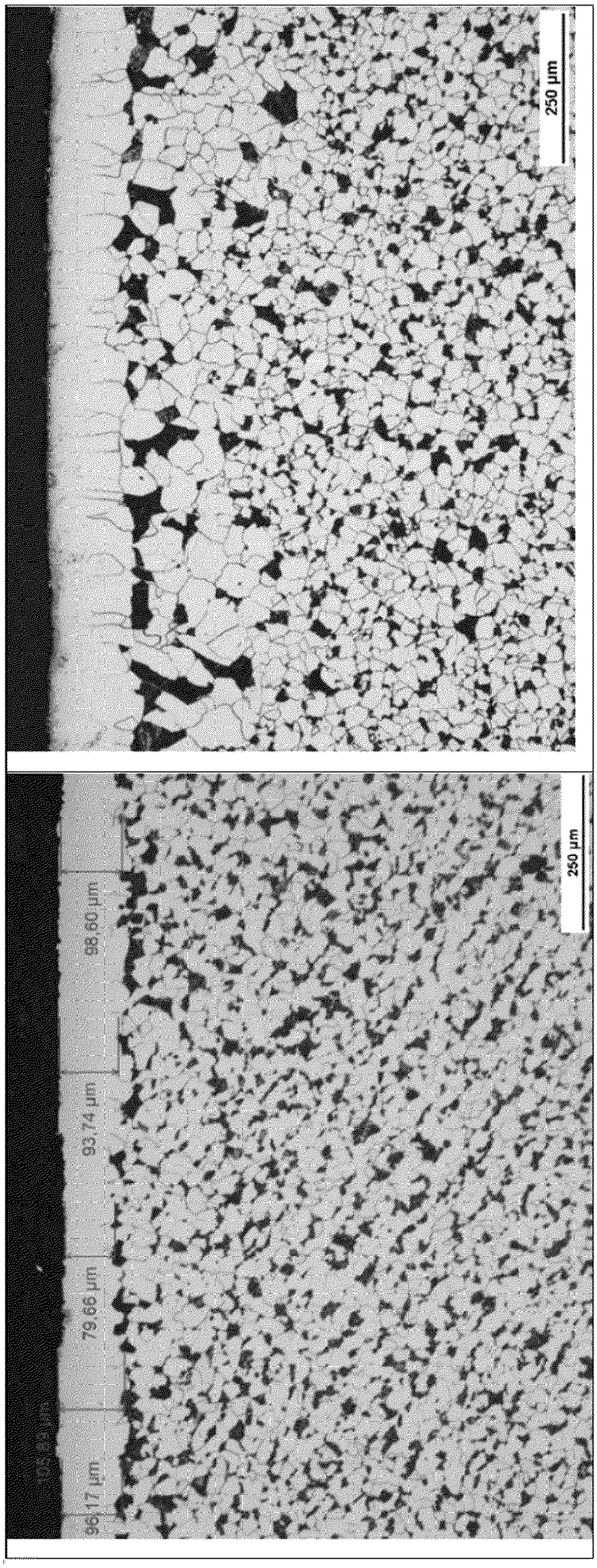


Fig. 1

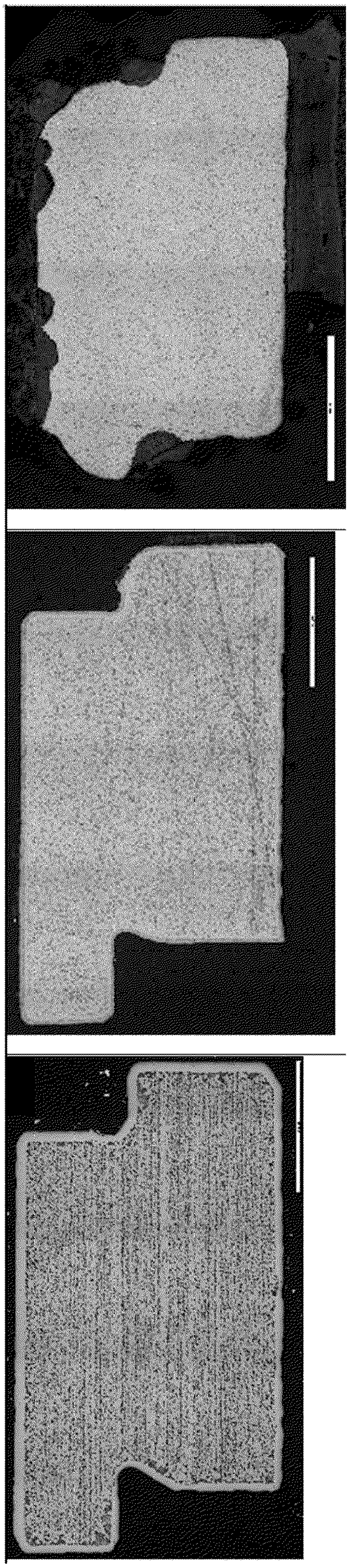
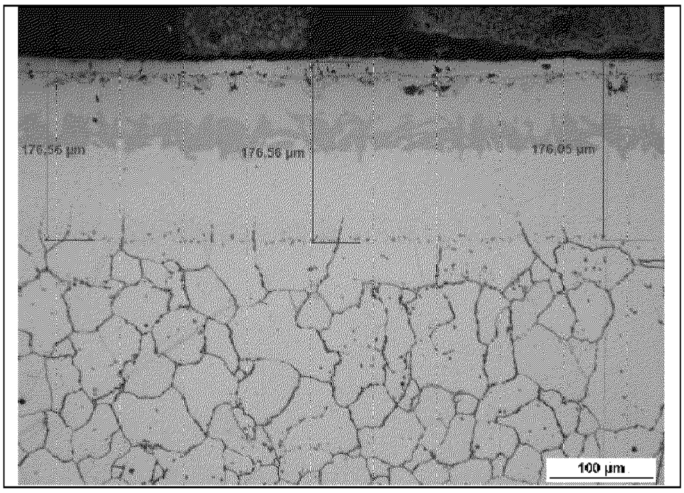
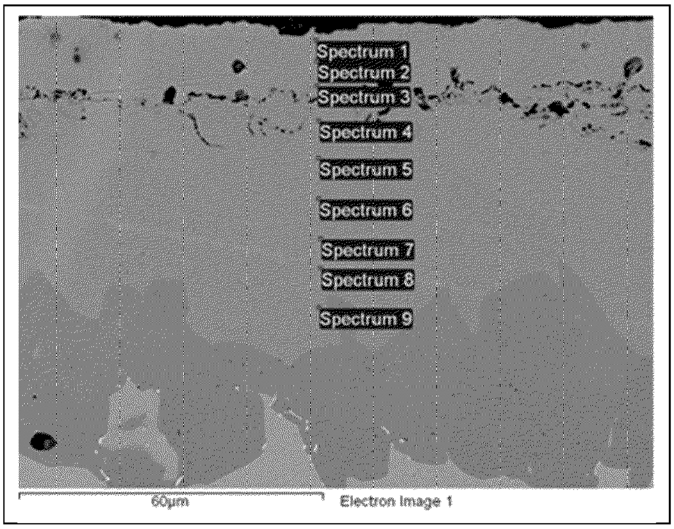


Fig. 2





	Al	Cr	Fe	Mo
1	13.67	0.43	85.90	
2	14.13	0.76	85.11	
3	13.80	0.50	85.70	
4	14.33	0.45	85.22	
5	13.54	0.77	85.69	
6	13.80	0.73	85.47	
7	13.54	0.62	85.83	
8	13.16	0.68	86.16	
9	12.78	0.60	85.53	1.09

Fig. 3

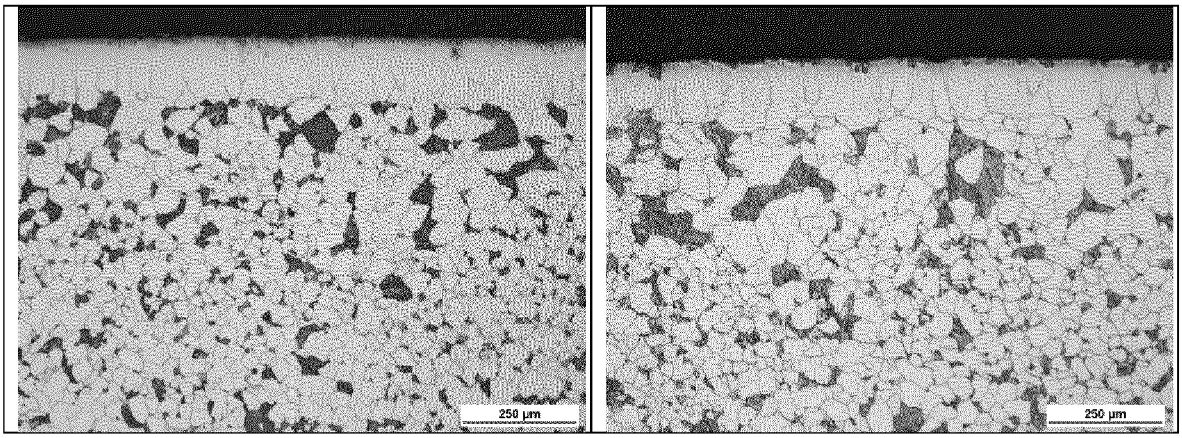


Fig. 4.

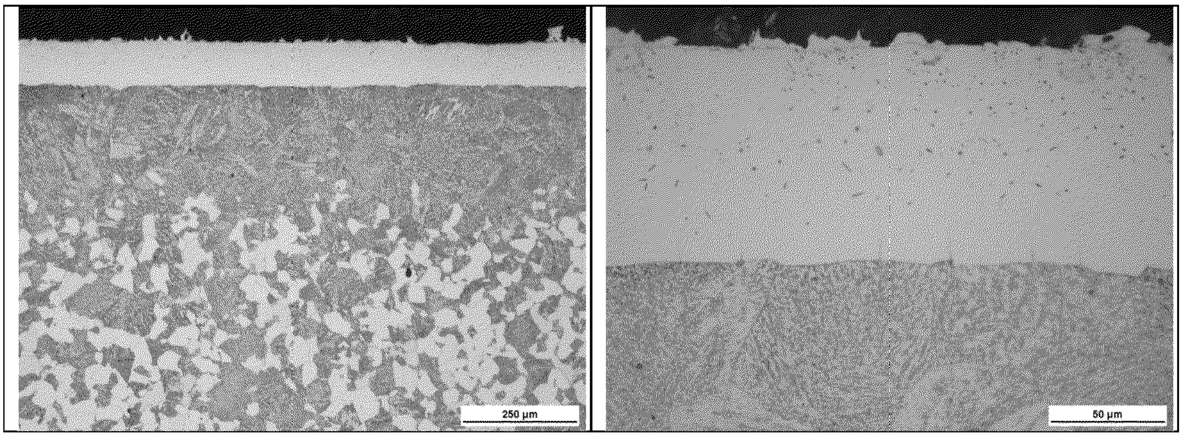


Fig. 5.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 24 17 9433

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	EP 0 294 987 A1 (EXXON RESEARCH ENGINEERING CO [US]) 14 December 1988 (1988-12-14)	1-6, 11-14	INV. C23C10/32 C23C10/52 C23C10/54 C23C10/56 C23C10/58 C23C10/60 C23C30/00
A	* columns 3, 9-11; claims 1-11 *	7-10	
A	GB 236 033 A (PERCY FRANCIS SUMMERS) 2 July 1925 (1925-07-02) * claims 1-2 *	1-14	
A	EP 0 690 145 A1 (SUMITOMO ELECTRIC INDUSTRIES [JP]) 3 January 1996 (1996-01-03) * claims 1-7 *	1-14	

TECHNICAL FIELDS SEARCHED (IPC)

C23C

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	3 July 2024	Chalaftris, Georgios

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 24 17 9433

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-07-2024

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0294987	A1	14-12-1988	CA	1324918	C	07-12-1993
			DE	3883857	T2	05-01-1994
			EP	0294987	A1	14-12-1988
			JP	2567456	B2	25-12-1996
			JP	S6456861	A	03-03-1989
			US	4835010	A	30-05-1989
GB 236033	A	02-07-1925	NONE			
EP 0690145	A1	03-01-1996	CA	2152216	A1	29-12-1995
			DE	69504433	T2	06-05-1999
			EP	0690145	A1	03-01-1996
			JP	3567488	B2	22-09-2004
			JP	H0813129	A	16-01-1996
			KR	100209342	B1	15-07-1999
			US	5582867	A	10-12-1996
			US	5803991	A	08-09-1998

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

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3948687 A **[0008]**
- EP 0946784 A **[0008]**