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(54) Conversion coating process for magnesium alloys

Umwandlungsbeschichtungsverfahren für Magnesiumlegierungen

Procédé de revêtement par conversion pour alliages de magnésium

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EP 2 944 707 B1

Description

FIELD OF THE INVENTION

[0001] The present invention is related to an improved phosphate-permanganate based conversion treatment for corrosion protection of Mg alloys, to the obtained protected Mg alloys substrates, its use for manufacturing parts, said parts, and to the solutions used for forming the protective coating.

BACKGROUND OF THE INVENTION

[0002] Mg-based alloys present a unique corrosion protection challenge. Unlike other active light metals, such as Al and Ti, Mg alloys do not form a naturally passivating oxide film. Upon atmospheric exposure, Mg rapidly develops oxide/hydroxide/carbonate films. These films are porous, poorly bonded and inhomogeneous, and unable to provide satisfactory protection to the underlying metal against corrosion. One of the most effective ways to improve the corrosion resistance of Mg alloys is to form a coating on the surface to isolate the base material from the environment, by acting as a functional barrier layer. The coating may also form a good base for subsequent organic coatings, like paints. Several surface coating treatment techniques have been developed, among which chemical conversion treatment represents an effective, comparatively low-cost and easily implemented method, which has been widely adopted in industrial processes. In the conversion coating process, the substrate to be protected is immersed in a solution that reacts with the surface, altering the metal ion concentration and the pH at the metal-solution interface. The localized change in composition causes precipitation from the solution onto the surface of the substrate, forming the coating.

[0003] A commonly used low cost corrosion resistance treatment for magnesium alloys is a dichromate based conversion coating. While it provides good corrosion protection, it is based on hexavalent chromium, which exerts harmful effects on the environment and human physiology. To overcome this serious drawback, many alternative chromate-free chemical conversion treatments have been developed. For example document US 2002/0174915 discloses a surface treating method, which comprises contacting a suitably pre-treated magnesium alloy substrate with a chemical conversion reagent comprising phosphate ion and permanganate ion and a pH value between 1.5 and 7. ES 2 178 917 discloses another method in which after a pre-treatment the Mg alloy substrate is contacted with an aqueous solution comprising alkaline metal permanganate and an alkaline metal phosphate, like potassium permanganate and sodium phosphate.

[0004] CN 1388270A discloses a surface treatment method of Mg alloys with a Cr-free conversion coating solution providing corrosion resistance and adhesion.

[0005] Although many methods have been developed, none of them is at present completely satisfactory in terms of corrosion protection if compared to the Cr-based ones. Thus, there is still the need in the state of the art of providing an alternative conversion coating process which provides good corrosion resistance and good adhesion for subsequent coatings.

DETAILED DESCRIPTION OF THE FIGURES

[0006]

Figure 1: Conversion coating according to the invention (left) and Cr-Mn reference (right) over EV31 A Mg alloy after 168 hrs in salt spray fog (SSF)

Figure 2: Conversion coating according to the invention (left) and Cr-Mn reference (right) over EV31 A Mg alloy, post-treated with resin + primer after 1500 hrs in SSF

Figure 3: AZ91 Mg alloy treated with a conversion coating according to the invention + resin + primer after 2000 hrs in SSF. Left: sample placed in SSF chamber as is. Right: sample with artificial damage

Figure 4: images from EV31A magnesium alloy after being submitted to the process of the invention with the chemical conversion coating solution, CC1 (left), and with the not according to the invention chemical conversion coating solution, CC2 (right).

Figure 5: Energy-dispersive X-ray spectroscopy (EDS) analysis of a EV31A sample treated with CC1

Figure 6: EDS analysis of a EV31A sample treated with CC2

DETAILED DESCRIPTION OF THE INVENTION

[0007] In one aspect the present invention relates to a process for surface treating a magnesium alloy, which comprises the following steps, carried out in the following sequence:

- (i) blasting a magnesium alloy substrate,
- (ii) degreasing the substrate,
- (iii) pickling the substrate,
- (iv) activating the substrate,
- (v) contacting the substrate with a chemical conversion coating solution according to claim 1 comprising potassium permanganate and sodium phosphate and calcium nitrate and yttrium nitrate. The present inventors have surprisingly found that this process,

hereinafter the process of the invention, results in a significantly improved corrosion protection for magnesium alloys.

[0008] In principle any magnesium alloy can be surface treated according to the process of the invention. In a preferred embodiment the Mg alloy is one selected from EV31A, AZ91 and AM60. In order to insure that the process of the invention achieves a homogenous covering of the substrate's surface and an improved overall performance of the resulting coated substrate, a pre-treatment comprising the combination of above mentioned steps (i) to (iv) in this sequence, is crucial.

[0009] The step of blasting is carried out to remove possible impurities present on the Mg alloy substrate. In a particular embodiment, blasting is carried out using alumina F-220 or F-500 (aluminium oxide particles of different sizes). After blasting, any remaining powder can be removed by conventional means such as with compressed air.

[0010] The step of degreasing in practice is not particularly restricted and can be carried out with any alkaline solution. In a preferred embodiment degreasing is carried out in alkaline solution, preferably hot, of sodium hydroxide or an alkaline cleaner such as Oakite®90 to remove oil from the surface. The substrate is generally treated by dipping it in the hot solution. The hot solution is usually at a temperature comprised between 70 and 90 °C, and in a particular embodiment at a temperature of 80 °C. Dipping times vary depending on the nature of the solution, the temperature, and the substrate but are typically comprised between 1 and 10 min. In a particular embodiment degreasing is carried out with an alkaline cleaner, like Oakite®90. In another particular embodiment degreasing is carried out with NaOH. Typical concentrations of Oakite®90 in the alkaline hot solution are between 60 and 70 g/L, and in a particular embodiment 65 g/L. When NaOH is used, typical concentrations are between 2.0 and 3.0 M, in a particular embodiment 2.5 M.

[0011] Pickling is carried out to remove surface impurities and contaminants. Pickling is carried out with an aqueous acidic solution. In a particular embodiment a phosphoric acid solution is used, and more particularly phosphoric acid is used in a concentration comprised between 10-85 wt%. In a more preferred embodiment, phosphoric acid is used in an amount of 25 wt%. The pickling step takes usually between 1 and 60 sec depending for example on the acid concentration. In a particular embodiment pickling takes 15 sec. Pickling may be carried out at temperatures preferably in the range from room temperature to 50°C to avoid surface damage.

[0012] The activating of the substrate is carried out with a solution of ammonium bifluoride or hydrofluoric acid. The substrate is generally treated by immersing it in the solution. In a particular embodiment activating is carried out with ammonium bifluoride. In a more particular embodiment ammonium bifluoride is present in a concentration of between 25 and 75 g/L, like for example 50 g/L.

In another particular embodiment activating is carried out with HF. According to a more particular embodiment HF is used in a concentration of between 9 and 15 wt%, like for example 12 wt%. Activating is typically carried out at room temperature for times usually comprised between 1 and 30 minutes. In a particular embodiment activation takes 10 min.

[0013] The chemical conversion coating solution comprises potassium permanganate, sodium phosphate, calcium nitrate and yttrium nitrate in concentrations according to claim 1. This chemical conversion coating solution, hereinafter also referred to as CC1 comprises between 0.1 and 0.3 M potassium permanganate, preferably between 0.15 and 0.25 M, and more preferably 0.2 M, and between 0.01 and 0.2 M sodium phosphate, preferably between 0.05 and 0.15 M, and more preferably 0.1 M. CC1 further comprises calcium nitrate and yttrium nitrate. Calcium nitrate is present in an amount of between 1.0 and 5 g/L in CC1, preferably between 1.5 and 3.5 g/L. Examples of calcium nitrate concentrations in CC1 are, 2 g/L, 2.5 g/L and 3.0 g/L. Yttrium nitrate is in an amount of between 1.5 and 5 g/L, preferably between 1.5 and 3.5 g/L. Examples of yttrium nitrate concentrations in CC1 are 2 g/L, 2.5 g/L and 3.0 g/L.

[0014] It is to be noted that all possible combinations of the particular or preferred ranges, subranges and examples for CC1 above disclosed are to be considered as individually disclosed embodiments in the present application. In a particularly preferred embodiment the chemical conversion coating solution comprises 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2 g/L of yttrium nitrate. According to an embodiment not according to the invention the chemical conversion coating solution, also referred in this description as CC2, comprises potassium permanganate, sodium phosphate, calcium nitrate and sodium vanadate. CC2 comprises between 0.1 and 0.3 M potassium permanganate, preferably between 0.15 and 0.25 M, and more preferably 0.2 M, and between 0.01 and 0.2 M sodium phosphate, preferably between 0.05 and 0.15 M, and more preferably 0.1 M. CC2 further comprises calcium nitrate and sodium vanadate. Calcium nitrate is present in a particular embodiment in an amount of between 1.0 and 5 g/L in CC2, preferably between 1.5 and 3.5 g/L. Examples of calcium nitrate concentrations in CC2 are 2 g/L, 2.5 g/L and 3.0 g/L. Sodium vanadate is present in a particular embodiment in an amount of between 1.5 and 5 g/L, preferably between 1.5 and 3.5 g/L. Examples of sodium vanadate concentrations in CC2 are 2 g/L, 2.5 g/L and 3.0 g/L.

[0015] It is to be noted that all possible combinations of the particular or preferred ranges, subranges and examples for CC2 above disclosed are to be considered as individually disclosed embodiments in the present application. In a particularly preferred embodiment the chemical conversion coating solution comprises 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2.5 g/L of sodium vanadate.

[0016] The pH of the chemical conversion coating solution CC1 or CC2 is adjusted to a pH comprised between 2.5 and 5, preferably to pH between 2.8 and pH 4.0 such as for example pH 3.0 in a particular embodiment, or pH 3.5. Adjustment is usually carried out with an acid, like phosphoric acid.

[0017] The substrate is contacted with the chemical conversion coating solution for times which may vary depending on the substrate, the chemical composition of the solution, the pH, and the temperature at which contact takes place. In a particular embodiment the substrate is contacted at room temperature. Contact is usually carried out by immersing the activated substrate in the chemical conversion coating solution.

[0018] The process of the invention may further comprise steps of washing and rinsing the substrate in a conventional manner, such as with deionized water, between the degreasing and the pickling step and/or between the pickling and the activating step and /or between the activating and the contacting step (v). Washing and rising may be carried out each time once or more times.

[0019] The process optionally further comprises rinsing the coated substrate obtained after step (v) with deionized water and ethanol; drying in a conventional manner, such as with hot air and storing the coated substrate in a controlled atmosphere without humidity. As it is used in the present invention, a controlled atmosphere without humidity refers to the conditions found for example in a sealed container filled with silica beads to absorb excess humidity.

[0020] In another aspect the present invention relates to a magnesium alloy substrate obtained according to the process of the invention. According to a particular embodiment the magnesium alloy is selected from the group from EV31A, AZ91 and AM60. In a more particular embodiment the Mg alloy is EV13A. Figure 4 shows images from this alloy after being submitted to the process of the invention with the chemical conversion coating solution, CC1 (left), and with the chemical conversion coating solution not according to the invention CC2 (right). Figure 5 shows the Energy-dispersive X-ray spectroscopy (EDS) analysis of the EV13A alloy after being submitted to the process of the invention with CC1. Figure 6 shows the Energy-dispersive X-ray spectroscopy (EDS) analysis of the EV13A alloy after being submitted to the process not according to the invention with CC2. In both Figures 5 and 6 Mg from the Mg alloy is observed. F is detected which comes from the treatment with HF and/or NH_4HF_2 ; P is detected originating from the phosphate component of CC1 and CC2. Ca, from the calcium nitrate used as additive in both CC1 and CC2, is also detected. V is detected in Figure 6 as it is used as additive in CC2. Nd although in small concentration, is also detected as it is part of the EV31A alloy. However, the inventors have also noticed that the presence of a Nd peak also corresponds to particles which are on the coating of the substrate, hence it probably forms compounds with other elements. Y is not visible in the spectra for the sample

treated with CC1. According to the inventors, this is probably due to the fact that the amount of yttrium in the coating is quite low, and/or because one of the peaks expected for yttrium is at 14.9eV, hence out of the measurement range.

[0021] Since the process of the invention imparts the Mg alloy with very good properties as it is explained further below, the substrates find application in a broad range of fields, such as the aerospace and automotive sectors.

[0022] In this sense a further aspect of the invention relates to the use of the magnesium alloy substrate of the invention for manufacturing a part for use in the aerospace and automotive sectors. Part as used herein refers to any part (item, element, piece, etc.) conventionally used in these sectors and made using magnesium alloy materials such as for example transmission gears for helicopters.

[0023] In another aspect the invention relates thus, to a part for use in the aerospace or automotive sector comprising the magnesium alloy substrate of the invention.

[0024] In a further aspect the invention relates to a chemical conversion coating solution for use in the process of the invention. The chemical conversion coating solution according to claim 13 comprises potassium permanganate, sodium phosphate, calcium nitrate and yttrium nitrate. This chemical conversion coating solution CC1 comprises between 0.1 and 0.3 M potassium permanganate, preferably between 0.15 and 0.25 M, and more preferably 0.2 M, and between 0.01 and 0.2 M sodium phosphate, preferably between 0.05 and 0.15 M, and more preferably 0.1 M. CC1 further comprises of calcium nitrate and yttrium nitrate. Calcium nitrate is present in an amount of between 1.0 and 5 g/L in CC1, preferably between 1.5 and 3.5 g/L. Examples of calcium nitrate concentrations in CC1 are, 2 g/L, 2.5 g/L and 3.0 g/L. Yttrium nitrate is in an amount of between 1.5 and 5 g/L, preferably between 1.5 and 3.5 g/L. Examples of yttrium nitrate concentrations in CC1 are 2 g/L, 2.5 g/L and 3.0 g/L..

[0025] As already stated above, it has to be remarked that all possible combinations of the particular or preferred ranges, subranges and examples for CC1 above disclosed are to be considered as individually disclosed embodiments in the present application. In a particularly preferred embodiment the chemical conversion coating solution comprises 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2 g/L of yttrium nitrate. According to an example not according to the invention the chemical conversion coating solution, CC2, comprises potassium permanganate, sodium phosphate, calcium nitrate and sodium vanadate. CC2 comprises between 0.1 and 0.3 M potassium permanganate, preferably between 0.15 and 0.25 M, and more preferably 0.2 M, and between 0.01 and 0.2 M sodium phosphate, preferably between 0.05 and 0.15 M, and more preferably 0.1 M. CC2 further comprises calcium nitrate and sodium vanadate. Calcium nitrate is present in a par-

ticular embodiment in an amount of between 1.0 and 5 g/L in CC2, preferably between 1.5 and 3.5 g/L. Examples of calcium nitrate concentrations in CC2 are 2 g/L, 2.5 g/L and 3.0 g/L. Sodium vanadate is present in a particular embodiment in an amount of between 1.5 and 5 g/L, preferably between 1.5 and 3.5 g/L. Examples of sodium vanadate concentrations in CC2 are 2 g/L, 2.5 g/L and 3.0 g/L.

[0026] It is to be noted that all possible combinations of the particular or preferred ranges, subranges and examples for CC2 above disclosed are to be considered as individually disclosed embodiments in the present application.

[0027] In a particularly preferred embodiment the chemical conversion coating solution comprises 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2.5 g/L of sodium vanadate.

[0028] The pH of the chemical conversion coating solution CC1 or CC2 is adjusted to a pH comprised between 2.5 and 5, preferably to pH between 2.8 and pH 4.0 such as for example pH 3.0 in a particular embodiment, or pH 3.5. Adjustment is usually carried out with an acid, like phosphoric acid.

[0029] The process of the invention provides a magnesium alloy substrate with a reproducible conversion coating with good appearance and surface morphology. The magnesium alloy substrate of the invention has been evaluated and the results obtained were compared to those achieved by treating the same magnesium alloy with a standard Cr-Mn coating as reference.

The magnesium alloy substrate of the invention was analysed according to the following testing procedures:

Testing procedures

Appearance

[0030] The appearance of both the conversion treated samples and the conversion treated and permanent resin and primer coated samples are evaluated by means of visual inspection.

Composition and morphology

[0031] The surface composition and morphology of the samples treated with the conversion coatings are determined using optical microscopy and Scanning Electron Microscopy (SEM, JEOL JSM 5910 LV) coupled with an energy dispersive X-ray (EDS) analyser (INCA), taking into account the following parameters: uniformity, grade of coverage of the substrate, defects and grain morphology.

Mild environment corrosion testing

[0032] The corrosion resistance of the conversion treated and oiled samples to the effects of a warm and humid atmosphere, is evaluated by means of mild envi-

ronment corrosion testing according to MIL STD 810-Method 507.4 standard.

[0033] The humidity tests is carried out at 60°C and 95%RH following the procedure described in Section 4.5.2 of MIL STD 810-Method 507.4 standard. The procedure consists of 10 cycles of 48 hours and the samples are exposed in the climatic chamber for about 500 hours.

Salt spray fog (SSF) environment corrosion testing

[0034] The corrosion resistance of the conversion treated and primer coated samples is evaluated by means of neutral salt spray fog corrosion testing according to the ASTM B117 standard.

[0035] According to Section 8.1 and 10.1 of ASTM B117 standard, the salt solution consists of 5 ± 1 parts of NaCl in 95 parts by mass of deionised water and the temperature in the exposure zone shall be maintained at 35 ± 2 °C. The samples are supported at an inclination 60° from the vertical, in agreement with some aeronautic specifications. *Samples with conversion coating only:* The corrosion performance of the conversion treated samples is evaluated after exposure to SSF for approximately 168 hours in order to compare them with the reference samples.

[0036] *Samples treated with conversion coating, resin and primer:* Both unscribed and scribed samples are tested. The scribe is performed following the indications of Section 5.1 of ASTM D1654 standard. The corrosion resistance of the samples treated with conversion coating, resin and primer is evaluated after 2000-hours exposure in SSF chamber. The unscribed samples are evaluated taking into account the presence and quantity of pits of corrosion and blisters on the surface. The scribed samples are also evaluated taking into account the following parameters: presence of corrosion products, blisters, lifts and coating curling in the scribe.

Adhesion

[0037] The adhesion of the conversion coatings to the above mentioned resin and primer is evaluated by means of cross-cut tape adhesion tests, following the indications of Section 6 in the ISO 2409 standard.

[0038] The corrosion resistance of substrates submitted to the process of the invention and oiled, in mild environment (10 cycles of 48 hours each at 95% of RH and temperature interval between 20°C and 60°C) is very good, and comparable to that of the Cr-Mn reference samples after completion of the test, as they passed 500 hours of exposure without showing signs of corrosion.

[0039] The substrates treated with the conversion coating only (e.g., without resin and primer) also show a very good corrosion performance, and even significantly better than the Cr-Mn reference samples after 168 hours of exposure to the salt spray fog (SSF) (see Fig. 1). The results are especially good when the chemical conversion coating solution CC1 is used.

[0040] Regarding the salt spray test for the substrates submitted to the process of the invention, and then coated with resin and primer, both CC₁ (according to the invention) and CC2 (not according to the invention) conversion coatings provide good corrosion protection, comparable to that provided by the Cr-Mn reference treatment after 1500 hours of SSF exposure (see Fig. 2). This effect was observed in the fully covered surfaces (no corrosion attack was evident after 2000 hours of SSF exposure) and around the artificial damage areas (where the corrosion of the base metal did not progress further) (see Fig. 3). Overall, the CC1 and CC2 treated samples passed 2000 hours of exposure without showing evident signs of corrosion.

[0041] The process of the invention also imparts the Mg alloy with good adhesion of organic coatings such as the primer and the resin mentioned in the invention.

[0042] The process of the present invention is illustrated below by reference to the examples, which are intended to be only illustrative and are not construed to limit the present invention in any way.

EXAMPLES

Example 1: Process for surface treating a EV31A magnesium alloy with a chemical conversion coating solution CC1 and obtaining a coated substrate

[0043] A EV31A Mg alloy was first blasted using alumina F-220 or F-500 to remove impurities present on the magnesium alloy substrate. The remaining powder was then removed with compressed air. The degreasing step was carried out with an alkaline hot solution at 80 °C of Oakite 90 (65 g/L) for 5 minutes by dipping the substrate in the solution while stirring. The substrate was rinsed thereafter with deionized water.

[0044] Pickling was thereafter carried out by mild acid treatment with phosphoric acid (25%) at room temperature during 15 seconds. The substrate was rinsed thereafter with deionized water. Activation was done by immersing the substrate in a solution of ammonium bifluoride (50 g/L) at room temperature during 10 min. The substrate was rinsed thereafter with deionized water.

[0045] A chemical conversion coating solution CC1 was prepared by adding directly the additives to a phosphate-permanganate batch comprising 0.2 M KMnO₄ and 0.1 M Na₃PO₄ in an amount of 2 g/L of Ca(NO₃)₂ and 2 g/L of Y(NO₃)₃. The pH was adjusted to pH 3 with phosphoric acid.

[0046] The substrate was immersed in the CC1 solution at room temperature.

[0047] Afterwards, the substrate was washed with deionized water and ethanol, dried with hot air, and stored under controlled atmosphere without humidity.

Example 2: not according to the invention: Process for surface treating a EV31A magnesium alloy with a chemical conversion coating solution CC2 and obtaining a coated substrate

[0048] A EV31A Mg alloy was first blasted using alumina F-220 or F-500 to remove impurities present on the magnesium alloy substrate. The remaining powder was then removed with compressed air. The degreasing step was carried out with an alkaline hot solution at 80 °C of Oakite 90 (65 g/L) for 5 minutes by dipping the substrate in the solution while stirring. The substrate was rinsed thereafter with deionized water.

[0049] Pickling was thereafter carried out by mild acid treatment with phosphoric acid (25%) at room temperature during 15 seconds. The substrate was rinsed thereafter with deionized water. Activation was done by immersing the substrate in a solution of ammonium bifluoride (50 g/L) at room temperature during 10 min. The substrate was rinsed thereafter with deionized water.

[0050] A chemical conversion coating solution CC2 was prepared by adding directly the additives to a phosphate-permanganate batch comprising 0.2 M KMnO₄ and 0.1 M Na₃PO₄ in an amount of 2 g/L of Ca(NO₃)₂ and 2.5 g/L of NaVO₃. The pH was adjusted to pH 3 with phosphoric acid.

[0051] The substrate was immersed in the CC2 solution at room temperature.

[0052] Afterwards, the substrate was washed with deionized water and ethanol, dried with hot air, and stored under controlled atmosphere without humidity.

Example 3: performance of the treated substrates

[0053] Both substrates treated according to Examples 1 and 2 (hereinafter the samples) were tested in terms of coating appearance; evaluation of composition and morphology; mild environment corrosion resistance; salt fog corrosion resistance; and resin and primer adhesion according to the procedures described above.

[0054] Samples obtained according to Examples 1 and 2 were also conventionally coated with commercial resins and primers (both chromium-free) used in aeronautic sectors, in order to check the overall performance in terms of corrosion protection. The resin and the primer were applied using a conventional air spray gun. The resin was applied to a final thickness of 10-15 µm. Subsequently, one layer of primer was applied to satisfy the thickness requirements (15-30 µm) and then cured at room temperature for 7 days.

Claims

1. A process for surface treating a magnesium alloy which comprises the following steps, carried out in the following sequence:

- (i) blasting a magnesium alloy substrate,
(ii) degreasing the substrate,
(iii) pickling the substrate,
(iv) activating the substrate,
(v) contacting the substrate with a chemical conversion coating solution comprising between 0.1 and 0.3 M potassium permanganate, between 0.01 and 0.2 M sodium phosphate, between 1.0 and 5 g/L calcium nitrate and between 1.5 and 5 g/L yttrium nitrate, and a pH comprised between 2.5 and 5 .
2. A process according to claim 1 wherein the magnesium alloy is EV31A, AZ91 or AM60.
3. A process according to claim 1 or 2, wherein blasting is carried out with alumina F-220 or F-500.
4. A process according to any one of claims 1 to 3, wherein degreasing is carried out in alkaline solution of sodium hydroxide or alkaline cleaner.
5. A process according to any one of claims 1 to 4, wherein pickling is carried out with phosphoric acid.
6. A process according to any one of claims 1 to 5, wherein activating is carried out with a solution of ammonium bifluoride or hydrofluoric acid.
7. A process according to any one of claims 1 to 6, wherein the chemical conversion coating solution comprises 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2 g/L of yttrium nitrate.
8. A process according to claim 7, in which the pH of the chemical conversion coating solution is comprised between pH 2.5 and pH 5.0 and adjusted with phosphoric acid.
9. A process according to any one of claims 1 to 8, further comprising washing and rinsing the coated substrate obtained after step (v) with deionized water and ethanol, drying and storing the coated substrate in a controlled atmosphere without humidity.
10. A magnesium alloy substrate obtained according to the process of any one of previous claims.
11. Use of the magnesium alloy substrate according to claim 10, for manufacturing a part for use in the aerospace and automotive sectors.
12. A part for use in the aerospace or automotive sector comprising a magnesium alloy substrate according to claim 10.
13. A chemical conversion coating solution comprising between 0.1 and 0.3 M potassium permanganate, between 0.01 and 0.2 M sodium phosphate, between 1.0 and 5 g/L calcium nitrate and between 1.5 and 5 g/L yttrium nitrate and a pH comprised between 2.5 and 5.
14. A chemical conversion coating solution according to claim 13, comprising, 0.2 M potassium permanganate, 0.1 M sodium phosphate, 2 g/L of calcium nitrate and 2 g/L of yttrium nitrate.
15. A chemical conversion coating solution according to any one of claims 13 or 14, which pH is pH 3.0.

Patentansprüche

1. Verfahren zur Oberflächenbehandlung einer Magnesiumlegierung, das die folgenden Schritte, durchgeführt in der folgenden Reihenfolge, umfasst:
- (i) Strahlen eines Magnesiumlegierungssubstrats,
(ii) Entfetten des Substrats,
(iii) Beizen des Substrats,
(iv) Aktivieren des Substrats,
(v) Inkontaktbringen des Substrats mit einer chemischen Umwandlungsbeschichtungslösung, umfassend zwischen 0,1 und 0,3 M Kaliumpermanganat, zwischen 0,01 und 0,2 M Natriumphosphat, zwischen 1,0 und 5 g/l Calciumnitrat und zwischen 1,5 und 5 g/l Yttriumnitrat, und einen zwischen 2,5 und 5 liegenden pH-Wert.
2. Verfahren nach Anspruch 1, wobei die Magnesiumlegierung EV31A, AZ91 oder AM60 ist.
3. Verfahren nach Anspruch 1 oder 2, wobei das Strahlen mit Aluminiumoxid F-220 oder F-500 durchgeführt wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Entfetten in einer alkalischen Lösung von Natriumhydroxid oder eines alkalischen Reinigers durchgeführt wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei das Beizen mit Phosphorsäure durchgeführt wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das Aktivieren mit einer Lösung von Ammoniumhydroxidfluorid oder Flusssäure durchgeführt wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, wobei die chemische Umwandlungsbeschichtungslösung 0,2 M Kaliumpermanganat, 0,1 M Natriumphosphat, 2 g/L Calciumnitrat und 2 g/L Yttriumnitrat umfasst.

8. Verfahren nach Anspruch 7, wobei der pH-Wert der chemischen Umwandlungsbeschichtungslösung zwischen pH 2,5 und pH 5,0 liegt und mit Phosphorsäure eingestellt wird.
9. Verfahren nach einem der Ansprüche 1 bis 8, weiterhin umfassend Waschen und Spülen des nach Schritt (v) erhaltenen beschichteten Substrats mit deionisiertem Wasser und Ethanol, Trocknen und Lagern des beschichteten Substrats in einer kontrollierten Atmosphäre ohne Feuchtigkeit.
10. Magnesiumlegierungssubstrat, erhalten gemäß dem Verfahren nach einem der vorangehenden Ansprüche.
11. Verwendung des Magnesiumlegierungssubstrats nach Anspruch 10, zur Herstellung eines Teils zur Verwendung im Luft- und Raumfahrtsektor und Automobilsektor.
12. Teil zur Verwendung im Luft- und Raumfahrtsektor oder Automobilsektor, umfassend ein Magnesiumlegierungssubstrat nach Anspruch 10.
13. Chemische Umwandlungsbeschichtungslösung, umfassend zwischen 0,1 und 0,3 M Kaliumpermanganat, zwischen 0,01 und 0,2 M Natriumphosphat, zwischen 1,0 und 5 g/L Calciumnitrat und zwischen 1,5 und 5 g/L Yttriumnitrat und einen zwischen 2,5 und 5 liegenden pH-Wert.
14. Chemische Umwandlungsbeschichtungslösung nach Anspruch 13, umfassend 0,2 M Kaliumpermanganat, 0,1 M Natriumphosphat, 2 g/L Calciumnitrat und 2 g/L Yttriumnitrat.
15. Chemische Umwandlungsbeschichtungslösung nach einem der Ansprüche 13 oder 14, deren pH-Wert pH 3,0 ist.

Revendications

1. Procédé de traitement de surface d'un alliage de magnésium qui comprend les étapes suivantes, mises en oeuvre selon la séquence suivante :
 - (i) grenaillage d'un substrat en alliage de magnésium,
 - (ii) dégraissage du substrat,
 - (iii) décapage du substrat,
 - (iv) activation du substrat,
 - (v) mise en contact du substrat avec une solution de revêtement à conversion chimique comprenant entre 0,1 et 0,3 M de permanganate de potassium, entre 0,01 et 0,2 M de phosphate de sodium, entre 1,0 et 5 g/L de nitrate de calcium

et entre 1,5 et 5 g/L de nitrate d'yttrium, et un pH compris entre 2,5 et 5.

2. Procédé selon la revendication 1 dans lequel l'alliage de magnésium est EV31A, AZ91 ou AM60.
3. Procédé selon la revendication 1 ou 2, dans lequel le grenaillage est mis en oeuvre avec de l'alumine F-220 ou F-500.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le dégraissage est mis en oeuvre dans une solution alcaline d'hydroxyde de sodium ou un agent nettoyant alcalin.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le décapage est mis en oeuvre avec de l'acide phosphorique.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'activation est mise en oeuvre avec une solution de bifluorure d'ammonium ou d'acide fluorhydrique.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la solution de revêtement à conversion chimique comprend 0,2 M de permanganate de potassium, 0,1 M de phosphate de sodium, 2 g/L de nitrate de calcium et 2 g/L de nitrate d'yttrium.
8. Procédé selon la revendication 7, dans lequel le pH de la solution de revêtement à conversion chimique est compris entre pH 2,5 et pH 5,0 et est ajusté à l'aide d'acide phosphorique.
9. Procédé selon l'une quelconque des revendications 1 à 8, comprenant en outre le lavage et le rinçage du substrat revêtu obtenu après l'étape (v) à l'eau désionisée et à l'éthanol, le séchage et le stockage du substrat revêtu dans une atmosphère contrôlée sans humidité.
10. Substrat en alliage de magnésium obtenu par le procédé selon l'une quelconque des revendications précédentes.
11. Utilisation du substrat en alliage de magnésium selon la revendication 10, pour la fabrication d'une pièce destinée à être utilisée dans les secteurs de l'aviation et de l'automobile.
12. Pièce pour son utilisation dans le secteur de l'aviation ou de l'automobile comprenant un substrat en alliage de magnésium selon la revendication 10.
13. Solution de revêtement à conversion chimique comprenant entre 0,1 et 0,3 M de permanganate de potassium, entre 0,01 et 0,2 M de phosphate de so-

dium, entre 1,0 et 5 g/L de nitrate de calcium et entre 1,5 et 5 g/L de nitrate d'yttrium et un pH compris entre 2,5 et 5.

14. Solution de revêtement à conversion chimique selon la revendication 13, comprenant 0,2 M de permanganate de potassium, 0,1 M de phosphate de sodium, 2 g/L de nitrate de calcium et 2 g/L de nitrate d'yttrium.

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15. Solution de revêtement à conversion chimique selon l'une quelconque des revendications 13 ou 14, dont le pH est pH 3,0.

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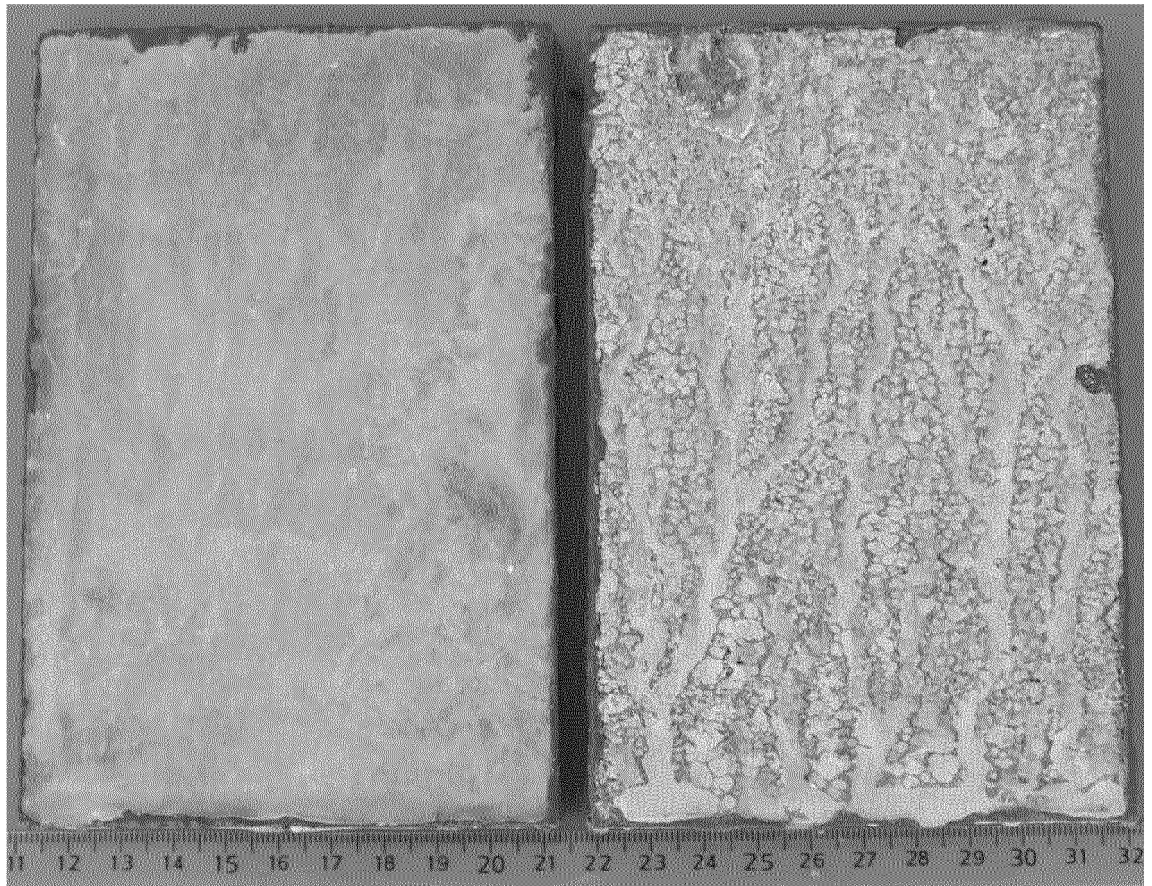


FIG. 1

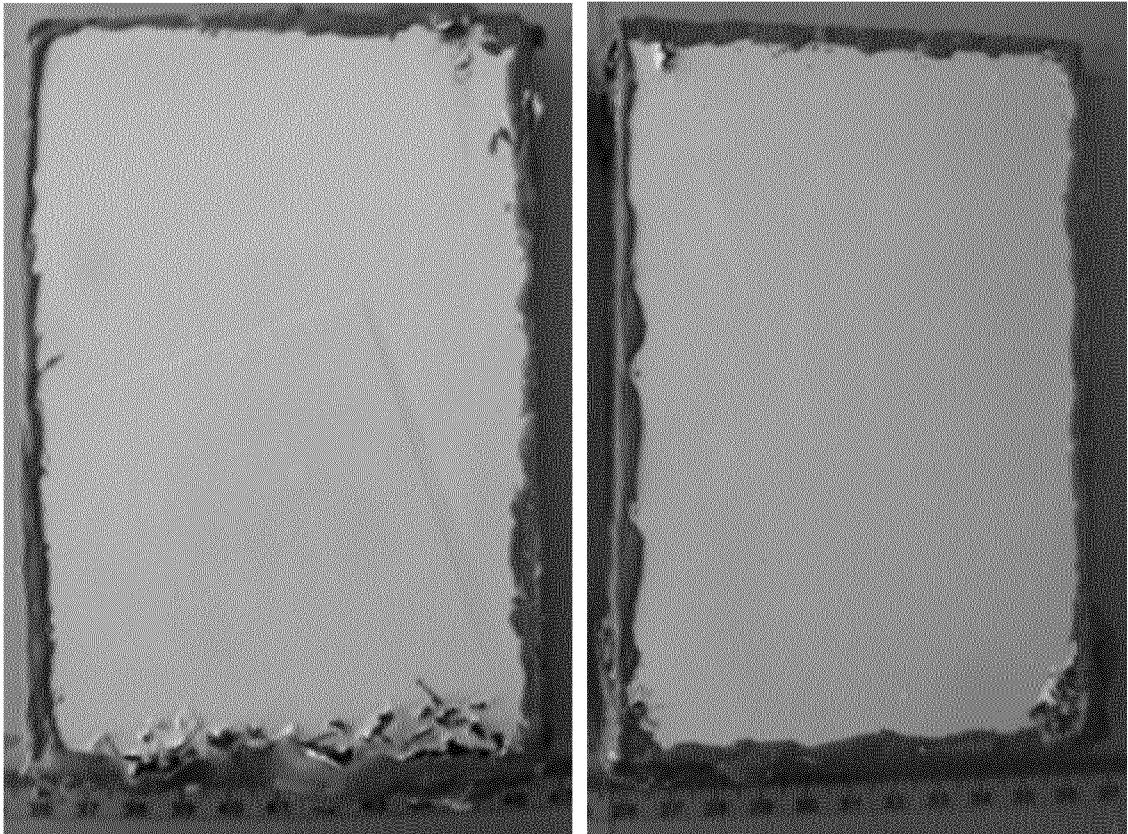


FIG. 2

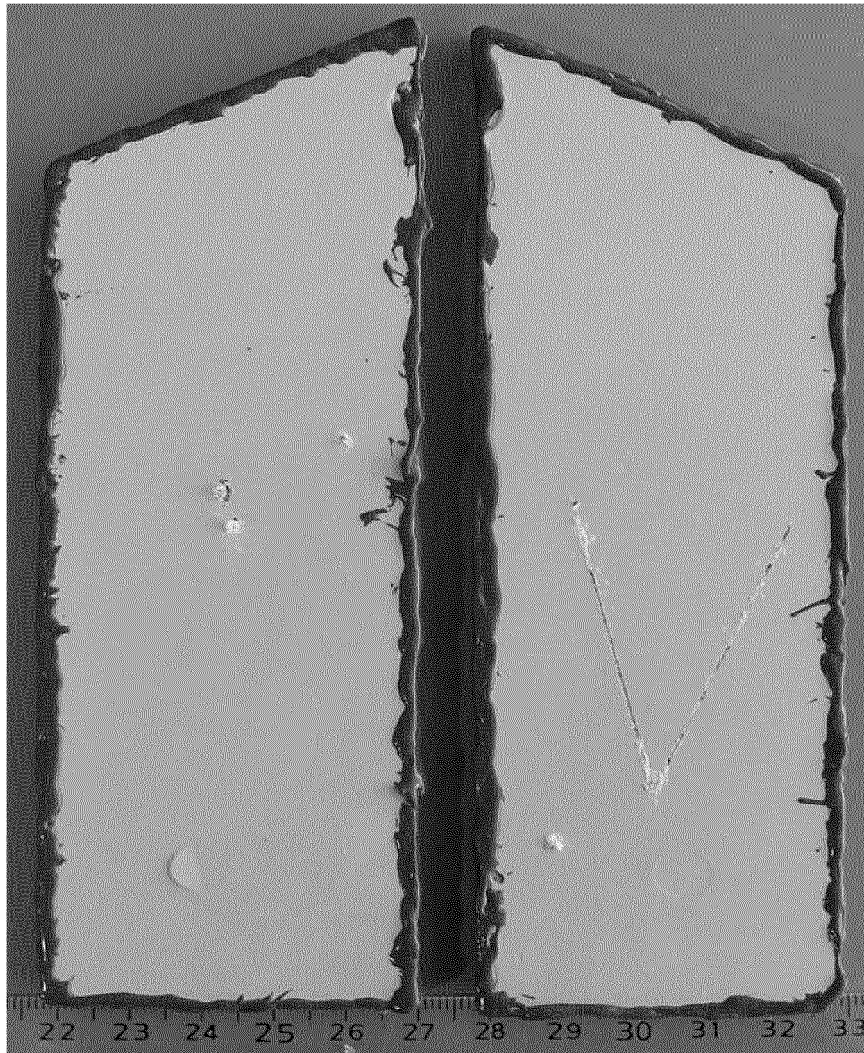


FIG. 3

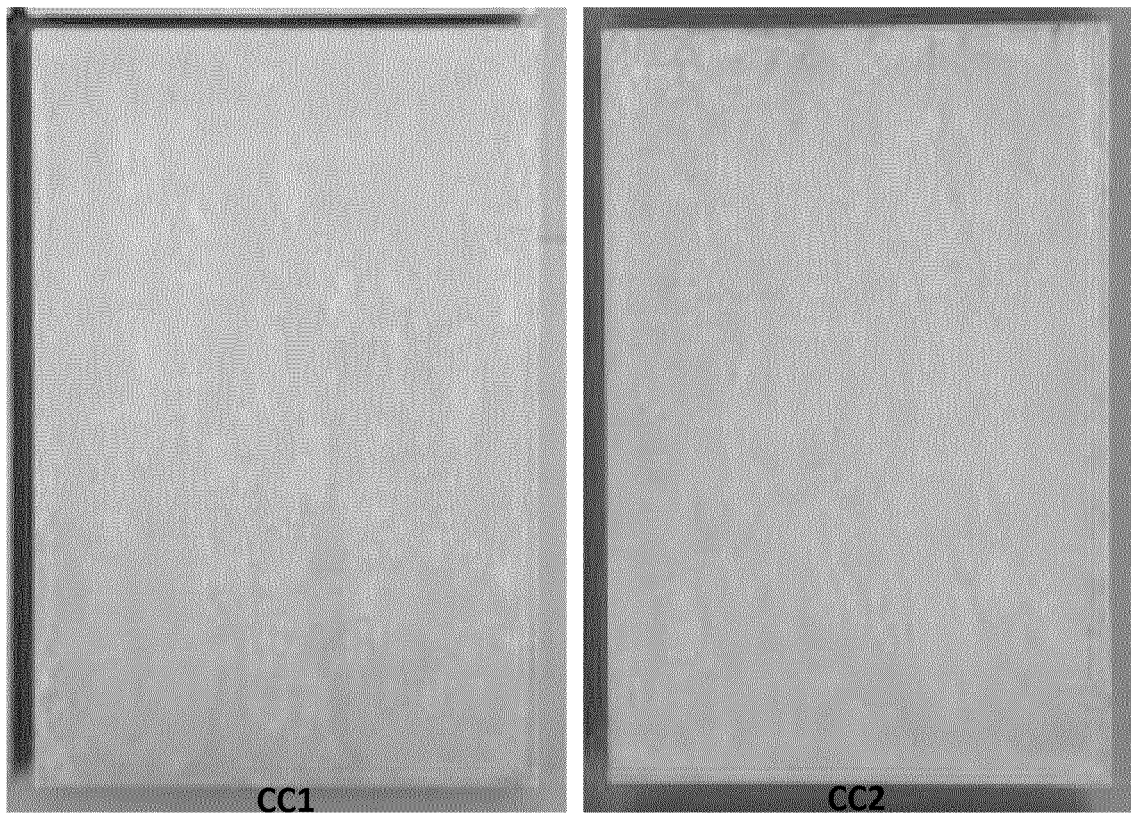


FIG. 4

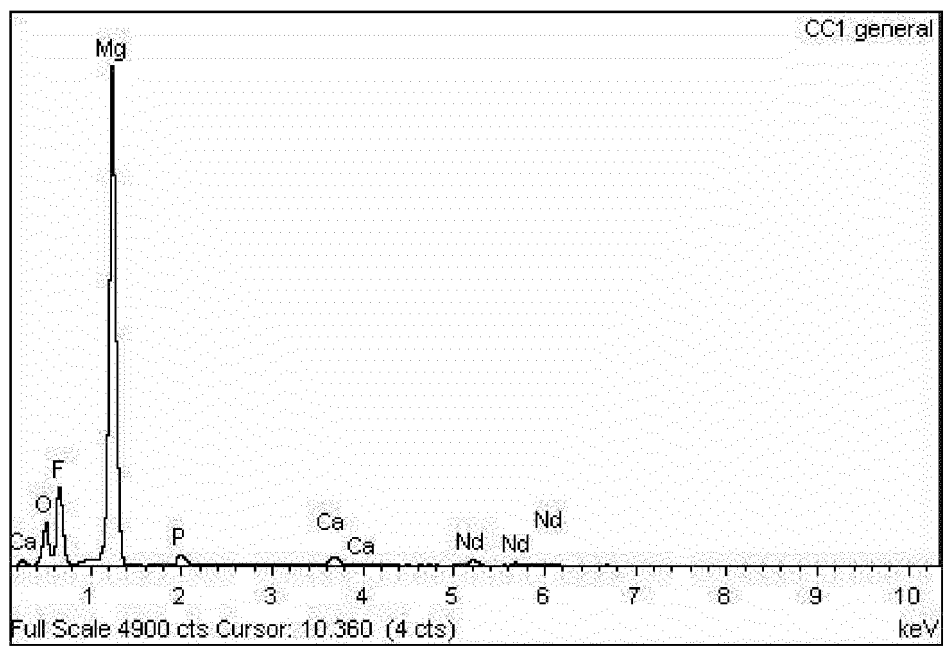


FIG. 5

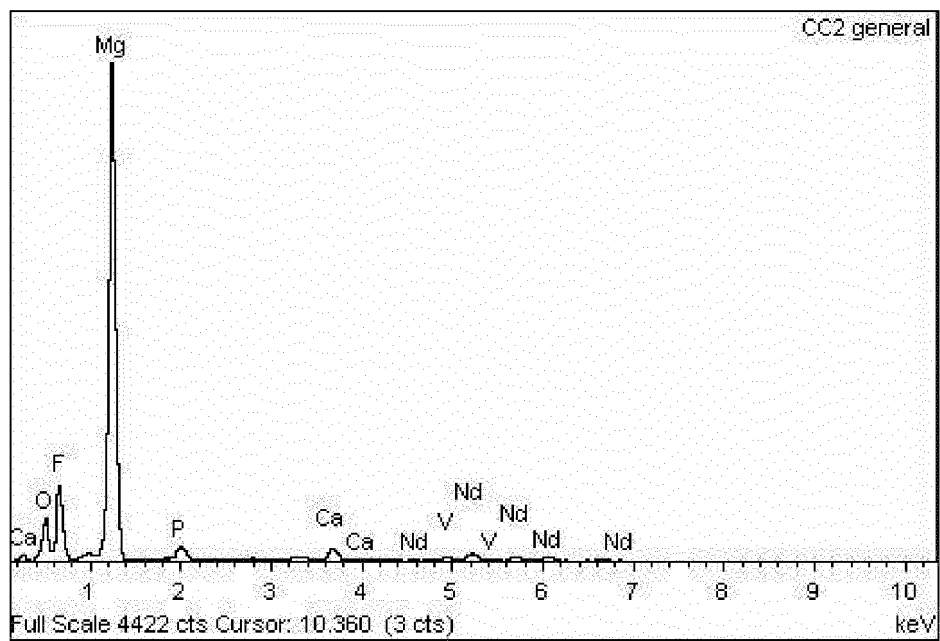


FIG. 6

REFERENCES CITED IN THE DESCRIPTION

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