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(54) **CONTINUOUS SURFACE TREATMENT FOR COILS MADE OF ALUMINUM ALLOYS SHEETS**

KONTINUIERLICHE OBERFLÄCHENBEHANDLUNG FÜR COILS AUS ALUMINIUMLEGIERTEN
BLECHEN

TRAITEMENT DE SURFACE EN CONTINU DES BOBINES EN TÔLES D'ALLIAGES D'ALUMINIUM

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Description

FIELD OF THE INVENTION

5 **[0001]** The invention relates to the field of continuous surface treatment of sheets and strips made of an aluminum alloy, and parts stamped from these sheets, and particularly 5xxx or 6xxx type alloy according to the Aluminum Association, intended for manufacturing bodywork parts for automobile vehicles

BACKGROUND

10 **[0002]** Aluminum is increasingly used in automobile construction to reduce the weight of vehicles and therefore fuel consumption and releases of pollutants and greenhouse effect gases. Sheets are used particularly for manufacturing bodywork skin parts, such as hoods and doors and structural parts. This type of application requires a set of sometimes contradicting mechanical strength, corrosion resistance and formability properties; with an acceptable cost for mass production.

15 **[0003]** For automobile parts, surface preparation adapted to assembly operations, and particularly adhesive bonding and welding, may be necessary. These pre-treatments take time and are expensive, in particular because the bath are corrosive and require special precaution of health and environment. Recent treatments are chromium-free for environmental reasons and use elements such as organophosphorous, silane and derivatives, titanium and/or zirconium. For example, such treatments are described in patents and applications US 5,514,211, US 5,879,437, US 6,167,609, US2013/284049, US2011/041957, US2016/319440.

[0004] The patent FR2856079 describes an alternative treatment simplified by using an atmospheric plasma.

[0005] Patent US 5,868,872 discloses a chromium-free no-rinse process in particular, to applications in the food packaging industry. This patent does not disclose an etching step prior to treatment but merely acidic or alkaline cleaners.

25 **[0006]** Patent US 6,562,148 discloses a method for the pretreatment of work pieces having a surface made of aluminium or aluminium alloys comprising rinsing with an aqueous, acidic solution containing a mineral acid, rinsing with water, bringing into contact with an aqueous, acidic solution which is chromium-free and polymer-free and contains Ti and Zr as complex fluorides in a weight ratio of Ti:Zr of 2:1 to 1:2.

30 **[0007]** Patent application EP 2 537 674 A1 discloses an aluminum or aluminum alloy material having a surface treatment coating film on a surface of a substrate formed by an aluminum or aluminum alloy, the surface treatment coating film being capable of maintaining hydrophilicity, high corrosion resistance, antibacterial properties and deodorizing properties for a long period of time.

[0008] Surface preparation is usually carried out with a continuous coil surface treatment line that enables the surface treatment of coils of sheets.

35 **[0009]** The surface treatment line may comprise continuous solution heat treating and quenching or may be a line dedicated to surface treatment. Several surface treatment steps are applied to progressively modify the surface properties in order to comply with an application of the products in the automotive sector, by optimizing the weight of a chemical layer. A first surface treatment step is usually a degreasing step of the sheet, which is used to remove oil residues on the sheet, present after the last rolling steps. Following the rolling processes, the surface of the aluminum includes a "disturbed area" also named "disturbed layer" or "disturbed surface layer", and etching is used in a second surface treatment step to remove the oxide layers and the disturbed area, ensuring a uniform surface, which is more favorable to deposit a product such as a Ti / Zr conversion layer and for further corrosion/bonding durability properties. A third surface treatment step is a conversion coating, the objective of the conversion being to precisely deposit a layer weight (for example comprising of Ti and/or Zr) which promotes adhesion and corrosion resistance. It has been generally admitted that the use of fluorine in the second etching treatment is necessary to eliminate the "disturbed area" and obtain a surface favorable to deposit the conversion layer. The use of fluorine containing bath requires however special precaution of health and environment. Another requirement is that the surface treatment lines dedicated to automotive applications have to be able to treat alternatively coils of 5XXX and 6XXX alloys sheets. It is thus economically advantageous to keep the same treatment for different types of alloys.

50 **[0010]** It is a purpose of this invention to develop improved surface treatment methods that are more environmentally friendly to produce the treated surfaces in an efficient and reliable manner providing treated surfaces for both 5XXX and 6XXX alloys.

SUMMARY OF THE INVENTION

55 **[0011]** An object of the invention is a continuous coil surface treatment process suitable for both a coil of a 5XXX aluminum alloy sheet and of a 6XXX aluminum alloy sheet having a surface comprising the successive steps of:

- a) optionally cleaning the surface of the aluminum alloy sheet;
- b) etching the surface of the optionally cleaned aluminum alloy sheet with a fluorine-free acidic solution;
- c) rinsing the surface of the etched aluminum alloy sheet with deionized water;
- d) applying to the surface of the etched aluminum alloy sheet a conversion solution comprising titanium and zirconium, with a zirconium to titanium weight ratio of from 3.0 to 5.0 preferably from 3.2 to 4.0,
- e) optionally rinsing the surface of the converted aluminum alloy sheet with deionized water; and,
- f) drying the surface of the aluminum alloy sheet.

DESCRIPTION OF THE FIGURES

[0012] Figure 1a is a SEM micrograph of a 6016 surface etched with a fluorine containing etching solution and Figure 1 b is a SEM micrograph of a 6016 surface etched with a fluorine-free etching solution.

DESCRIPTION OF THE INVENTION

[0013] All aluminium alloys referred to in the following are designated using the rules and designations defined by the Aluminium Association in Registration Record Series that it publishes regularly, unless mentioned otherwise.

[0014] Unless otherwise specified, the definitions of standard EN 12258 apply.

[0015] The method according to the invention is a continuous coil surface treatment process suitable for both a coil of a 5XXX alloy sheet and of a 6XXX alloy sheet. One significant advantage of the invention is that there is no need to change or modify the treatments when switching the line from a 5XXX alloy to a 6XXX alloy.

[0016] The method is suitable for the treatment of a coil made of 5XXX alloy sheet and for the treatment of a coil made of a 6XXX alloy sheet. Preferably the coil is a coil of a sheet made from an aluminum alloy selected from the group consisting of AA5754, AA5182, AA6451, AA6605, AA6005, AA6005A, AA6016, AA6116, AA6022, AA6013, AA6056, AA6156, AA6111 and AA6014.

[0017] In a first step, the sheet surface may optionally be cleaned. The cleaning may be used to remove residual oil left by the rolling process. Optionally, the cleaning may be carried out by hot water spraying and/or by using organic solvents and/or by using surfactants and/or detergents such as alkaline detergents. For some continuous treatment lines, the sheets may have been sufficiently degreased by the previous thermal treatments and the cleaning step may not be needed. Also in some instances cleaning and etching may be carried out simultaneously to simplify the process. For productivity and cost reasons, it is usually preferable to avoid having a cleaning step.

[0018] In a next step, the surface of the optionally cleaned aluminum alloy sheet is etched with a fluorine-free acidic solution. The present inventors have found that by combining a fluorine-free acidic solution with a conversion bath comprising Ti and Zr in specific quantities it is possible to treat 5XXX and 6XXX sheets with a same bath and obtain satisfactory conversion. Preferably etching with a fluorine-free acidic solution is carried out chemically and not electro-chemically.

[0019] Preferably, the fluorine-free acidic solution comprises sulfuric acid, nitric acid, phosphoric acid, or mixtures thereof. Advantageously, the fluorine-free acidic solution comprises at least 80% sulfuric acid and phosphoric acid, or mixtures thereof. In an embodiment the fluorine-free acidic solution does not contain nitric acid. It is advantageous if the mixture of acids, if used, comprises at least 80 % sulfuric acid. Advantageously, the concentration of sulfuric acid of the fluorine-free acidic solution is from about 2 g/l to about 60 g/l, preferably from 15 g/l to 50 g/l. Optionally, the fluorine-free acidic solution can include one or more additives (e.g., surfactants and/or detergents) and/or one or more accelerators. The surfactant and/or detergent additives can be included in the fluorine-free acidic solution at concentrations ranging from about 0.05 wt. % to 3 wt. %. Preferably, the surfactant and/or detergent additives can be included in the fluorine-free acidic solution at a concentration ranging from about 0.1 wt. % to 2.5 wt. %, from about 0.2 wt. % to 2 wt. %, from about 0.3 wt. % to 1.5 wt. % or from about 0.4 wt. % to 1.3 wt. %. A suitable accelerator that can be included in the fluorine-free acidic solution includes ferric sulfate. The accelerators can be included in the fluorine-free acidic solution at concentrations ranging from about 0.005 wt. % to 0.4 wt. %. For example, the accelerators can be included in the fluorine-free acidic solution at a concentration ranging from about 0.01 wt. % to 0.3 wt. %, from about 0.03 wt. % to 0.2 wt. %.

[0020] The fluorine-free acidic solution can be heated to a temperature of from about 55° C. to about 85° C. The fluorine-free acidic solution can be controlled within the outlined temperature and concentration ranges using, for example, heat exchangers and metering pumps and overflows and suitably replaced or replenished.

[0021] The fluorine-free acidic solution can be applied by spraying the solution onto the sheet or by immersing the sheet in a bath. Preferably, the fluorine-free acidic solution is applied by immersion. Optionally, the fluorine-free acidic solution can be circulated to ensure a fresh solution is continuously exposed to the sheet surfaces. In an advantageous embodiment, the fluorine-free acidic solution is continuously treated with an exchange resin in order to maintain a limited quantity of Al and Mg ions in the solution. Preferably, the fluorine-free acidic solution comprises less than about 3 g/l of aluminum ions and magnesium ions. Advantageously, the fluorine-free acidic solution can contain less than 2 g/l of

aluminum and magnesium ions. The contact time for the acid etching step can be from about 5 seconds to about 30 seconds or preferably from about 10 to about 20 seconds.

[0022] Advantageously, the etching removal is from 0.01 to 0.2 g/m², preferably from 0.01 to 0.1 g/m² for 6XXX alloys and from 0.1 to 0.2 g/m² for 5XXX alloys. With the fluorine-free acidic solution of the invention, the etching removal is substantially lower than the etching removal known from prior art fluorine containing acid solution. This is advantageous to limit Al and Mg ions in the solution. Also, the etching of the invention provides an advantageous smoother surface than the prior art etching, with in particular less or even no pitting.

[0023] After etching it is needed to rinse the surface of the etched aluminum alloy sheet with deionized water. Preferably, the deionized water in this step has a conductivity of less than or equal to 50 µS/cm. The rinsing step is preferably performed at a temperature ranging from about 37° C. to about 70° C. Advantageously, the rinsing step can be performed at a temperature of from about 40° C. to about 65° C. and preferably from about 45° C. to about 60° C. The rinse can be a progressive cascading system. Preferably, sprays are used for the rinsing step.

[0024] The following step is applying to the surface of the etched aluminum alloy sheet a conversion solution comprising titanium and zirconium, with a zirconium to titanium weight ratio of from 3.0 to 5.0 preferably from 3.2 to 4.0. The present inventors have found that by combining etching with the fluorine-free acidic solution and conversion with the conversion solution according to the invention, it is possible to obtain a Zr/Ti weight ratio on the treated sheet surface of from about 0.8 to about 1.3 for 5XXX and 6XXX alloys. This ratio is important for the adhesive bonding properties of the sheets. A benefit of the invention that it is not needed to modify the conversion solution composition in order to treat both 5XXX and 6XXX alloys. The conversion solution can be applied at a temperature of from about 35° C. to about 65° C. Preferably, the conversion solution is applied at a different temperature for 5XXX and 6XXX, typically at a temperature of from about 40° C to about 50° C for 5XXX alloys and of from about 45° C to 55° C for 6XXX alloys. The conversion solution may be applied for a contact time of from about 5 seconds to about 20 seconds. Preferably, the conversion solution is applied at during a different contact time for 5XXX and 6XXX, preferably with a contact time of from about 5 seconds to about 9 seconds for 5XXX alloys, typically with a contact time of about 7 seconds for 5XXX alloys and preferably with a contact time of from about 8 seconds to about 12 seconds for 6XXX alloys, typically with a contact time of about 10 seconds for 6XXX alloys.

[0025] Preferably, the conversion solution comprises titanium and zirconium, with a titanium content of from about 20 to about 200 mg/l and preferably from 60 to 140 mg/l. Advantageously the conversion solution comprises hexafluotitanic acid, hexafluozirconic acid, hydrofluoric acid and optionally ammonium hydrogendifluoride. The additional fluoride (under the form of hydrofluoric acid and optionally ammonium hydrogendifluoride) is advantageously added to complex the Al generated during treatment with the conversion solution. The pH of the conversion solution, is advantageously adjusted upward to a pH from about 2.5 to about 4.5, preferably from 3.5 to 4 by the addition of an alkali such as ammonium hydroxide or ammonium hydrogendifluoride. In an advantageous embodiment, the conversion solution is continuously treated with an exchange resin in order to maintain a limited quantity of Al and Mg ions in the solution. Preferably, the conversion solution comprises less than about 80 ppm of aluminum ions and magnesium ions.

[0026] The conversion solution can be applied by spraying the solution onto the sheet or by immersing the sheet in a bath. Preferably the conversion solution is applied by spraying the aluminum alloy sheet with the conversion solution, with preferably at least 5 spraying ramps. Applying the inventive described conversion solution by roll-coating would not be optimal because the Ti/Zr ratio on the sheet would be the same as the Ti/Zr ratio in the conversion solution,

[0027] The following step is optionally rinsing the surface of the converted aluminum alloy sheet with deionized water.

[0028] The final step is drying the surface of the aluminum alloy sheet. The drying step removes any water from the surface of the sheet. The drying step can be performed using an air dryer or an infrared dryer. The drying step can be performed for a time period of up to five minutes. The drying step may also be used for a metallurgical purpose, in particular for 6xxx alloys if needed, so that the coiling temperature is advantageously of from 50 °C to 120 °C or preferably from 60 °C to 100 °C.

EXAMPLE

[0029] The surface of aluminum alloy sheets was treated on a continuous line according to the methods described herein. The sheets included 5182 aluminum alloy sheets and 6016 aluminum alloy sheets. The sheets were cleaned and etched by spray with a sulfo fluorhydric bath (H₂SO₄ 8 g/l HF 0,4 g/l, 50 °C) for trials 1 and 2 or with a sulfuric acid bath (H₂SO₄ 43 g/l 70 °C) for trials 3 to 6. SEM micrograph of the surface obtained for 6016 alloy etched with the sulfo fluorhydric bath (trial 2) and micrograph of the surface obtained for 6016 alloy etched with the sulfuric acid bath (trial 6) are presented in Figure 1a and 1b respectively. The etching of the invention provides an advantageous smoother surface than the prior art etching, with much less pitting. Following etching the sheets were rinsed with deionized water and treated by spray with Ti/Zr conversion surface treatment with a pH of 3.8 comprising hexafluotitanic acid, hexafluozirconic acid, hydrofluoric acid and ammonium hydrogendifluoride. The contact time, concentration and temperature are shown in Table 1 .

[0030] The quantity of Zr and Ti deposited on the surface was measured by XRF on three positions across the width for 6 samples. The average value of the measurement is provided in Table 1.

Table 1

	Conversion bath	Ti concentration in conversion solution (mg/l)	Zr /Ti weight ratio in conversion solution	Alloy	Temperature	Contact time	Ti (mg/m2)	Zr (mg/m2)	Zr/Ti weight ratio on the sheet surface
1	A	40	2.8	5182	45°C	6	5,2	5,5	1,0
2				6016	50°C	8	5,4	5,1	0,9
3	B	100	2.2	5182	45°C	7	5,4	5,1	0,9
4				6016	50°C	10	6,1	3,4	0,6
5	C	100	3.5	5182	45°C	7	5,1	6,9	1,3
6				6016	50°C	10	5,4	4,6	0,9

[0031] Conversion coating with bath C is according to the invention. With the method of the invention it is possible to obtain a Zr/Ti ratio between 0.8 and 1.3 with a single bath for both 5XXX and 6XXX alloys, and obtain an advantageous smoother surface.

Claims

1. A continuous coil surface treatment process suitable for both a coil of a 5XXX aluminum alloy sheet and of a 6XXX aluminum alloy sheet having a surface comprising the successive steps of:
 - a) optionally cleaning the surface of the aluminum alloy sheet;
 - b) etching the surface of the optionally cleaned aluminum alloy sheet with a fluorine-free acidic solution;
 - c) rinsing the surface of the etched aluminum alloy sheet with deionized water;
 - d) applying to the surface of the etched aluminum alloy sheet a conversion solution comprising titanium and zirconium, with a zirconium to titanium weight ratio of from 3.0 to 5.0 preferably from 3.2 to 4.0;
 - e) optionally rinsing the surface of the converted aluminum alloy sheet with deionized water; and,
 - f) drying the surface of the aluminum alloy sheet.
2. The process of claim 1, wherein the conversion solution comprises titanium and zirconium, with a titanium content of from 20 to 200 mg/l and preferably of from 60 to 140 mg/l.
3. The process of claim 1 or claim 2 wherein the conversion solution comprises hexafluotitanic acid, hexafluozirconic acid, hydrofluoric acid and optionally ammonium hydrogendifluoride.
4. The process of anyone of claims 1 to 3, wherein the fluorine-free acidic solution comprises sulfuric acid, nitric acid, phosphoric acid, or mixtures thereof.
5. The process of anyone of claims 1 to 4, wherein the concentration of sulfuric acid of the fluorine-free acidic solution is from 2 g/l to 60 g/l, preferably from 15 g/l to 50 g/l.
6. The process of anyone of claims 1 to 5, wherein the aluminum alloy sheet is made from an aluminum alloy selected from the group consisting of AA5754, AA5182, AA6451, AA6005, AA6605, AA6005A, AA6016, AA6116, AA6022, AA6013, AA6056, AA6156, AA6111 and AA6014.
7. The process of anyone of claims 1 to 6, wherein the applying in step (d) is performed by immersing the aluminum alloy sheet in the conversion solution.
8. The process of anyone of claims 1 to 6, wherein the applying in step (d) is performed by spraying the aluminum alloy sheet with the conversion solution.

9. The process of anyone of claims 1 to 8, wherein the etching in step (b) is performed by spraying the aluminum alloy sheet with the fluorine-free acidic solution.
10. The process of anyone of claims 1 to 9, wherein the fluorine-free acidic solution in step (b) comprises less than 2 g/l of aluminum ions and magnesium ions.
11. The process of anyone of claims 1 to 10 wherein the fluorine-free acidic solution, comprises surfactant additives or accelerators and is used at a temperature of from 55° C. to 85° C. for a period of 5 to 30 seconds.

Patentansprüche

1. Kontinuierliches Oberflächenbehandlungsverfahren für Coils, das sowohl für einen Coil aus einem 5XXX aluminiumlegiertem Blech geeignet ist als auch für einen aus 6XXX aluminiumlegiertem Blech, die eine Oberfläche aufweisen, die die aufeinanderfolgenden Schritte umfasst:
 - a) gegebenenfalls Reinigen der Oberfläche des aluminiumlegierten Blechs;
 - b) Ätzen der Oberfläche des gegebenenfalls gereinigten aluminiumlegierten Blechs mit einer fluorfreien Säurelösung;
 - c) Spülen der Oberfläche des geätzten aluminiumlegierten Blechs mit deionisiertem Wasser;
 - d) Aufbringen auf die Oberfläche des geätzten aluminiumlegierten Blechs einer Konversionslösung, die Titan und Zirkonium umfasst, mit einem Gewichtsverhältnis von Zirkonium zu Titan von 3,0 bis 5,0, vorzugsweise von 3,2 bis 4,0;
 - e) gegebenenfalls Spülen der Oberfläche des konvertierten aluminiumlegierten Blechs mit deionisiertem Wasser; und
 - f) Trocknen der Oberfläche des aluminiumlegierten Blechs.
2. Verfahren nach Anspruch 1, wobei die Konversionslösung Titan und Zirkonium umfasst, mit einem Titangehalt von 20 bis 200 mg/l und vorzugsweise von 60 bis 140 mg/l.
3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Konversionslösung Hexafluorotitansäure, Hexafluorozirkoniumsäure, Fluorwasserstoffsäure und gegebenenfalls Ammoniumhydrogendifluorid umfasst.
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die fluorfreie Säurelösung Schwefelsäure, Salpetersäure, Phosphorsäure oder Mischungen davon umfasst.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Konzentration an Schwefelsäure der fluorfreien Säurelösung 2 g/l bis 60 g/l beträgt, vorzugsweise 15 g/l bis 50 g/l.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das aluminiumlegierte Blech aus einer Aluminiumlegierung hergestellt ist, die aus der Gruppe ausgewählt ist, die besteht aus: AA5754, AA5182, AA6451, AA6005, AA6605, AA6005A, AA6016, AA6116, AA6022, AA6013, AA6056, AA6156, AA6111 und AA6014.
7. Verfahren nach einem der Ansprüche 1 bis 6, wobei das Aufbringen in Schritt (d) durch Eintauchen des aluminiumlegierten Blechs in die Konversionslösung durchgeführt wird.
8. Verfahren nach einem der Ansprüche 1 bis 6, wobei das Aufbringen in Schritt (d) durch Besprühen des aluminiumlegierten Blechs mit der Konversionslösung durchgeführt wird.
9. Verfahren nach einem der Ansprüche 1 bis 8, wobei das Ätzen in Schritt (b) durch Besprühen des aluminiumlegierten Blechs mit der fluorfreien Säurelösung durchgeführt wird.
10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die fluorfreie Säurelösung in Schritt (b) weniger als 2 g/l Aluminiumionen und Magnesiumionen umfasst.
11. Verfahren nach einem der Ansprüche 1 bis 10, wobei die fluorfreie Säurelösung Tensidadditive oder Härter umfasst und bei einer Temperatur von 55 °C bis 85 °C für einen Zeitraum von 5 bis 30 Sekunden verwendet wird.

Revendications

1. Procédé de traitement de surface en continu adapté aux bobines de tôles en alliage d'aluminium 5XXX et en alliage d'aluminium 6XXX, dont les étapes successives sont les suivantes :

- a) nettoyage facultatif de la surface de la tôle en alliage d'aluminium ;
- b) attaque chimique de la surface de la tôle en alliage d'aluminium, éventuellement nettoyée, avec une solution acide sans fluor ;
- c) rinçage à l'eau déionisée de la surface de la tôle en alliage d'aluminium attaquée ;
- d) application sur la surface de la tôle en alliage d'aluminium attaquée d'une solution de conversion comprenant du titane et du zirconium, avec un rapport massique zirconium/titane variant de 3,0 à 5,0, de préférence de 3,2 à 4,0 ;
- e) rinçage facultatif à l'eau déionisée de la surface de la tôle en alliage d'aluminium convertie ; et,
- f) séchage de la surface de la tôle en alliage d'aluminium.

2. Procédé selon la revendication 1, dans lequel la solution de conversion comprend du titane et du zirconium, avec une teneur en titane allant de 20 à 200 mg/l et de préférence de 60 à 140 mg/l.

3. Procédé selon la revendication 1 ou 2, dans lequel la solution de conversion comprend de l'acide hexafluorotitanique, de l'acide hexafluorozirconique, de l'acide fluorhydrique et de l'hydrogénodifluorure d'ammonium.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la solution acide sans fluor comprend de l'acide sulfurique, de l'acide nitrique, de l'acide phosphorique ou un mélange de ces derniers.

5. Procédé selon la revendication 4, dans lequel la concentration en acide sulfurique de la solution acide sans fluor varie de 2 g/l à 60 g/l, de préférence de 15 g/l à 50 g/l.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la tôle en alliage d'aluminium est fabriquée à partir d'un alliage d'aluminium choisi parmi le groupe comprenant les alliages AA5754, AA5182, AA6451, AA6005, AA6605, AA6005A, AA6016, AA6116, AA6022, AA6013, AA6056, AA6156, AA6111 et AA6014.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'application de l'étape (d) est réalisée en immergeant la tôle en alliage d'aluminium dans la solution de conversion.

8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'application de l'étape (d) est réalisée en pulvérisant la solution de conversion sur la tôle en alliage d'aluminium.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel l'attaque chimique de l'étape (b) est réalisée en pulvérisant la solution acide sans fluor sur la tôle en alliage d'aluminium.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel la solution acide sans fluor de l'étape (b) affiche une concentration en ions aluminium et en ions magnésium inférieure à 2 g/l.

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel la solution acide sans fluor comprend des additifs tensioactifs ou des accélérateurs, et est utilisé à une température comprise entre 55 °C et 85 °C pendant une période de 5 à 30 secondes.

Figure 1a

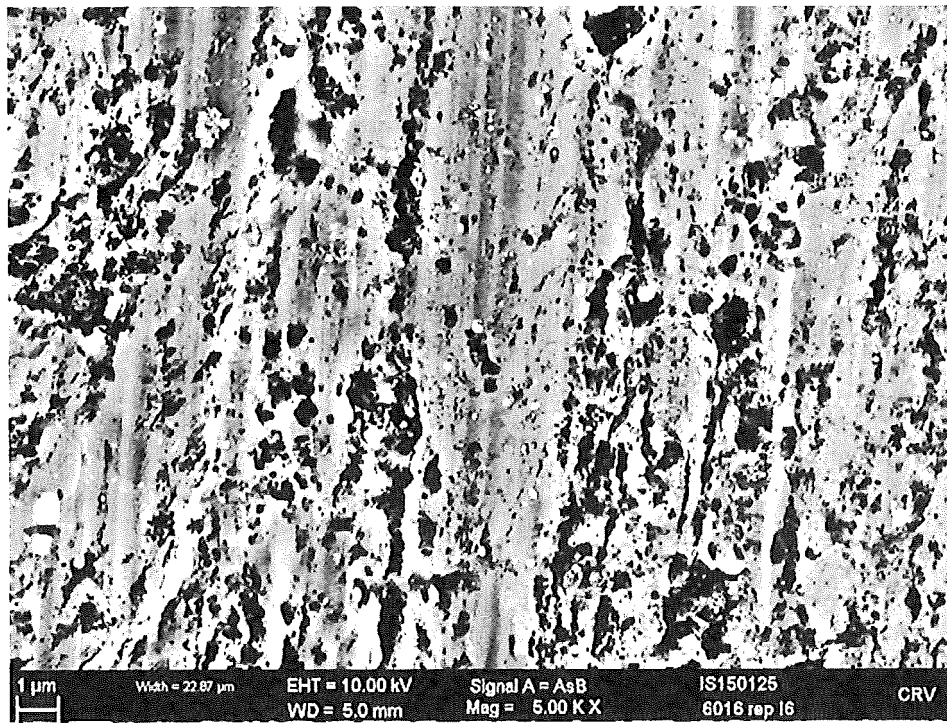
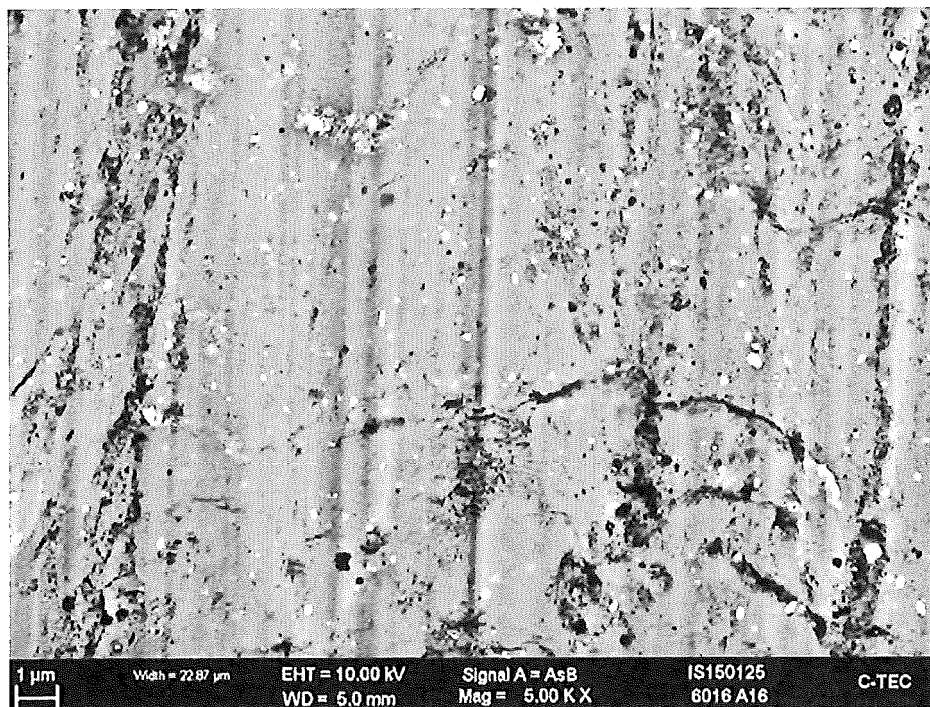


Figure 1b



REFERENCES CITED IN THE DESCRIPTION

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