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(54) **METHOD OF CONDITIONING THE SURFACE OF A LITHO-SHEET OR LITHO-STRIP**

VERFAHREN ZUR KONDITIONIERUNG DER OBERFLÄCHE EINES LITHOBANDS

PROCÉDÉ DE CONDITIONNEMENT DE LA SURFACE D'UNE PELLICULE DE LITHOGRAPHIE

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(73) Proprietor: **Hydro Aluminium Rolled Products GmbH**
41515 Grevenbroich (DE)

(72) Inventors:
- **KERNIG, Bernhard**
50969 Köln (DE)
- **BRINKMAN, Henk-Jan**
53175 Bonn (DE)

(74) Representative: **Cohausz & Florack**
Patent- und Rechtsanwälte
Partnerschaftsgesellschaft
Bleichstraße 14
40211 Düsseldorf (DE)

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EP 2 024 190 B9

Description

[0001] The invention relates to a method of conditioning the surface of a litho-sheet or litho-strip consisting of an aluminium alloy, which method comprises at least the step of degreasing the surface of the litho-sheet or litho-strip with a degreasing medium.

[0002] Work pieces such as strips or sheets consisting of an aluminium alloy are often surface treated after finishing rolling to prepare them for the next manufacturing step. In particular strips or sheet for lithographic printing are conditioned to achieve a predetermined surface roughness in a subsequent graining process. Litho-strips or sheets are usually degreased after finishing rolling. As known from the US-patent specification US 5,997,721, degreasing respectively cleaning of the surface is done in one step by anodising the aluminium alloy sheet with AC current in an acidic electrolyte bath. Another way to degrease or clean aluminium slivers is known from the German patent DE 43 17 815 C1 namely the use of an alkaline medium. But from the use of alkaline media it is known that they do not remove every features of the subsurface microcrystalline layer, in particular oxide particles, which are present on or near the surface of the rolled aluminium strips.

[0003] However, prior electro-chemical graining the litho-strips are usually subjected to sodium hydroxide in a pre-treatment to degrease and clean the surface again, which process together with the electro-chemical graining is herein further called surface roughening process of litho-strips. In principle surface roughening is done by the manufacture of lithographic printing plates. Due to the increasing manufacturing speed of surface roughening of the litho-strips time for the pre-treatment of the surface of the litho-strips and for the electro-chemical graining decreases. It has been found that due to the increasing manufacturing speed the pre-treatment with sodium hydroxide is not sufficient enough to remove all contaminants from the surface of the litho-strip. As a consequence, the results in electro-chemical graining are not stable and surface defects occur on electro-chemically grained litho-strips or sheets. However, a reduction of the manufacturing speed causes higher production costs for lithographic printing plates.

[0004] Furthermore, methods of conditioning the surface of a litho-strip including two steps require relative high expenses related to facility equipments.

[0005] US 5,114,607 discloses a cleaning solution for cleaning and etching a metal surface with sodium hydroxide and an alkali metal salt of gluconic acid. US 4,602,363 discloses a method for cleaning metals with a cleaner comprising sodium tripolyphosphates and sodium hydroxide.

[0006] It is an object of the invention to provide a method for conditioning the surface of a litho-sheet or litho-strip and a litho-sheet or litho-strip consisting of an aluminium alloy enabling an increasing manufacturing speed in surface roughening and maintaining at the same time a high quality of the grained surface of the litho-sheet or litho-strip with relative low effort related to facility equipment.

[0007] According to a first teaching of the present invention the above mentioned object is solved by a method of conditioning the surface of an aluminium work piece consisting of an aluminium alloy, which method comprises at least the step of degreasing the surface of the litho-sheet or litho-strip with a degreasing medium, wherein the aqueous degreasing medium contains 1,5 to 3 % by weight of a composite of 5 - 40 % sodium tripolyphosphate, 3 - 10 % sodium gluconate, 3 - 8 % of a composite of non-ionic and anionic surfactants and optionally 0,5 % to 70 % soda, preferably 30 - 70 % soda, wherein sodium hydroxide is added to the aqueous degreasing medium such that the concentration of sodium hydroxide in the aqueous degreasing medium is 0,01 to 5 % by weight, preferably 0,1 to 1,5 % by weight, more preferably 1 to 2,5 % by weight.

[0008] It has been surprisingly found that the combination of the use of the degreasing medium together with added sodium hydroxide ensures an increased manufacturing speed during surface roughening including electro-chemical graining with sufficient results despite of the fact that oxide particles are not removed completely during degreasing. The reason for the good results is seen in the fact that due to the addition of sodium hydroxide the degreasing medium has an increased pickling rate which removes more aluminium from the surface at the same time. In combination with the described pre-treatment of for example litho-strips it has been surprisingly found that the electro-chemical graining process of litho-strips can be done with a lower charge entry therefore enabling a higher manufacturing speed. While the addition of 0,1 % to 1,5 % by weight sodium hydroxide is suitable even for lower manufacturing speeds during degreasing, with the addition of 1 % to 2,5 % by weight sodium hydroxide highest manufacturing speeds during degreasing are achievable ensuring at the same time high manufacturing speeds during plate manufacturing, i.e. during electro-chemical graining. The optional addition of soda in an amount of 0,5 - 70 %, preferably 30 to 70 % by weight allows to control pH-value of the degreasing medium.

[0009] According to a preferred embodiment of the invention the time of application of the degreasing medium to the surface of the aluminium work piece is 1 to 7 s, preferably 2 to 5 s. These application times ensure high production speeds at the same time ensuring that the oxide islands can easily be removed by surface roughening.

[0010] To increase pickling effect of the degreasing medium the temperature of the degreasing medium is 50 to 85 °C, preferably 65 °C to 75 °C.

[0011] More preferably, the pH-value of the aqueous degreasing medium is from 10 to 14, preferably 10 to 13,5.

[0012] According to the invention, the work piece is a litho-strips or a litho-sheat. In this case the necessary electro-chemical graining process for manufacturing litho-strips or litho-sheets can be accomplished thoroughly within less time and the printing plate manufacturing speed can be increased. Furthermore, the charge entry needed can be reduced while providing a fully grained strip or sheet surface.

[0013] More preferably, the inventive conditioning method is accomplished subsequent the manufacturing of a litho-strip and the conditioned strip is reeled on a coil. In this case a coil of a conditioned litho-strip can be provided comprising an optimum performance in further surface roughening processes used to manufacture lithographic printing plates.

[0014] The above mentioned object is solved by a work piece consisting of an aluminium alloy conditioned by the inventive method. As outlined before, the work piece provides a cleaned surface with an optimum performance for a subsequent electro-chemical graining process.

[0015] The work piece is a litho-strip or a litho-sheet. Litho-strip or sheets are produced for lithographic printing plates and differ from "normal" sheets due to the aluminium alloy they consist of and their specific thickness, which is typically less than 1 mm, preferably 0,14 to 0,5 mm, more preferably 0,25 to 0,3 mm. Furthermore, the surface of litho-strips and sheets has to be prepared for a roughening process, since manufacturing of lithographic printing plates generally comprises an electro-chemical graining process to prepare the surface of the lithographic printing plates for the printing process. With the litho-sheets or litho-strips, the necessary electro-chemical graining of the surface can be accomplished in shorter time with a reduced charge entry.

[0016] Beside an optimised surface of the work piece the mechanical features and an improved graining structure during electro-chemical graining can be provided if the aluminium alloy of the work pierce is one of the aluminium alloys AA1050, AA1100, AA3103 or AlMg0,5. These aluminium alloys provide the mechanical strength needed for lithographic printing plates while enabling due to the low amount of alloying constituents a homogeneous graining of the surface. However, work pieces consisting of other aluminium alloys may provide the same advantages.

[0017] According to a more preferably embodiment of the work piece the aluminium alloy contains the following alloying constituents in percent by weight:

0,05 % ≤ Si ≤ 0,15 %,
0,3 % ≤ Fe ≤ 0,4 %,
Cu ≤ 0,01 %,
Mn ≤ 0,05 %,
Mg ≤ 0,01 %,
Zn ≤ 0,015 %,
Ti ≤ 0,015 %,

impurities each less than 0,005 % in sum max. 0,15 %, rest Al
or

0,05 % ≤ Si ≤ 0,25 %,
0,30 % ≤ Fe ≤ 0,40 %,
Cu ≤ 0,04 %,
Mn ≤ 0,05 %,
0,1 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % and

impurities each less than 0,005 % in sum max.

0,15 %, rest Al

or

0,05 % ≤ Si ≤ 0,5 %,
0,40 % ≤ Fe ≤ 1 %,
Cu ≤ 0,04 %,
0,08 % ≤ Mn ≤ 0,3 %,
0,05 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % and

impurities each less than 0,005% in sum max.

0,15 %, rest Al.

[0018] Work pieces consisting of one of the three aluminium alloys and conditioned with the inventive method have state of the art mechanical and graining properties, in particular if the work pieces are litho-strips which are grained electro-chemically after conditioning. It was surprisingly observed that in particular the latter aluminium alloys conditioned with the inventive conditioning method show a higher sensitivity in subsequent surface roughening processes. As a result despite of the inventive single step conditioning method, which reduces the expenses for the conditioning equipment significantly, an increase in plate manufacturing speed for litho-strips and sheets is achievable.

[0019] There are a lot of possibilities to develop further the invention. Hereunto it is refer to the dependent claims of claim 1 as well as to embodiments of the invention in combination with the drawings. The drawings show in

Fig. 1 a microscopic view of the surface of a litho-strip degreased conventionally and
Fig. 2 a microscopic view of the surface of a litho-strip degreased with the inventive method.

[0020] To verify the inventive method four strips made of two different aluminium alloys were tested on the one hand with different degreasing parameters and on the other with different strip velocities during electro-chemical graining on different plate manufacturing lines. The different aluminium alloys have the following compositions of alloying constituents in weight percent:

alloy A:

0,05 % ≤ Si ≤ 0,25 %,
0,3 % ≤ Fe ≤ 0,40 %,
Cu ≤ 0,04 %,
Mn ≤ 0,05 %,
0,1 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 %, and

impurities each less than 0,005 % in sum max.

0,15 %, rest Al.

alloy B:

0,05 % ≤ Si ≤ 0,15 %,
0,3 % ≤ Fe ≤ 0,4 %,
Cu ≤ 0,01 %,
Mn ≤ 0,05 %,
Mg ≤ 0,01 %,
Zn ≤ 0,015 %,
Ti ≤ 0,015 %,

impurities each less than 0,005 % in sum max.

0,15 %, rest Al

[0021] Litho-strips made from the aluminium alloys mentioned above where tested with regard to their graining behaviour on industrial plate manufacturing lines.

[0022] For the inventive examples the degreasing medium used contains 1,5 to 3 % by weight of a composite of 5 to 40 % sodium tripolyphosphate, 3 to 10 % sodium gluconate, 30 to 70 % soda and 3 to 8 % of a composite of non-ionic and anionic surfactants, with an addition of sodium hydroxide in the amount of 1 % by weight. The comparative examples were degreased with the same conditions without the addition of sodium hydroxide to the degreasing medium. The results of the examples are shown in table 1

Strip	Al Alloy	$T_{Degr.}$ (°C)	$t_{Degr.}$ (s)	$V_{Graining}$ (m/min.)	Type	Appearance after graining
Strip 1	A	75	3,4	55	prior art	0

(continued)

Strip	Al Alloy	$T_{Degr.}$ (°C)	$t_{Degr.}$ (s)	$V_{Graining}$ (m/min.)	Type	Appearance after graining
				50	prior art	+
Strip 2	A	75	3,4	55 50	invention invention	+ +
Strip 3	B	75	3,4	> 60	prior art	0
Strip 4	B	75	3,4	> 60	invention	++

[0023] with T_{Degr} as the temperature during degreasing, t_{Degr} the contact time of the degreasing medium with the strip surface and $V_{Graining}$ the velocity of the strips in the plate manufacturing lines, i.e. the velocity during electro-chemical graining. Strip 1 and 2 produced from one mother strip were tested on the same plate manufacturing line. The same applies to strip 3 and 4. The different values of $V_{Graining}$ for strip 1,2 and strip 3,4 are caused by different characteristics of the plate manufacturing lines.

[0024] As can be derived from table 1 the litho-strips degreased with the inventive method generally show a good appearance after electro-chemical graining even if the graining velocity was increased. However, litho-strips degreased with the inventive method show even better graining results, because the surface of the litho-strip grained with the inventive method have a finer, more homogeneous and more shallow graining structure. This graining structure provides improved printing characteristics of the litho-strips. Additionally, the inventive method provides said improved graining structure even at higher manufacturing speeds, as can be derived from the results of strip 1 and strip 2. Strip 1 degreased conventionally shows merely good appearance results after electro-chemical graining at a graining velocity of 50 m/min. However, strip 2 degreased with the inventive method allows 55 m/min graining velocity.

[0025] The different graining structures of the conventional and inventive degreasing method are shown in Fig. 1 and Fig. 2. Fig. 2 shows, as already mentioned, a microscopic view of the surface of a litho-strip consisting of the aluminium alloy A degreased with the inventive method after electro-chemical graining. Fig. 1 shows the graining result of the same litho-strip degreased conventionally. The graining pattern achieved with the inventive method is finer and more shallow compared to the graining pattern achieved with a conventionally degreased litho-strip. As a result, the printing characteristics of the litho-strips are improved significantly.

[0026] The present embodiments of the invention have been achieved by the addition of 1 % per weight sodium hydroxide. It is expected that a higher concentration of sodium hydroxide combined with a decreased contact time of the strip with the degreasing medium will lead to similar results.

Claims

1. Method of conditioning the surface of a litho-sheet or litho-strip consisting of an aluminium alloy, which method comprises at least the step of degreasing the surface of the litho-sheet or litho-strip with a degreasing medium,
   characterized in that
   the aqueous degreasing medium contains 1,5 to 3 % by weight of a composite of 5 - 40 % sodium tripolyphosphate, 3 - 10 % sodium gluconate, 3 - 8 % of a composite of non-ionic and anionic surfactants and optionally 0,5 - 70 % soda, preferably 30 - 70 % soda, wherein sodium hydroxide is added to the aqueous degreasing medium such that the concentration of sodium hydroxide in the aqueous degreasing medium is 0,01 to 5 % by weight, preferably 0,1 to 1,5 %, more preferably 1 to 2,5 % by weight.

2. Method according to claim 1, wherein
   the time of application the degreasing medium is 1 to 7 s, preferably 2 to 5 s.

3. Method according to claim 1 or 2, wherein
   the temperature of the degreasing medium is 50 to 85 °C, preferably 65 °C to 75 °C.

4. Method according to claim 1 to 3, wherein
   the pH-value of the aqueous degreasing medium is from 10 to 14, preferably 10 to 13,5.

5. Method according to claim 1 to 4, wherein the litho-strip is conditioned and the conditioning is accomplished subsequently to manufacturing, respectively rolling of the strip whereby the conditioned strip is reeled on a coil.

6. Method according to claim 1 to 5, wherein the aluminium alloy is one of the aluminium alloys AA1050, AA1100, AA3103 or AlMg0,5.

7. Method according to claim 1 to 5, wherein the aluminium alloy contains the following alloying constituents in percent by weight:

0,05 % ≤ Si ≤ 0,15 %,
0,3 % ≤ Fe ≤ 0,4 %,
Cu ≤ 0,01 %,
Mn ≤ 0,05 %,
Mg ≤ 0,01 %,
Zn ≤ 0,015 %,
Ti ≤ 0,015 %,

impurities each less than 0,005 % in sum max.

0,15 %, rest Al

or

0,05 % ≤ Si ≤ 0,25 %,
0, 30 % ≤ Fe ≤ 0,40 %,
Cu ≤ 0,04 %,
Mn ≤ 0,05 %,
0,1 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % and

impurities each less than 0,005 % in sum max.

0,15 %, rest Al

or

0,05 % ≤ Si ≤ 0,5 %,
0,40 % ≤ Fe ≤ 1 %,
Cu ≤ 0,04 %,
0,08 % ≤ Mn ≤ 0,3 %,
0,05 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % and

impurities each less than 0,005 % in sum max.

0,15 %, rest Al.

Patentansprüche

1. Verfahren zur Konditionierung der Oberfläche eines Lithobleches oder eines Lithobandes bestehend aus einer Aluminiumlegierung, welches Verfahren mindestens den Schritt des Entfettens der Oberfläche des Lithobleches oder des Lithobandes mit einem Entfettungsmedium umfasst,
dadurch gekennzeichnet, dass
das wässrige Entfettungsmedium 1,5 bis 3 Gew.-% eines Verbundstoffes aus 5 - 40 % Natriumtripolyphosphat, 3 - 10 % Natriumglukonat, 3 - 8 % eines Verbundstoffes aus nichtionischen und anionischen Tensiden und wahlweise 0,5 - 70 % Natriumkarbonat, bevorzugt 30 - 70 % Natriumkarbonat enthält, wobei Natriumhydroxid dem wässrigen Entfettungsmedium so hinzugegeben wird, dass die Konzentration von Natriumhydroxid in dem wässrigen Entfettungsmedium 0,01 bis 5 Gew.-%, bevorzugt 0,1 bis 1,5 Gew.-% , besonders bevorzugt 1 bis 2,5 Gew.-% beträgt.

2. Verfahren nach Anspruch 1, wobei die Auftragszeit des Entfettungsmediums 1 bis 7 s, bevorzugt 2 bis 5 s beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei die Temperatur des Entfettungsmediums 50 bis 85 °C, bevorzugt 65 °C bis 75 °C beträgt.

4. Verfahren nach Anspruch 1 bis 3, wobei der pH-Wert des wässrigen Entfettungsmediums 10 bis 14, bevorzugt 10 bis 13,5 beträgt.

5. Verfahren nach Anspruch 1 bis 4, wobei das Lithoband konditioniert wird und das Konditionieren nach dem Herstellen bzw. Aufrollen des Bandes durchgeführt wird, wobei das konditionierte Band auf eine Spule aufgewickelt wird.

6. Verfahren nach Anspruch 1 bis 5, wobei die Aluminiumlegierung eine der Aluminiumlegierungen AA1050, AA1100, AA3103 oder AlMg0,5 ist.

7. Verfahren nach Anspruch 1 bis 5, wobei die Aluminiumlegierung folgende Legierungsbestandteile in Gewichtsprozent enthält:

0,05 % ≤ Si ≤ 0,15 %,
0,3 % ≤ Fe ≤ 0,4 %,
Cu ≤ 0,01 %,
Mn ≤ 0,05 %,
Mg ≤ 0,01 %,
Zn ≤ 0,015 %,
Ti ≤ 0,015 %,

Verunreinigungen von jeweils weniger als 0,005 %, insgesamt maximal 0,15 %, wobei der Rest Al ist oder

0,05 % ≤ Si ≤ 0,25 %,
0,30 % ≤ Fe ≤ 0,40 %,
Cu ≤ 0,04 %,
Mn ≤ 0,05 %,
0,1 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % und

Verunreinigungen von jeweils weniger als 0,005 %, insgesamt maximal 0,15 %, wobei der Rest Al ist oder

0,05 % ≤ Si ≤ 0,5 %,
0,40 % ≤ Fe ≤ 1 %,
Cu ≤ 0,04 %,
0,08 % ≤ Mn ≤ 0,3 %,
0,05 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % und

Verunreinigungen von jeweils weniger als 0,005 %, insgesamt maximal 0,15 %, wobei der Rest Al ist.

Revendications

1. Procédé de conditionnement de la surface d'une feuille de lithographie ou d'une pellicule de lithographie constituée d'un alliage d'aluminium, ledit procédé comprenant au moins l'étape consistant à dégraisser la surface de la feuille de lithographie ou de la pellicule de lithographie avec un milieu dégraissant,
caractérisé en ce que
le milieu dégraissant aqueux contient 1,5 à 3 % en poids d'un composite de 5 à 40 % de tripolyphosphate de sodium, 3 à 10 % de gluconate de sodium, 3 à 8 % d'un composite de surfactants non ioniques et anioniques et facultativement 0,5 à 70 % de soude, de préférence de 30 à 70 % de soude, de l'hydroxyde de sodium étant ajouté au milieu dégraissant aqueux de manière à ce que la concentration en hydroxyde de sodium dans le milieu dégraissant aqueux soit de 0,01 à 5 % en poids, de préférence de 0,1 à 1,5 %, de manière davantage préférée de 1 à 2,5 % en poids.

2. Procédé selon la revendication 1, dans lequel la durée d'application du milieu dégraissant est de 1 à 7 secondes, de préférence de 2 à 5 secondes.

3. Procédé selon la revendication 1 ou 2, dans lequel la température du milieu dégraissant est de 50 à 85°C, de préférence de 65°C à 75°C.

4. Procédé selon les revendications 1 à 3, dans lequel la valeur de pH du milieu dégraissant aqueux est de 10 à 14, de préférence de 10 à 13,5.

5. Procédé selon les revendications 1 à 4, dans lequel la pellicule de lithographie est conditionnée et le conditionnement est réalisé après la fabrication, respectivement en enroulant la pellicule, la pellicule conditionnée étant ainsi enroulée sur une bobine.

6. Procédé selon les revendications 1 à 5, dans lequel l'alliage d'aluminium est l'un des alliages d'aluminium AA1050, AA1100, AA3103 ou AlMg0,5.

7. Procédé selon les revendications 1 à 5, dans lequel l'alliage d'aluminium contient les constituants d'alliage suivants, en pourcentage en poids :

0,05 % ≤ Si ≤ 0,15 %,
0,3 % ≤ Fe ≤ 0,4 %,
Cu ≤ 0,01 %,
Mn ≤ 0,05 %,
Mg ≤ 0,01 %,
Zn ≤ 0,015 %,
Ti ≤ 0,015 %,

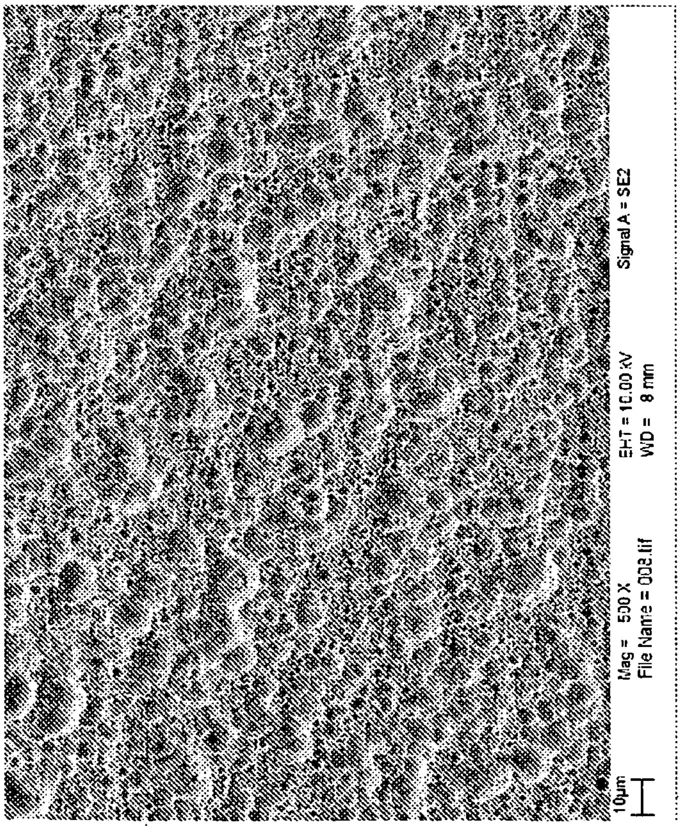
chacune des impuretés étant présente à hauteur de moins de 0,005 % et leur somme atteignant un maximum de 0,15 %, le reste étant de l'Al
ou

0,05 % ≤ Si ≤ 0,25 %,
0,30 % ≤ Fe ≤ 0,40 %,
Cu ≤ 0,04 %,
Mn ≤ 0,05 %,
0,1 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % et

chacune des impuretés étant présente à hauteur de moins de 0,005 % et leur somme atteignant un maximum de 0,15 %, le reste étant de l'Al
ou

0,05 % ≤ Si ≤ 0,5 %,
0,40 % ≤ Fe ≤ 1 %,
Cu ≤ 0,04 %,
0,08 % ≤ Mn ≤ 0,3 %,
0,05 % ≤ Mg ≤ 0,3 %,
Ti ≤ 0,04 % et

chacune des impuretés étant présente à hauteur de moins de 0,005 % et leur somme atteignant un maximum de 0,15 %, le reste étant de l'Al.


10µm
Mag = 500 X
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EHT = 10.00 kV
WD = 8 mm
Signal A = SE2

Fig. 1

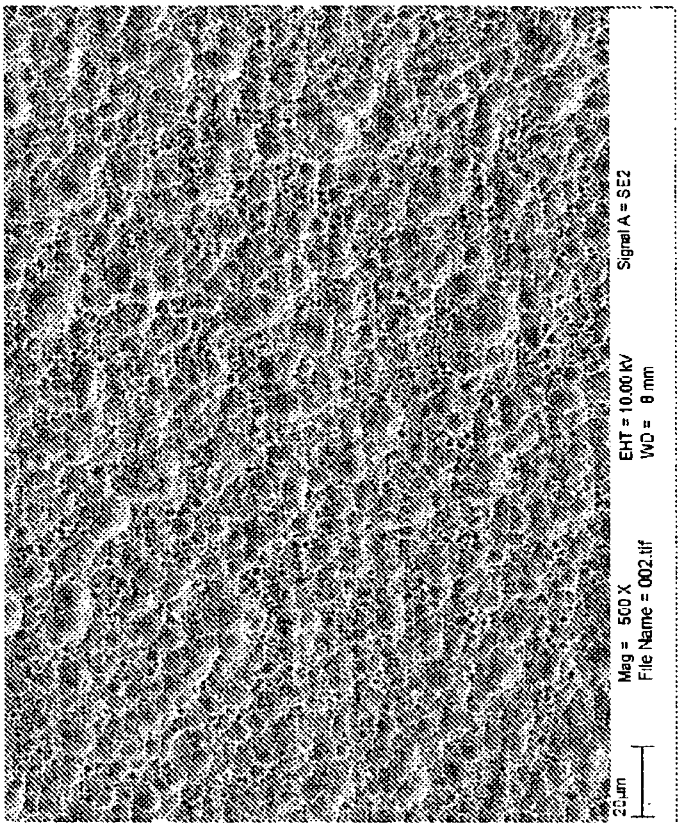
20µm
Mag = 500 X
File Name = 002.tif
EHT = 10.00 kV
WD = 8 mm
Signal A = SE2

Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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