(11) **EP 2 177 638 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

21.04.2010 Bulletin 2010/16

(51) Int Cl.: C22C 21/00 (2006.01)

(21) Application number: 08018013.6

(22) Date of filing: 15.10.2008

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

Designated Extension States:

AL BA MK RS

(71) Applicant: "IMPEXMETAL" S.A. 00842 Warszawa (PL)

(72) Inventors:

- Rutecki, Pawel 62-510 Konin (PL)
- Frontczak, Andrzej 62-510 Konin (PL)

- Sauczek, Pawel 62/510 Konin (PL)
- Kosmalski, Grzegorz 62-510 Konin (PL)
- Smorawinski, Zdzislaw 62-510 Konin (PL)
- (74) Representative: Klassek, Maciej Adam Inventconsult, Kancelaria Patentowa, ul. Sowinskiego 1 40-272 Katowice (PL)

Remarks:

Amended claims in accordance with Rule 137(2) EPC.

(54) Aluminium alloy, in particular for heat exchangers manufacturing

(57) The invention refers to the aluminum alloy, designated in particular for heat exchangers manufacturing, in particular for automotive industry. Aluminum alloy contains: silicon Si from 0.05 % to 1.2 % by weight, iron Fe from 0.1 % to 0.5 % by weight, manganese Mn from 0.7 % to 2.0 % by weight, titanium Ti up to 0.25 % by weight, beryllium Be up to 0.1 % by weight, wherein the ratio of

beryllium and titanium [Be/Ti] by weight is from 0.5 to 2.5. The alloy contains at least one potential regulator in the form of zinc Zn from 0.1~% to 2.0~% by weight and/or copper Cu from 0.2~% to 2.0~% by weight and at least one strengthening additive in the form of nickel Ni from 0.05~% to 0.40~% by weight and/or chromium Cr from 0.05~% to 0.40~% by weight and/or magnesium Mg up to 1.1~% by weight.

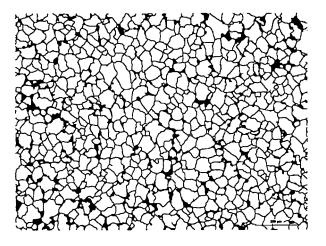


Fig. 1a

EP 2 177 638 A

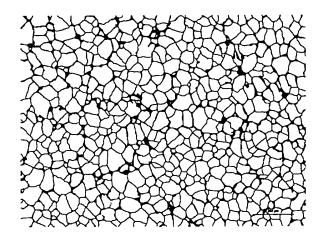


Fig. 1b

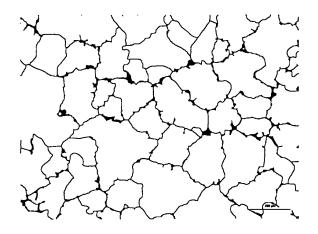


Fig. 1c

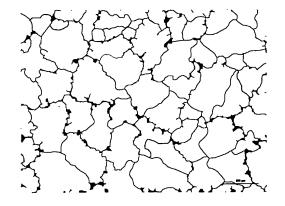


Fig. 1d

Description

10

20

30

35

40

45

50

55

[0001] The invention refers to the aluminum alloy, designated in particular for heat exchangers manufacturing, in particular for automotive industry.

- **[0002]** Known aluminum alloys for heat exchangers manufacturing, in particular for radiators, apart from the main ingredient, that is aluminum, contain the additions, which can be divided into three groups:
 - Group I basic additions, which constitute the so-called base alloy with the main element, that is aluminum,
 - · Group II additions being basic potential regulators, and
 - Group III alloy strengthening additions.

In known alloys, Group I additions include silicon, iron, manganese, Group II additions include zinc or copper used separately or together, and Group III additions include nickel, chromium, magnesium and zirconium, used separately or together.

[0003] The known standard composition of aluminum alloy type 3003, specified in standard PN-EN573, in addition to aluminum includes also silicon Si - 0.6 %, iron Fe - 0.7 % and manganese Mn - from 1.0% to 1.5 %. The alloy may also contain potential regulators in the form of zinc Zn - up to 0.10% and copper Cu - from 0.05% to 0.20%.

[0004] The known alloys are used, among others, for manufacturing of heat exchangers for automotive industry, such as radiators and condensers. Known alloys are based on standard alloys type 3003 and 3003+ 1.5 % Zn, enriched with additions of different chemical elements, which are to regulate the corrosion potential, corrosion resistance, strength properties, thermal resistance, plasticity and formability.

[0005] In the processes for heat exchangers manufacturing, aluminum alloys are used, which according to their eventual purpose differ in mechanical properties and corrosion potential level. The alloys vary in scope of zinc content, wherein the alloys used for the manufacturing of pipes do not contain zinc, whereas the alloys used for the manufacturing of the flanges with a developed surface area, which surround the pipes and are known as fins, contain zinc, which is a known corrosion potential regulator for the alloy. In the combined working system of the heat exchanger, the fins are used as pipes protectors.

[0006] The properties of the known alloys are influenced by their chemical composition, manufacturing method and type of thermal treatment.

[0007] The properties of any aluminum alloys depend on the composition of solution α , and also crystallographic composition and structure, in particular the size and distribution of inter-metallic precipitations at grain boundaries. The direct-chill casting processes for the known aluminum alloys are characterized by a dendrite structure, which is decisive for non-homogeneity of the material, variable size of precipitations and their distribution. This material structure is then reflected in the final properties of the product, that is the properties of the rolled strip. Following local variations in microcrystalline structure, there are considerable corrosion potential gradients between precipitations and solution in the known alloys, which leads to local corrosion centers. In the process of heat exchangers manufacturing, the known process for structure homogenization is not used, as in the final product, the expected length of grains at the cross-section of the strip should be relatively low, which is connected with a large grain size. Small grains are an obstacle in the process of heat exchangers brazing.

[0008] Patent Description No. 185567 specifies the composition of aluminum alloy for fins manufacturing, with the following basic additions /group I/: silicon Si from 0.05% to 0.50% by weight, iron Fe 0.5% by weight, manganese Mn from 0.1% to 1.5 % by weight, and titanium from 0.03 % to 0.35 % by weight and additions with the purpose of potential regulators /group II/, that is zinc Zn from 0.06% to 1.0 % by weight, copper Cu 0.03 % by weight, and alloy strengthening additions /group III/including nickel Ni below 0.01 % by weight, chromium Cr 0.5 % by weight, and magnesium Mg 1.0 % by weight, and zirconium Zr 0.,3 % by weight. The alloy is designed for fins production.

[0009] European Patent Document EP 1435397B1 refers to the aluminum alloy containing silicon Si from 0.5% to 1.0 % by weight, iron Fe 0.3 % by weight, manganese Mn from 0.3 % to 0.7% by weight and zinc Zn 4 % by weight, and magnesium Mg from 0.25% to 0.6 % by weight, and zirconium Zr from 0.05% to 0.25 % by weight. This alloy is also designed for fins manufacturing.

[0010] Furthermore, European Patent Document EP 1580286 A2 refers to the alloy for the manufacturing of heat exchanger pipes, which contains silicon Si 0.1 % by weight, manganese Mn from 1.55 % to 1.9 % by weight, and copper from 0.6 % to 1.0% by weight and magnesium Mg 0.4 % by weight, and zirconium Zr from 0.05 % to 1.5 % by weight. [0011] It is commonly known that with increasing content of additions, alloys strength and thermal resistance increase, whereas their resistance to corrosion and plasticity deteriorate. In the currently used technologies for the production of alloys to be used in the manufacturing of heat exchangers, this fact considerably limits the natural tendency to reduce the thickness of a material, in particular in the case of the strip designed for fins production. The desired properties of the material for the pipes include plasticity of material related to its formability and appropriate corrosion potential correlated with the fins potential so that the protecting effect is provided.

[0012] Material for fins manufacturing should also be characterized by good formability. Therefore, a difference in the composition of the alloy for pipes manufacturing and fins manufacturing is in corrosion potential regulators, which in the known alloys have the form of Zn and/or Cu additions and alloy strengthening additions, which in the known alloys have the form of Ni, C, Mg, Zr, which are added together or separately.

[0013] International patent application WO 2005/011889 refers to aluminum alloy designed for the production of pipes and fins for heat exchangers, containing silicon Si 0.3 % by weight, iron Fe up to 0.5 % by weight, manganese Mn from 0.5 % to 0.7 % by weight, titanium Ti below 0.2 % by weight, and zinc Zn up to 2.0 % by weight, and copper Cu from 0.06 % to 1.5 % by weight.

[0014] In order to meet the ambitious requirements for aluminum alloys designed for the manufacturing of heat exchangers, especially radiators for automotive industry, said radiators composed of pipes surrounded by fins, the base alloy was developed, which together with the complementing and modifying additions is the object of this invention. Aluminum alloy according to the present invention contains:

silicon Si from 0.05 % to 1.2 % by weight iron Fe from 0.1 % to 0.5 % by weight, manganese Mn from 0.7 % to 2.0 % by weight, titanium Ti 0.25 % by weight, beryllium Be up to 0.1 % by weight,

15

30

40

wherein beryllium Be to titanium Ti ratio by weight [Be/Ti] is from 0.5 to 2.5; and at least one potential regulator, in the form of zinc Zn from 0.1 % to 2.0% by weight, copper Cu 0,2 to 2,0 % by weight; and

at least one strengthening addition in the form of nickel Ni from 0.05% to 0.40 % by weight, chromium Cr from 0.05% to 0.40 % by weight, and magnesium Mg up to 1.1 % by weight.

[0015] The alloy according to the invention shows the properties of the globular primary structure, which is a result of its new chemical composition. The result of crystallizing the alloy in the globular form in the presence of the elements which act as alloy strengthening additions, such as Ni, Cr, Mg and Si guarantees even distribution of undissolved elements in the form of fine inter-metallic phases at the boundary, which are formed as a result of grain crystallization process, wherein the grain size is not reflected in the final product, which is made from the alloy according to the present invention. The globular structure which is formed, makes it possible in the conventional treatment process to have the final product, i.e. rolled strip, with solution and precipitation strengthening and at the same time with high plasticity of the alloy and its good thermal and corrosion resistance.

The alloy according to the invention is designed for the manufacturing of the elements of heat exchangers, in particular radiators for automotive industry, wherein the alloy may be used for the manufacturing of both pipes and fins.

35 Analysis of microcrystalline structure of the alloy

[0016] The microcrystalline structure of the alloy according to the present invention was analyzed by comparing the structure of the alloy according to the present invention, of the composition as follows:

 $\label{eq:continuous} Fe - 0.274\%; Si - 0.392\%; Cu - 0.011\%; Zn - 1.413\%; Ti 0.157\%; Mg - 0.022\%; Mn - 1.510\%; Ni - 0.136\%; Be - 0.045\%; Zr - 0.019; remaining Al- alloy HF 311 (Fig. 1a) and$

Fe - 0.366%; Si - 0.362%; Cu - 0.370%; Zn - 0.050%; Ti - 0.142%; Mg - 0.006%; Mn - 0.850%; Ni - 0.139%; Be - 0.025%; Zr - 0.003%; remaining Al - alloy LT325 (Fig. 1b)

with the structure of standard alloy 3003+1.5 % of zinc Zn according to PN-EN 573, of the composition as follows:

Fe - 0.290%; Si - 0.382%; Cu - 0.076%; Zn - 1.469%; Ti - 0.033%; Mg - 0.009%; Mn - 1.265%; Ni - 0.04%; Be - 0.000%; Zr - 0.033%; remaining Al - alloy LT325 (Fig. 1c).

and with the structure of reference alloy FA6815 of the following chemical composition:

Fe - 0.267%; Si - 0.974%; Cu - 0.011%; Zn - 1.473%; Ti - 0.035%; Mg - 0.030%; Mn - 1.565%; Ni - 0.009%; Be - 0.001%; Zr - 0.115%; Al - remaining %. (Fig. 1d).

The specimens of the above mentioned alloys were made, which then were used as crystalline microsections. Fig. 1a - 1d show the pictures of the primary microstructure of the tested specimens.

Strength properties tests

[0017] Strength tests were made according to the method compliant with PN-EN 10002-1. Using the strip specimens, made of the alloy according to the present invention. For the measurements, the testing device Type 1120.25 by Zwick GmbH Germany was used, and the following alloys were tested:

- alloy HF 311 for fins manufacturing, of the following chemical composition:

```
Fe - 0.274%; Si - 0.392%; Cu - 0.011%; Zn - 1.413%; Ti 0.157%; Mg - 0.022%; Mn - 1.510%; Ni - 0.136%; Be - 0.045%; Zr - 0.019; remaining Al,
```

and

- alloy LT 325 for pipes manufacturing, of the following chemical composition:

```
Fe - 0.366%; Si - 0.362%; Cu - 0.370%; Zn - 0.050%; Ti - 0.142%; Mg - 0.006%; Mn - 0.850%; Ni - 0.139%; Be - 0.025%; Zr - 0.003%; remaining Al.
```

[0018] The results of strength tests for both alloys according to the invention are shown in table no. 1.

Table No. 1.

Mechanical properties of the alloys

-		ť	1

20

25

30

35

40

45

5

10

R_m [Mpa] A₅₀ [%] Alloy type R_{02} [Mpa] HF311 205 195 2 145 55 after brazing LT325 165 155 4 LT325 after brazing 156 58

Where:

R_m - tensile strength,

R₀₂ - notional yield point,

A₅₀ - elongation.

Thermal resistance tests

[0019] Thermal resistance tests for the alloy according to the invention were made based on the sagging distance (SD) method using the strip specimens. The tests were made on the equipment comprised of the laboratory oven and the rack, fig. 2. In order to increase the sensitivity of the measurement, test conditions were changed and instead of the circular support the edge support was used. Moreover, the length of the protruding strip was changed for the tests, given different thicknesses and widths of the strips used, on the basis of the following criterion:

strip length I measured from the support, which should be equal to the ratio between the mass of strip 1 in the length 1 to the cross-section of strip F. For the tested alloys, the ratio was specified as follows:

HF
$$311 = 1.30 - 1.40 \text{ g/mm}^2$$

LT $325 = 1.40 - 1.50 \text{ g/mm}^2$.

[0020] During the measurement, the adjustments of heating and holding in a temperature were made using a thermocouple located under the tested material near the support in the axis of the measurement device.

[0021] Diagram of the SD test equipment is shown in Fig. 2

Table 2.

50	
55	

Thermal propert	Thermal properties of the alloys		
Alloy type	SD [mm]		
HF311	max 25		
LT325	max 30		

Testing of alloys corrosion resistance

[0022] Tests in scope of corrosion resistance of the alloys according to the invention were made in line with the method as per ASTM G 69-97. The tests were made using the apparatus Potencjostat - Galwanostat ATLAS 0531 EU and the following properties were determined:

density of passivation current I_p , passivation potential E_p i re-passivation potential E_R .

[0023] The lower passivation current and the higher pitting potential, the better resistance to corrosion.

[0024] The results of tests are shown in Table No. 3.

Table 3.

15	

20

25

30

35

45

50

55

10

Corrosion properties of the alloys

Alloy type $\begin{bmatrix} I_P \\ [\mu A/cm^2] \end{bmatrix}$ $\begin{bmatrix} E_P \\ [mV] \end{bmatrix}$ $\begin{bmatrix} [mV] \end{bmatrix}$ HF311 82 -882 -800

LT325 72 -736 -626

Claims

Ciali

1. Aluminum alloy, in particular for heat exchangers manufacturing, containing:

silicon Si from 0.05 % to 1.2 % by weight, iron Fe from 0.1 % to 0.5 % by weight, manganese Mn from 0.7 % to 2.0 % by weight. titanium Ti up to 0.25 % by weight, beryllium Be up to 0.1 % by weight,

wherein the ratio of beryllium and titanium [Be/Ti] by weight is from 0.5 to 2,5.

- 2. Alloy according to claim 1, containing at least one potential regulator in the form of zinc Zn from 0.1 % to 2.0 % by weight and/or copper Cu from 0.2 % to 2.0 % by weight.
- 3. Alloy according to claim 1 or 2, containing at least one strengthening addition in the form of nickel Ni from 0.05 % to 0.40 % by weight and/or chromium Cr from 0.05 % to 0.40 % by weight and/or magnesium Mg up to 1.1 % by weight.

Amended claims in accordance with Rule 137(2) EPC.

1. Aluminum alloy, in particular for heat exchangers manufacturing, consisting of:

silicon Si from 0.05 % to 1.2 % by weight, iron Fe from 0.1 % to 0.5 % by weight, manganese Mn from 0.7 % to 2.0 % by weight. titanium Ti up to 0.25 % by weight, beryllium Be up to 0.1 % by weight,

wherein the ratio of beryllium and titanium [Be/Ti] by weight is from 0.15 to 2.5 and containing:

at least one potential regulator in the form of zinc Zn from $0.1\,\%$ to $2.0\,\%$ by weight and/or copper Cu from $0.2\,\%$ to $2.0\,\%$ by weight and

at least one strengthening addition in the form of nickel Ni from 0.05 % to 0.40 % by weight and/or chromium Cr from 0.05 % to 0.40 % by weight and/or magnesium Mg up to 1.1 % by weight

and the reminder being aluminum Al with unavoidable impurities.

5			
10			
15			
20			
25			
30			
35			
40			
45			
50			
55			

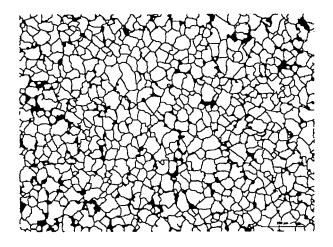


Fig. 1a

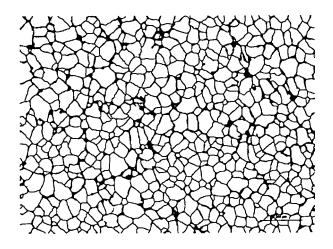


Fig. 1b

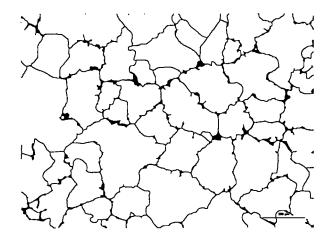


Fig. 1c

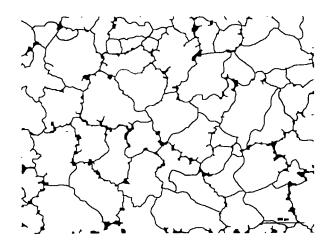
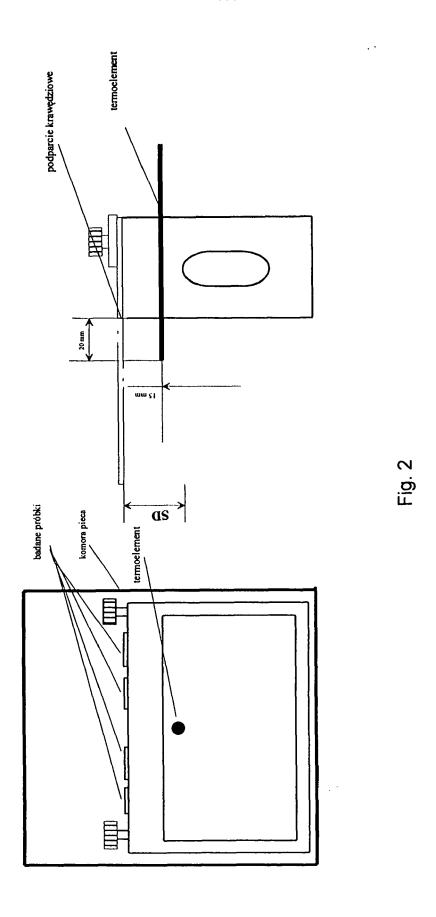


Fig. 1d





EUROPEAN SEARCH REPORT

Application Number EP 08 01 8013

	DOCUMENTS CONSIDERE			
Category	Citation of document with indicati of relevant passages	on, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 04 048045 A (NIPPON NIKKEI TECHNO RES CO L 18 February 1992 (1992 * abstract * * page 3; example 10;	TD) -02-18)	1-3	INV. C22C21/00
A	JP 04 318144 A (KOBE S 9 November 1992 (1992- * abstract * * page 4; examples 1,1	11-09)	1-3	
А	JP 2000 273563 A (SKY 3 October 2000 (2000-1 * abstract * * page 6; example M; t	0-03)	1-3	
A	GB 1 423 844 A (ELEKTR 4 February 1976 (1976- * the whole document *		1-3	
А	GB 1 330 560 A (SUMITO INDUSTRIES; SUMITOMO C 19 September 1973 (197 * the whole document *	HEMICAL CO)	1-3	TECHNICAL FIELDS SEARCHED (IPC)
А	JP 06 272001 A (FURUKA KAWASAKI STEEL CO) 27 September 1994 (199 * abstract *	•	1-3	
	The present search report has been	drawn up for all claims		
	Place of search Munich	Date of completion of the search 2 March 2009	Pat	Examiner Eton, Guy
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another ument of the same category inological backgroundwritten disclosure rmediate document	T : theory or principl E : earlier patent do after the filing dat D : document cited i L : document cited for a : member of the sa document	e underlying the i cument, but publi te n the application or other reasons	nvention shed on, or

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

EP 08 01 8013

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.

02-03-2009

GB 1423844 A 04-02-1976 BE 798413 A1 16 CA 983291 A1 10 CH 587541 A5 13 DE 2317994 A1 15 DK 140505 B 17 FI 60462 B 30 FR 2182212 A1 07 IT 980911 B 10 JP 49107906 A 14 NL 7305733 A 30 NO 129579 B 29 SE 360391 B 24 US 4233066 A 11 GB 1330560 A 19-09-1973 AU 3749871 A 05 CA 945400 A1 16 CH 560762 A5 15	
JP 2000273563 A 03-10-2000 JP 4040787 B2 36 GB 1423844 A 04-02-1976 BE 798413 A1 16 CA 983291 A1 16 CH 587541 A5 13 DE 2317994 A1 15 DK 140505 B 17 FI 60462 B 36 FR 2182212 A1 07 IT 980911 B 16 JP 49107906 A 14 NL 7305733 A 36 NO 129579 B 29 SE 360391 B 24 US 4233066 A 11 GB 1330560 A 19-09-1973 AU 3749871 A 05 CA 945400 A1 16 CH 560762 A5 15	
GB 1423844 A 04-02-1976 BE 798413 A1 16 CA 983291 A1 10 CH 587541 A5 13 DE 2317994 A1 15 DK 140505 B 17 FI 60462 B 30 FR 2182212 A1 07 IT 980911 B 10 JP 49107906 A 14 NL 7305733 A 30 NO 129579 B 29 SE 360391 B 24 US 4233066 A 11 GB 1330560 A 19-09-1973 AU 3749871 A 05 CA 945400 A1 16 CH 560762 A5 15	
CA 983291 A1 10 CH 587541 A5 13 DE 2317994 A1 15 DK 140505 B 17 FI 60462 B 36 FR 2182212 A1 07 IT 980911 B 16 JP 49107906 A 14 NL 7305733 A 36 NO 129579 B 29 SE 360391 B 24 US 4233066 A 11 GB 1330560 A 19-09-1973 AU 3749871 A 05 CA 945400 A1 16 CH 560762 A5 15	0-01-20
CA 945400 A1 16 CH 560762 A5 15	6-08-19 0-02-19 3-05-19 5-11-19 7-09-19 0-09-19 0-10-19 4-10-19 0-10-19 4-09-19
JP 52004485 B 04	5-07-19 6-04-19 5-04-19 4-02-19
JP 6272001 A 27-09-1994 JP 2925884 B2 28	 8-07-19
JP 6272001 A 27-09-1994 JP 2925884 B2 28	3 3-07-1

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

- EP 1435397 B1 [0009]
- EP 1580286 A2 **[0010]**

• WO 2005011889 A [0013]