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(54) **ALUMINIUM ALLOYS FOR MANUFACTURING OF ALUMINIUM CANS BY IMPACT EXTRUSION**

(57) The present invention provides aluminium alloys for manufacturing of aluminium cans by impact extrusion. Alloys according to the invention consist of 0.050-0.200 wt. % Si, 0.150-0.250 wt. % Fe, 0.300-0.800 wt. % Cu, 0.010-0.400 wt. % Mn, 0.050-0.200 wt. % Mg,

0.003-0.050 wt. % Cr, 0.010-0.100 wt. % Ti, 0.001-0.050 wt. % B, less than 0.15 wt. % of secondary alloying elements with less than 0.05 wt. % of any secondary alloying element, and aluminium as the remainder.

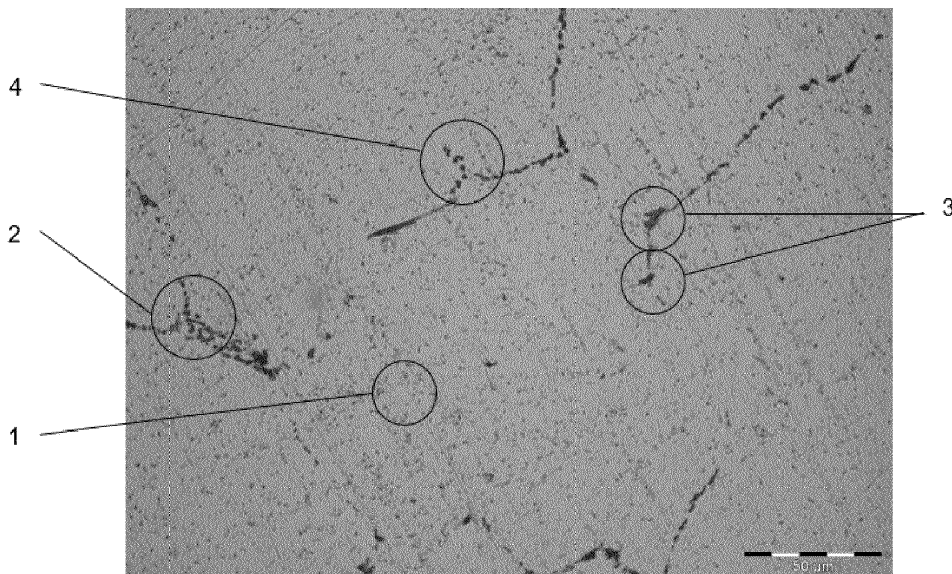


FIG. 2

DescriptionFIELD OF THE INVENTION

5 **[0001]** The field of the invention is related to aluminium alloys. Specifically, the present invention relates to aluminium alloys for manufacturing of aluminium cans by impact extrusion.

BACKGROUND ART

10 **[0002]** Aluminium cans, for example aerosol cans, are typically manufactured from aluminium slugs by impact extrusion from alloys of series 1XXX and from the series 3XXX, which are previously stamped from an aluminium narrow strip. According to the 4-digit international labelling system, the first digit (Xxxx) indicates the main alloying element, which has been added to the aluminium alloy; the second digit (xXxx) indicates a modification of the specific alloy; and the third and fourth digits are numbers given to identify a specific alloy in the series and can refer, for example, to the purity
15 of the aluminium or to the specific combination of alloying elements.

[0003] Usually, in a first step, the body of the can may be formed by impact extrusion from slug. In the next step the cans are internally coated and dried (polymerization) at around 250 °C. After polymerization the external coating, printing and lacquering follow. Drying of the external colour, printing and lacquering usually takes place at around 150 - 190 °C. In the last step the neck of the can may be formed, for example, on a multi-die necking machine.

20 **[0004]** Aluminium alloys from 1XXX series are used for production of cans because they have good manufacturability at impact extrusion, being the most common aluminium grades EN AW 1050A having a minimum Al (aluminium) content of 99.5% by weight, and EN AW 1070 having an Al minimum content of 99.7% by weight. These two aluminium alloys are very ductile, but have reduced mechanical strength after lacquering, so the can weight cannot be lightened.

25 **[0005]** In the case of 3000-series aluminium alloys for cans according to the European Standard EN 573-3, the most common aluminium grades are EN AW 3102 having an Mn (manganese) content of approximately 0.3% by weight and EN AW 3207 having an Mn content of approximately 0.6% by weight. New aluminium alloys from Al-Mg-Si system were developed, which enable the production of cans with reduced thickness and weight. However, while aluminium alloys EN AW 3102 and EN AW 3207 improve high-temperature strength, thus making it possible to manufacture thinner and lighter cans compared to the 1000-series alloys, they also disadvantageously require the use of a higher tonnage
30 extrusion presses because, due to the same reason, higher tonnage machine pressures also required during the process. Also, as a result of this, faster tool wearing and degradation occurs.

[0006] However, manufacturing of cans using known alloy compositions typically results in a significant decrease in mechanical properties after polymerization (*i.e.* high-temperature curing after lacquering). Recrystallization steps, *i.e.* the growth of the grain size which starts at such high temperatures, have also been found to lead to a decrease in
35 mechanical properties.

[0007] Many developments have been produced to increase the mechanical properties of aluminium alloys for cans and reduce the decrease of mechanical properties in the lacquering process. Many of them are based on a determinate alloy composition and sometimes involve the addition of specific alloying elements such as Zr (zirconium) to increase the recrystallization threshold as in the example patents mentioned below.

40 **[0008]** US7520044B2 discloses an alloy for can production based on system Al-Mg-Si system that comprises 0.12 to 0.20 weight % Fe (iron), 0.35 to 0.45 weight % Si (silicon), 0.25 to 0.40 weight % Mg (magnesium), 0.05 to 0.15 weight % Mn (manganese), and the rest is Al (aluminium). However, the presence of a high percentage of Si (> 0.35 wt.%) promotes a quick wear of transformation tools, and also a higher tonnage press is needed to deform the slug to obtain the cans. The presence of a high percentage of Mg (> 0.25 wt.%) also promotes a quicker degradation of the tooling
45 and requires higher deformation forces.

[0009] FR2773819A1 proposes a can alloy with Cu (copper) and Mn, where the composition of Cu and Mn is inside a polygon defined by a system of axis with Mn (wt.%) in abscissa and Cu (wt.%) in ordinates. A percentage of Mn between 0.2 and 0.4 wt.% promotes the maintenance of mechanical properties after lacquering. Cu is limited between 0.4 and 0.65 wt.% in order to obtain a high corrosion resistance and high mechanical characteristics. Ti should be within
50 a percentage between 0.005 and 0.05 wt.% to obtain small as-cast grain size. However, the high copper weight amounts (>0.4 wt.%) in combination with manganese amounts higher than 0.2 wt.% makes it difficult to deform the alloy, so higher forces are required, which could also lead to need powerful machinery. The high percentage of Cu also promotes a reduced corrosion resistance of the alloy.

55 **[0010]** FR2457328A1 discloses an alloy for can production with good cold deformation and resistant to the lacquering process. This document discloses an alloy having <0.4 wt % Fe, 0.15-0.35 wt. % Si, 0.15-0.35 wt. % Mg, <0.01 wt. % Cu, <0.2 wt. % Cr, <0.2 wt. % Mn, <0.15 wt. % Zr and <0.05 wt. % of any other alloying element. Also, the described alloy has low Ti amounts (<0.05 wt. %), thus significantly reducing the beneficial effects typically associated with higher Ti relative amounts. Cu weight percentage is very limited, which negatively impacts on the mechanical properties of the

alloy, compared to alloys with higher Cu amounts, and promotes the formation of Al_2Cu precipitates. Also, since low Mn amounts are present in these alloys, they are not in enough quantity to compensate for the presence of Fe, and acicular $\beta-Al_5FeSi$ phase formation occurs.

[0011] EP2881477B1 discloses a heat resistant alloy for can production with good cold deformation and resistant to the lacquering process. This document discloses an alloy according to EN AW 1050A with $Si \leq 0.25$ wt. %; $Fe \leq 0.4$ wt. %; $Cu \leq 0.05$ wt. %; $Mn \leq 0.05$ wt. %; $Zn \leq 0.07$ wt. %; $Ti \leq 0.05$ wt. %, characterized in that each composition contains added Zr in an amount ranging between 0.10 and 0.15% by weight. Again, since low Mn amounts are present in these alloys, they are not in enough quantity to compensate for the presence of Fe, and acicular $\beta-Al_5FeSi$ phase formation therefore inevitably occurs.

[0012] EP3075875A1 discloses an aluminium alloy for cans manufactured by the impact extrusion method with constant mechanical properties before and after polymerization. This document discloses an alloy that contains alloying elements in mass percent: 0.1-0.55 wt. % Fe, 0.05-0.2 wt. % Si, <0.01 wt. % Mg, <0.01 wt. % Cu, < 0.02 wt. % Zn, 0.0 - 0.03 wt. % Ti, 0.01 - 0.06 wt. % Mn, 0.05 - 0.2 wt. % Zr. The addition of Zr into the alloy in the range of 0.05 - 0.2 wt. % allows to maintain tensile test strength and improve deformable and burst pressure. The addition of Zr increase the recrystallization threshold above 300°C and other elements like Fe, Mn, Ti and Si in the form of intermetallic phases strengthen the aluminium matrix and provide higher mechanical properties, reflected on higher deformable and burst pressures. However, these alloys are more expensive because they contain zirconium. Besides, the use of such low amounts of copper and magnesium necessarily requires using high-purity raw materials produced by electrolysis, sometimes even by several consecutive electrolytic steps, to ensure that low amounts of any undesired specific metal, which may be a contaminant, are obtained. Due to this, the cost of these aluminium alloys becomes undesirably more expensive.

[0013] JPS6333185A discloses an aluminium alloy brazing sheet with excellent corrosion resistance and drooping resistance, composed by 0.2-1.5 wt.% Mn and 0.03-0.15 wt.% Zr. Zr promotes coarsening of the crystal grain at core material brazing time and crystal grain formation, thus preventing the restraining action of Fe, which is present as impurity. In order to achieve this, an amount of Zr is needed which corresponds to at least 20 wt.% of the Fe content. Zr is an expensive alloying element, in contrast with Fe. A higher percentage of Zr promotes an increase in the price of the alloy, and Fe is always present as an alloying element, but it can also be considered a contaminant depending on its wt.%. Reducing the Fe wt.% to low values in an alloy also supposes an increase in the price of the alloy, due to the need of working with high purity alloys.

[0014] WO2013040339A1 discloses aluminium alloys for impact extrusion manufacturing process employing recycled aluminium scraps with relatively pure aluminium. Disclosed alloys are composed at least about 97 wt.% Al, at least about 0.1 wt.% Si, at least about 0.25 wt.% Fe, at least about 0.05 wt.% Cu, at least about 0.07 wt.% Mn and at least about 0.05 wt.% Mg. These alloying elements in the disclosed amounts, however, negatively modify metallurgical and mechanical characteristics, and also increase solidification temperature range, increase yield strength values and decrease ductility. Due to this, and also because of the increased ultimate tensile strength and yield strength values, it is necessary to increase the tonnage loads when punching slugs. Furthermore, these alloys with low-alloying element content are normally more expensive than alloys with alloy compositions that can be obtained with less pure materials.

[0015] WO2018125199A1 discloses aluminium alloys for impact extrusion manufacturing processes employing recycled aluminium scraps with relatively pure aluminium. Alloy is composed by at least about 97.56 wt.% Al, at least about 0.07 wt.% Si, at least about 0.22 wt.% Fe, at least about 0.04 wt.% Mn, at least about 0.02 wt.% Mg and at most about 0.15 wt.% impurities and a balance comprising one of Cu, Zn, Cr, and Ti elements. Nevertheless, these alloys with low-alloying elements content are normally more expensive than the alloys with alloy compositions that can be obtained with less pure materials.

[0016] WO9937826A1 discloses aluminium alloys for the manufacture of containers. However, these alloys involve high Mg percentages (0.8-1.5 wt.%), which promote a quick degradation of tooling, and increase the tonnage loads when punching slugs.

[0017] WO2020048988A1 discloses an aluminium alloy consisting of: 0.07 wt.% to 0.17 wt.% silicon, 0.25 wt.% to 0.45 wt.% iron, 0.02 wt.% to 0.15 wt.% copper, 0.30 wt.% to 0.50 wt.% manganese, 0.05 wt.% to 0.20 wt.% chromium, 0.01 wt.% to 0.04 wt.% titanium, and the remainder aluminium and optionally additional admixtures. However, a content in Fe over 0.25 wt.% implies a reduction on the ductility of the alloy, more tool wearing and also it could lead to the need of higher pressing forces. On the other hand, the high percentages of Mn (>0.3 wt.%) were added to avoid the needle-like $\beta-Al_5FeSi$ compounds, but the combination of both elements increases the tooling wear, can reduce the ductility of the alloy and increase the risk of cracking. The use of Mg as is not described, but rather appears to be an impurity. Mg is known in the art to potentially provide better mechanical properties, its use in aluminium alloys is responsible for the formation of intermetallics with an effect of precipitation hardening at the temperatures used for baking an inner lacquer. Here, metastable clusters and / or precipitates based on magnesium are formed (as Mg_2Si), leading to an increase in strength and counteracting recrystallization, so a loss of strength is caused thereby. Also, the Cu content is limited to 0.02 wt.% to 0.15 wt.%, wherein such low amounts have been found to adversely affect strength and heat resistance of the aluminium alloy due to the reduced formation of Al_2Cu precipitates.

[0018] WO2020048994A1 discloses an aluminium alloy consisting of: 0.07 wt.% to 0.17 wt.% silicon, 0.25 wt.% to 0.45 wt.% iron, 0.05 wt.% to 0.20 wt.% copper, 0.30 wt.% to 0.50 wt.% manganese, 0.05 wt.% to 0.25 wt.% magnesium, 0.01 wt.% to 0.04 wt.% titanium, and the remainder aluminium and optionally additional admixtures. The content in Fe over 0.25 wt. % implies a reduction on the ductility of the alloy, more tool wearing and also it could lead to the need of higher pressing forces. Besides, high percentages of Mn (>0.3 wt.%) are added to avoid the formation of needle-like β -Al₅FeSi compounds, but the combination of both Fe and Mn elements disadvantageously increases the tooling wear, can reduce the ductility of the alloy and increase the risk of cracking.

[0019] Thus, problems arising during can manufacturing, such as the decrease in mechanical properties after polymerization, or also internal colour reduction, are still unresolved. Therefore, there is a significant need to find new aluminium alloys providing enhanced mechanical properties.

SUMMARY OF INVENTION

[0020] The present invention provides aluminium alloys for manufacturing of aluminium cans by impact extrusion, which solves the technical problems known in the art of:

- preservation of mechanical properties after polymerization (*i.e.* high-temperature curing after lacquering), which is expressed in higher deformation resistance and burst pressure of the can,
- providing good transformation (*e.g.* can conformability) and the provision of adequate surface of can after impact extrusion,
- avoiding the need of higher-tonnage extrusion machines to obtain the cans,
- avoiding a premature wear of die and impact extrusion tooling, and
- casting of the aluminium with an excellent surface and with minimal defects.

[0021] In a first aspect, the present invention provides an aluminium alloy by impact extrusion, wherein said alloy consists of:

- 0.050-0.200 % by weight of silicon,
- 0.150-0.250 % by weight of iron,
- 0.300-0.800 % by weight of copper,
- 0.050-0.200 % by weight of magnesium,
- 0.003-0.050 % by weight of chromium,
- 0.010-0.100 % by weight of titanium,
- 0.010-0.400 % by weight of manganese,
- 0.001-0.050 % by weight of boron,
- less than 0.15% by weight of other secondary elements with less than 0.05% by weight any secondary alloying element, and aluminium as the remainder.

[0022] Chemical composition of the alloy of the present invention allows to increase the recrystallization threshold to the higher temperatures and a higher back annealing resistance is obtained, resulting in improved container performance and mechanical properties.

[0023] Furthermore, elements like Fe, Mn, Ti, Cr and Si, which typically are in the form of intermetallic phases, strengthen the aluminium matrix and enable the achievement of higher mechanical properties. Higher mechanical properties are reflected in high deformable and burst pressures. The addition of Mn, Zr, V and other specific alloying elements can rise the recrystallization threshold of the material up above 300°C.

[0024] Aluminium alloys according to the invention enable the manufacturing of cans with the minimal decrease in mechanical properties or with the same mechanical properties as the starting material, *i.e.* alloy with minimal aluminium mass fraction of 99.5 wt. % Al. Cans made from aluminium alloys of the invention achieve 2-3 bar higher deformation resistance and burst pressure compared with an alloy containing 99.5 wt. % aluminium.

BRIEF DESCRIPTION OF DRAWINGS

[0025]

Figure 1. Microstructure at x50 augmentations of exemplary Alloy 1 of the invention, analyzed with an optic microscope.

1: Small polygonal intermetallics

- 2: Semi-globular dendrites
- 3: Fine eutectic structure

Figure 2. Microstructure at x500 augmentations of exemplary Alloy 1 of the invention, analyzed with an optic microscope.

- 1: Small polygonal intermetallics
- 2: Fine eutectic structure
- 3: Al₂Cu intermetallic particles
- 4: Mg₂Si intermetallic particles

DETAILED DESCRIPTION OF THE INVENTION

[0026] In a first aspect, the present invention provides an aluminium alloy by impact extrusion, wherein said alloy consists of:

- 0.050-0.200 % by weight of silicon,
- 0.150-0.250 % by weight of iron,
- 0.300-0.800 % by weight of copper,
- 0.050-0.200 % by weight of magnesium,
- 0.003-0.050 % by weight of chromium,
- 0.010-0.100 % by weight of titanium,
- 0.010-0.400 % by weight of manganese,
- 0.001-0.050 % by weight of boron,
- less than 0.15% by weight of other secondary elements with less than 0.05% by weight any secondary alloying element, and aluminium as the remainder.

[0027] Aluminium alloys of the invention may preferably have a silicon content in the range of 0.050-0.175wt. %, in the range of 0.050-0.150wt. %, in the range of 0.050-0.100wt. %, in the range of 0.075-0.200wt. % or in the range of 0.100-0.200wt. %. This silicon content in the aluminium alloys of the invention was found to surprisingly avoid an increase of wearing of transformation tools.

[0028] Aluminium alloys of the invention may also preferably have an iron content in the range of 0.150-0.240wt. %, in the range of 0.175-0.240wt. %, in the range of 0.175-0.230wt. %, in the range of 0.190-0.230wt. %, in the range of 0.200-0.250wt. %, or in the range of 0.210-0.250wt. %. Alloys of the invention including this iron content were found to significantly avoid an increase of wearing of transformation tools and a decrease on the ductility of the alloy.

[0029] Furthermore, aluminium alloys of the invention, may preferably have a copper content in the range of 0.300-0.650wt. %, in the range of 0.300-0.600wt. %, or in the range of 0.300-0.500wt. %. These aluminium alloys may also have a copper content in the range of 0.400-0.800wt. %, in the range of 0.500-0.800wt. %, in the range of 0.650-0.800wt. %, or in the range of 0.650-0.750 wt. % to allow heat treating the alloy, by creating small Al₂Cu precipitates. Alloys of the invention, which include this copper content, advantageously guarantee achievable manufacturing forces. Furthermore, the presence of such high amounts of copper increases the mechanical properties of the alloys, as evidenced in the examples provided below.

[0030] Aluminium alloys of the invention may also preferably have a magnesium content in the range of 0.050-0.150wt. %, in the range of 0.050 to 0.100wt. %, in the range of 0.100 to 0.150wt. %, or in the range of 0.150-0.200wt. %. With this magnesium content, aluminium alloys of the invention were surprisingly found to allow their heat treatment, while only producing reduced amounts of Mg₂Si precipitates. Besides, this magnesium content also made it possible to avoid an increase of wearing of transformation tools, and balance the yield strength increase with the minimum percentage of iron to avoid adversely affecting elongation.

Aluminium alloys of the invention may preferably have a chromium content which is in the range of 0.003-0.040wt. %, in the range of 0.003-0.030wt. %, in the range of 0.003-0.020wt. %, in the range of 0.030-0.010wt. %, or in the range of 0.010-0.050wt. % to create very fine Cr precipitates. With these Cr wt.% values, it was possible to advantageously produce fine precipitates, thus making it advantageously possible to reduce the ductility of the alloy.

[0031] Titanium content of the aluminium alloys may preferably be in the range of 0.010-0.075wt. %, in the range of 0.010-0.050wt. %, in the range of 0.050 to 0.100wt. %, or in the range of 0.050 to 0.075wt. %. This titanium content creates very fine TiB₂ particles and promote a very intensive grain refinement of the alloy which is difficult to achieve using other titanium ranges, thus increasing its mechanical properties. Specifically, the precipitation of such very fine intermetallics with Ti that are stable to thermal treatments counteracts the recrystallization effect. With the Ti amounts

used in the aluminium alloys of the invention, wearing on transformation tools was mitigated.

[0032] In the invention, boron content may preferably be in the range of 0.001-0.030wt. %, in the range of 0.001 to 0.010wt. %, in the range of 0.010% to 0.050wt. %, in the range of 0.010% to 0.030wt. %, or in the range of 0.030-0.050wt. %. The presence of this boron amount was found to lead to increased formation of TiB₂ particles and promote a better grain refinement of the alloy.

[0033] Aluminium alloys of the invention may preferably have a manganese content in the range of 0.010 to 0.100wt. %, in the range of 0.010 to 0.080wt. %, in the range of 0.100 to 0.250wt. %, in the range of 0.200 to 0.400wt. %, in the range of 0.200 to 0.300wt. %, or in the range of 0.250 to 0.400wt. %. The presence of Mn in such amounts was found to advantageously reduce the presence of β -Al₅SiFe intermetallic needles, by transforming them into α -Al₁₂(Mn,Fe)Si₂, and also resulted in an increased deformability of the obtained alloys and reduced tool wearing. This manganese content in the aluminium alloys of the invention was also found to avoid the necessity of much higher pressures of the machinery employed to make the deformation of the cans, thus making conformation easier. It also solved the sludge problem that occurs with high percentages of manganese in combination with iron, chromium and other alloying elements.

[0034] In the invention, secondary alloying elements can be any other alloying element or impurity in the alloy with the proviso that secondary alloying elements are always present in a weight percentage less than 0.15%, more preferably in a weight percentage less than 0.150%.

[0035] In the invention, secondary alloying elements can be any other alloying element or impurity in the alloy with the proviso that each individual secondary alloying element is always present in a weight percentage less than 0.05%, more preferably in a weight percentage less than 0.050%.

[0036] Phases formed with alloying elements Si, Fe, Cu, Mn, Mg, Cr, Ti and B, and secondary alloying elements, including V and Zr, were found to strengthen the aluminium matrix by forming small polygonal intermetallic compounds.

[0037] Aluminium alloys of the invention made it possible to provide enhanced mechanical properties. Specifically, they were found to better maintain the mechanical properties after polymerization, at the level of the starting material. This is reflected in achieving 2-3 bars higher deformable and burst pressures compared with the 99.5 wt. % Al alloy, in the case of Alloy 1 (see example below).

[0038] With these improved mechanical properties of the can material, it is possible to produce cans with thinner walls and reduced weight, for example, in the cosmetic and food industry.

[0039] It is postulated that the desired properties were obtained due to the formation of a very fine eutectic phase, the semi-globular shape of the dendrites, the absence of fragile β -iron needles and the presence of very small polygonal small intermetallic particles precipitated inside the grain, the presence of Al₂Cu precipitates and also Mg₂Si rounded particles on the border of the grains in the samples, due to the combination of the different elements between them in the new developed alloys of the invention.

[0040] Figure 1 illustrates an exemplary aluminium alloy of the invention with the described microstructures at x50 augmentations obtained from slugs annealed at 500°C for 5 hours.

[0041] On the other hand, the presence of well distributed small polygonal intermetallics with fine complex eutectics, Al₂Cu polygonal precipitates and Mg₂Si globular particles around the grain border can be observed in Figure 2 with x500 augmentations.

[0042] Cans made from the alloys of the present invention meet the burst requirements set forth by jurisdictional regulations, while being pliable enough to be formed using impact extrusion without an additional machine tonnage or a superior impact extrusion tooling, because mechanical properties at high temperature are advantageously improved. It is particularly surprising that, according to the invention, a defined percentage of Cu and Mg as alloying elements in combination with the rest of alloy components in the defined ranges of composition can bring about advantageous changes in the strength properties or the drop in strength in a can, preferably an aerosol can. The containers of the present invention can be light weighted (*i.e.* walls and bottom thickness can be thinned) and still meet the burst requirements, where cans made from conventional materials (*i.e.* EN AW 1070 or EN AW 1050) cannot. Light weighting the containers is both environmentally and financially beneficial.

[0043] Aluminium alloy melt is produced in a melting furnace which is fed with the T-form blocks of electrolytic aluminium or with the electrolytic aluminium and with the process scrap obtained from stamping. When aluminium in the furnace is in liquid state with the temperature of approximately 720 °C, dross is removed from the melt and melt is poured into the holding furnace, where alloying of aluminium melt is performed.

[0044] In accordance with the required chemical composition of the alloy, alloying elements, such as titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), silicon (Si), magnesium (Mg), copper (Cu) and others are added at this point.

[0045] The majority of alloying elements are added into the aluminium melt in the form of tablets, small blocks or wire, as master alloys or near pure elements, including high quality scraps as for the Cu. Master alloy AlTi5B1 (5% titanium; 1% boron (B)) is normally added in the form of wire, which also serves to refine the microstructure of the alloy. Other master alloy compositions can be added to the melt to refine the microstructure, such as AlTi3B1, AlTiC, or AlTi10B1. If titanium boride is added to a composition comprising EN AW 1070 and EN AW 3104, then the amount of boron in the composition may not show a discernible increase. In some embodiments, the amount of boron in the composition can

typically increase by less than about 0.0006 wt. %. The amount of titanium in the composition may also not show a discernible increase, though there might be an increase by about 0.003-0.0055 wt.%. However, even without there being an apparent significant increase in the boron amount, a beneficial effect on grain refinement was observed, as discussed below.

5 **[0046]** Care must be taken to ensure that alloying elements are alloyed at least in 15-minute intervals when there is the risk of forming complex intermetallic phases that can promote the sedimentation of those phases.

[0047] While not wishing to be bound by theory, it is believed that the Ti based grain refiners allows the aluminium alloy to be grain refined during nucleation and solidification of the aluminium alloy. When metals solidify, the metal requires a surface on which to nucleate. Once the solid is nucleated, it will begin to grow. If there are very few nuclei in the melt, the resulting grains can be large because the grains grow unimpeded by their neighboring grains.

10 **[0048]** A melt with few nucleants can begin to solidify from the mold walls and impurities floating in the liquid metal, which results in a coarse as-cast grain structure lacking in ductility. Lower ductility can negatively affect the ability to roll (hot or cold) the aluminium alloy. Also, large as-cast grains result in large second phase particles, which also reduce metal ductility. As the metal solidifies, solute elements can segregate to intergranular liquid pools, which become rich in the solute to form these particles or intermetallic compounds.

15 **[0049]** A Ti-based grain refiner can be added to a melt in order to form fine TiB₂ particles therein. When the melt begins to solidify, these particles can act as nuclei on which solidification can begin and from which grains can grow. However, since there are many nucleation and growth sites, the grains can impinge on each other limiting their growth. The size of the intermetallic compounds can decrease, and they will be more finely distributed in the metal matrix. Thus, a main objective of grain refinement using a Ti base grain refiner can be to reduce the as-cast grain size.

20 **[0050]** The finer the "as-cast grain size", the smaller size of intermetallics. If the as-cast grain size is very fine (less than about 10 microns) and well dispersed, then the grain growth during hot rolling and annealing can be reduced.

25 **[0051]** After alloying, gases must be removed from the melt. Gases are removed from the melt already in the melting and casting/holding furnace with the so - called porous plugs, with rotatory degassers or by specific equipment. Degassing of the melt with the inert gas argon or nitrogen allows to reduce the total amount of dissolved gases into the alloy and also reduce the presence of oxides. After degassing, filters (ceramic foam, blankets...) are used to remove metal and non-metal inclusions from the molten metal.

30 **[0052]** Different casting methods may be used and may be chosen from a wheel belt caster, a Hazelett caster and/or a block caster. When a wheel belt caster is used, the molten aluminium can be held between a flanged wheel and a thick metal belt during solidification. The belt wraps around the wheel at about 180°. Both the wheel and the belt are chilled with water on the back side to optimize and control heat extraction. This wheel belt caster process is commonly used in the process to make EN AW 1070 and EN AW 1050 slugs. However, the thick steel belt is inflexible and unable to deflect and maintain contact with the slab that is shrinking due to solidification. The effect is magnified by the using more alloyed alloys because it solidifies over a larger temperature range (between about 480°C and about 685°C) than the EN AW 1050 and EN AW 1070 (typically between about 645°C and about 655°C) purer alloys. The aluminium strip may reach a temperature of 530 °C at the casting wheel outlet. The aluminium strip travels to the hot rolling mill and then to the cold rolling mill through a roller track.

35 **[0053]** Alternatively, a Hazelett caster may be used. When a Hazelett caster is used, the molten aluminium can be held between two flexible steel belts during solidification. Steel dam blocks can be chain mounted and form the sides of the mold. The parallel belts can slope slightly downward to allow gravity to feed molten aluminum into the system. High pressure water is sprayed on the back side of both belts to optimize and control heat extraction. This highpressure water also deflects the belt to keep it in contact with the solidifying, contracting slab. This belt deflection enables the Hazelett caster to produce a wide range of aluminium (and other) alloys. The Hazelett caster process is commonly used to produce architectural aluminum strip and may be used to produce impact extrusion slugs.

40 **[0054]** Alternatively, a block caster can be used. When a block caster is used, the molten aluminum is held between a series of chain mounted steel blocks during solidification and form the sides of the mold. The blocks are water cooled to optimize and control heat extraction.

45 **[0055]** A lubricating powder may be applied to the caster components that contact the slab. More specifically, a graphite or silica powder may be applied as necessary. Temperature control is important during and following the casting process. During casting, regardless of the casting process used, the cooling rate and temperature profile of the slab must be carefully controlled during solidification. The wheel belt caster reduces the cooling water flow rate to achieve this. If the Hazelett caster is used, the water flow for general control and gas flow over the slab may be used to closely modify the temperature. Ambient conditions, especially air flow must be controlled near the caster. This air flow control is especially critical when gas flow is used to modify the slab temperature.

50 **[0056]** The temperature of the slab at the exit of the caster must also be carefully controlled. In some embodiments, the exit temperature of the slab through the Hazelett caster can be above about 520°C, however the maximum temperature of any part of the slab exiting the caster can be less than about 582°C. In some embodiments, the exit temperature of the slab can be between about 430°C and about 490°C, which can depend on the composition of the aluminium alloy.

[0057] The process of strip rolling is performed by the reduction of the input narrow strip with minimal transverse deformation. Longitudinal rolling is a continuous forming operation that reduces the cross-section of the material between the counter rotating rollers.

[0058] Reduction in the hot rolling mill is 40-70% of the strip thickness, while in the cold rolling mill it reaches 30-50%. Aluminium narrow strip is casted with the casting speed up to 10 m/min.

[0059] Rolled aluminium alloy narrow strip then travels to the stamping line, where slugs are stamped using a stamping machine. Stamping machines usually have from 60 to 625 strokes per minute.

[0060] Stamped slugs fall on the conveyor belt below the stamping machine. From here, they are led into the annealing containers and into the annealing furnaces, where the slugs are softened and the oil, which remained from stamping, is burned off.

[0061] After the annealing, the slugs are surface treated by sandblasting, vibrating or tumbling, since a certain degree of roughness is required for impact extrusion in order to homogeneously distribute lubricant on the surface of slugs before the impact extrusion process.

[0062] The manufacturing process of aluminium cans is composed of several stages, such as formation of the can body, lacquering, polymerization, printing, drying at high temperatures and formation of the neck of the can. First the body of the cans is formed from the slug by the impact extrusion. After impact extrusion, lacquering of the internal surface of can and polymerization of the coating at around 250 °C follows. The coating of the external surface follows and drying at around 150 °C follows in the next step. After external coating, printing and drying of the print at around 150 °C follows and after that, lacquering of the external surface and drying at around 170-190 °C. In the last stage formation of the can opening, neck and the dome in the multi-step necking machine takes place.

[0063] Aluminium narrow strip is casted from aluminium alloy of the invention using a "rotary strip caster / wheel belt caster", "Hazelett caster" and/or a "block caster" method(s), and advantageously enables the casting of narrow strip also without defects on the surface of the strip.

[0064] Additional advantages and features of the invention will become apparent to the person skilled in the art upon examination of the description, or may be learned by practice of the invention without undue burden.

[0065] The following examples and drawings are provided by way of illustration, and they shall not be construed as limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments here described.

Example 1. Exemplary aluminium can alloys according to the invention (Preparation, composition and mechanical properties)

[0066] Aluminium slugs with different compositions have been prepared by melting a standard EN-AW 1050 base alloy in a 60-kg electric furnace, alloying elements at 720°C, homogenizing and de-gassing with hydrogen for 2 minutes and later pouring of 8 cylindrical bars in a die casting probe die. The obtained cylindrical bars were preheated at 450°C for 1 hour 15 minutes and forged, with a 22% of section reduction in the forging operation. Slugs were machined from bars and annealing thermal treatment was held at 500°C for 5 hours. After the slugs were shot blasted with white corundum f36 at 3bar.

[0067] Several compositions were tested. In order to compare the obtained properties of the alloys according to the invention (sample hereinafter referred to as "Alloy 1"), one of comparative alloys was in compliance EN-AW 1050 standard (comparative sample hereinafter referred to as "A5") in accordance with European Standard EN 573-3:2013; a second one was based on EN-AW 3102 (comparative sample hereinafter referred to as "A3Mn") having an Mn content approximately 0.3 wt%; and a third one was based on EN-AW 3102 having an Mn content approximately 0.3 wt.% and 0.05 wt.% (comparative sample hereinafter referred to as "A3MnZr").

[0068] Tables 1, 2 and 3 present the changes in the Brinell hardness (HB), Yield strength (Rp0.2), Ultimate tensile strength (Rm) and Elongation (A) values during different steps of the manufacturing process of cans in relation to the composition of Al alloy.

Table 1

	Alloy 1	A5	A3Mn	A3MnZr
Si (% by weight)	0.107	0.088	0.080	0.090
Fe (% by weight)	0.217	0.205	0.300	0.200
Cu (% by weight)	0.464	0.001	0	0
Mn (% by weight)	0.022	0	0.320	0.240
Mg (% by weight)	0.052	0.003	0	0.130

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(continued)

	Alloy 1	A5	A3Mn	A3MnZr
Cr (% by weight)	0.004	0	0.030	0
Ni (% by weight)	0	0	0.010	0
Ti (% by weight)	0.015	0.014	0.020	0.020
Ag (% by weight)	0	0	0	0
V (% by weight)	0.013	0.011	0.010	0.010
Zr (% by weight)	0.013	0.001	0	0.050
B (% by weight)	0.002	0.002	0.003	0.003
Rp0.2 (MPa)	53.70	23.00	41.00	38.00
Rm (MPa)	105.50	77.00	86.00	89.00
A (%)	41.20	46.20	48.00	35.00
Brinell Hardness (HV)	37.03	28.90	31.63	29.03

[0069] Industrial cans were manufactured with standard equipment. Ø44.5x6.8 mm slugs were employed to obtain Ø45x190 cans with 0.28 mm wall thickness and 0.8 mm bottom thickness, for a pressurized can of 15bar. Test bars were obtained from manufactured cans before and after lacquering. The obtained results for cans before the lacquering process are specified in Table 2 and after lacquering in Table 3.

Table 2

	Alloy 1	A5	A3Mn	A3MnZr
Rp0.2 (MPa)	157.5	136.5	147.5	153.5
Rm (MPa)	173.5	145.5	156.0	168.5
A (%)	3.9	2.3	2.2	3.5

Table 3

	Alloy 1	A5	A3Mn	A3MnZr
Rp0.2 (MPa)	156.0	138.0	141.5	148.0
Rm (MPa)	174.5	141.0	149.0	162.5
A (%)	4.3	1.6	2.5	4.0

[0070] Table 4 presents the obtained results by performing the 15-bar test procedure over manufactured cans from the different alloys. Burst test results showed an increase of more than 2-3 Bar in the case of alloy 1 in comparison with A5 alloy and higher values than alloys A3Mn and A3MnZr. In the case of deformation test, Alloy 1 also showed about 2 bar increase in the case of Alloy 1 in comparison with A5 alloy, and slightly higher than A3MnZr alloy and A3Mn alloy.

Table 4

	Alloy 1	A5	A3Mn	A3MnZr
Deformation test (Bar)	20.4	17.77	22.74	19.12
Burst test (Bar)	24.34	22.93	25.40	26.51

[0071] With the specific defined composition of the proposed alloy with Cu, unexpectedly higher mechanical properties were achieved and maintained within the desired tolerance during the whole manufacturing process of cans. Based on the specific selection of alloying elements, the tensile strength of aluminium alloy of the invention and burst and defor-

mation test were found to be higher at the end of the process compared to the tensile strength of A5 after extrusion, and similar or better than A3Mn and A3MnZr alloys.

Analytical methods:

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[0072] In order to analyze the microstructure of obtained samples, the samples were cut from the slugs and prepared according to standard metallographic procedures, by hot mounting in conductive resin, grinding, and polishing. The microstructure, the different regions and the averaged overall chemical composition of each sample were investigated by an optic microscope model DMI5000 M (LEICA Microsystems, Wetzlar, Germany).

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[0073] Vickers microhardness FM-700 model (FUTURE-TECH, Kawasaki, Japan) was employed on the slugs and on obtained cans. At least 10 random individual measurements were made, and the obtained values were transformed to HB units.

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[0074] In order to determine the mechanical properties of the composite rods, three tensile tests were carried out in accordance with the UNE-EN ISO 6892-1 B:2010 standards at room temperature with a crosshead speed of 5 mm/min using an Instron 3369 electromechanical testing machine from slugs and cans. The tensile stress, ultimate tensile strength, and elongation were calculated from obtained stress-strain diagrams.

[0075] Internal pressure tests (Deformation and Burst tests) were performed in a calibrated test machine according to European Aerosol Federation standard FEA621 "Aerosol Containers: Measurement of internal pressure resistance of empty containers without valves".

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Claims

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1. Aluminium alloy for manufacturing of aluminium cans by impact extrusion, **characterized in that** said alloy consists of:

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- 0.050-0.200 % by weight of silicon,
- 0.150-0.250 % by weight of iron,
- 0.300-0.800 % by weight of copper,
- 0.050-0.200 % by weight of magnesium,
- 0.003-0.050 % by weight of chromium,
- 0.010-0.100 % by weight of titanium,
- 0.010-0.400 % by weight of manganese,
- 0.001-0.050 % by weight of boron,
- less than 0.15% by weight of secondary alloying elements with less than 0.05% by weight any other alloying element,
- and aluminium as the remainder.

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2. Aluminium alloy according to claim 1, wherein the copper content is in the range of from 0.300 to 0.650 % by weight.

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3. Aluminium alloy according to claim 1 or 2, wherein the copper content is in the range of from 0.300 to 0.600 % by weight.

4. Aluminium alloy according to any preceding claim, wherein the silicon content is in the range of from 0.050 to 0.175 % by weight.

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5. Aluminium alloy according to any preceding claim, wherein the silicon content is in the range of from 0.050 to 0.150 % by weight.

6. Aluminium alloy according to any preceding claim, wherein the iron content is in the range of from 0.175 to 0.240 % by weight.

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7. Aluminium alloy according to any preceding claim, wherein the iron content is in the range of from 0.190 to 0.230 % by weight.

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8. Aluminium alloy according to any preceding claim, wherein the copper content is in the range of from 0.300 to 0.650 % by weight.

9. Aluminium alloy according to any preceding claim, wherein the copper content is in the range of from 0.300 to 0.500

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% by weight.

5 **10.** Aluminium alloy according to any preceding claim, wherein the magnesium content is in the range of from 0.050 to 0.150 % by weight.

11. Aluminium alloy according to any preceding claim, wherein the chromium content is in the range of from 0.003 to 0.030 % by weight.

10 **12.** Aluminium alloy according to any preceding claim, wherein the chromium content is in the range of from 0.003 to 0.010 % by weight.

13. Aluminium alloy according to any preceding claim, wherein the titanium content is in the range of from 0.010 to 0.075 % by weight.

15 **14.** Aluminium alloy according to any preceding claim, wherein the boron content is in the range of from 0.001 to 0.030 % by weight.

20 **15.** Aluminium alloy according to any preceding claim, wherein the manganese content is in the range of from 0.001 to 0.250 % by weight.

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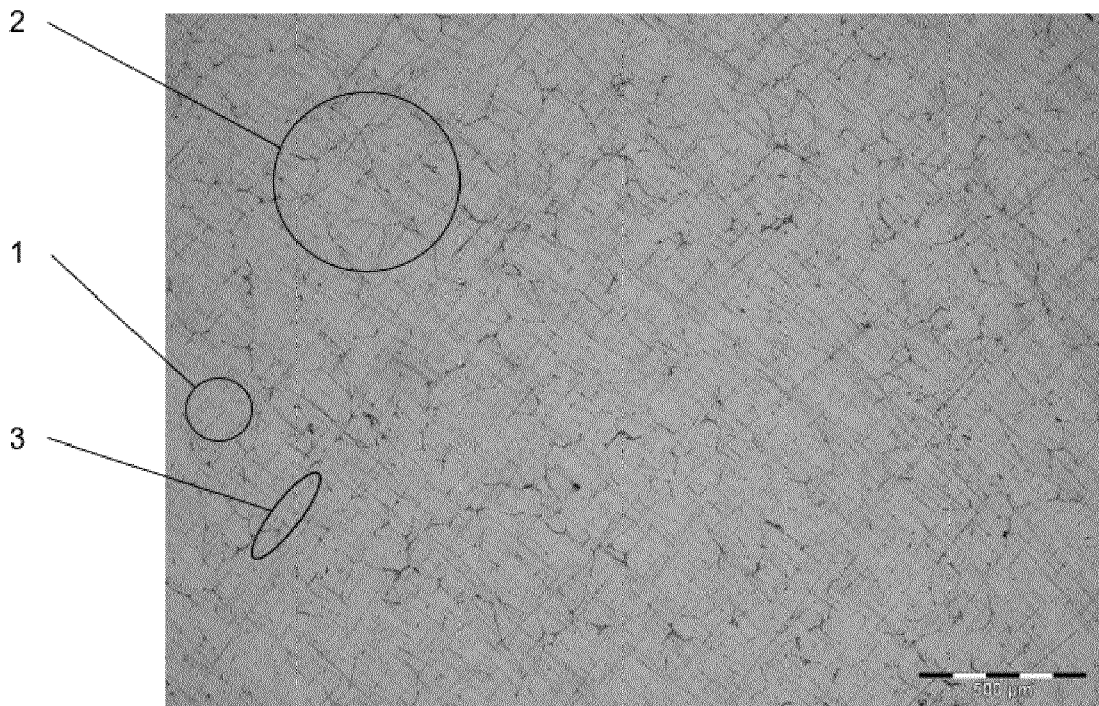


FIG. 1

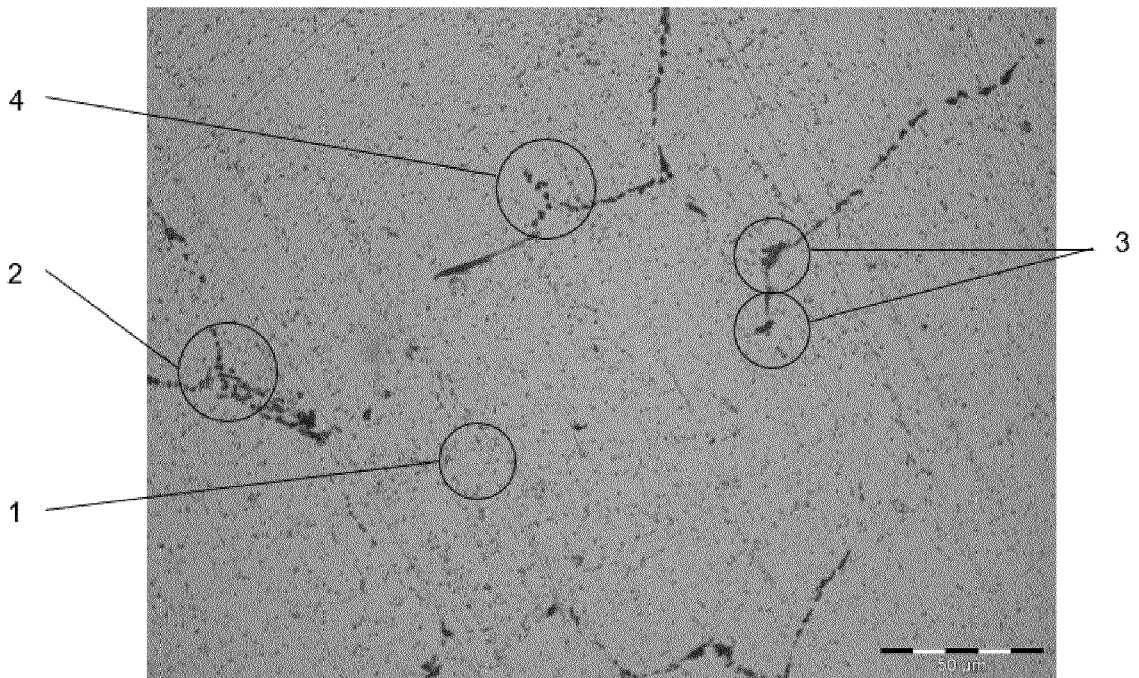


FIG. 2



EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	RU 2 718 370 C1 (AKTIONERNOE OBSHCHESTVO ARNEST [RU]) 6 April 2020 (2020-04-06) * abstract; tables 1, 2, AA5 * -----	1-15	INV. C22C21/12 C22C21/14 C22C21/16 C22F1/057
Y	WO 99/37826 A1 (CEBAL [FR]; HOFFMANN JEAN LUC [FR]; JUPIN ALAIN [FR]) 29 July 1999 (1999-07-29) * pages 4-7; claims 1-3 * -----	1-15	
A	US 2018/078982 A1 (SILES JOHN L [US] ET AL) 22 March 2018 (2018-03-22) * claims 1-31 * -----	1-15	
A,D	US 7 520 044 B2 (BOXAL FRANCE [FR]) 21 April 2009 (2009-04-21) * paragraphs [0020] - [0021]; claims 1-5; table 1 * -----	1-15	
A,D	FR 2 457 328 A1 (CEBAL) 19 December 1980 (1980-12-19) * pages 1-2; claims 1-3 * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC)
A,D	EP 3 075 875 A1 (TALUM D D KIDRICEVO [SI]) 5 October 2016 (2016-10-05) * paragraphs [0010] - [0033]; claims 1-4 * -----	1-15	C22C C22F
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 7 October 2020	Examiner Chebeleu, Alice
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

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

EP 20 38 2640

5

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.

07-10-2020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
RU 2718370	C1	06-04-2020	-----
WO 9937826	A1	29-07-1999	AR 014420 A1 28-02-2001
			AT 216738 T 15-05-2002
			AU 2060599 A 09-08-1999
			BR 9907215 A 24-10-2000
			CA 2318389 A1 29-07-1999
			CN 1288487 A 21-03-2001
			CZ 20002512 A3 12-12-2001
			DE 69901341 T2 28-11-2002
			EP 1064413 A1 03-01-2001
			ES 2175929 T3 16-11-2002
			FR 2773819 A1 23-07-1999
			HU 0100376 A2 28-05-2001
			KR 20010024776 A 26-03-2001
			PL 341380 A1 09-04-2001
			WO 9937826 A1 29-07-1999

US 2018078982	A1	22-03-2018	AU 2014251206 A1 12-11-2015
			CA 2908181 A1 16-10-2014
			CA 2990040 A1 16-10-2014
			CL 2015002985 A1 12-08-2016
			CN 105324316 A 10-02-2016
			CN 107985713 A 04-05-2018
			EP 2983998 A2 17-02-2016
			GT 201500310 A 04-01-2017
			JP 6255084 B2 27-12-2017
			JP 2016524536 A 18-08-2016
			RU 2015147899 A 15-05-2017
			US 2014298641 A1 09-10-2014
			US 2017036255 A1 09-02-2017
			US 2018078982 A1 22-03-2018
			WO 2014168873 A2 16-10-2014

US 7520044	B2	21-04-2009	AT 507317 T 15-05-2011
			EP 1624083 A2 08-02-2006
			ES 2365716 T3 10-10-2011
			FR 2873717 A1 03-02-2006
			US 2006021415 A1 02-02-2006

FR 2457328	A1	19-12-1980	NONE

EP 3075875	A1	05-10-2016	EP 3075875 A1 05-10-2016
			SI 24969 A 28-10-2016

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 7520044 B2 [0008]
- FR 2773819 A1 [0009]
- FR 2457328 A1 [0010]
- EP 2881477 B1 [0011]
- EP 3075875 A1 [0012]
- WO 2013040339 A1 [0014]
- WO 2018125199 A1 [0015]
- WO 9937826 A1 [0016]
- WO 2020048988 A1 [0017]
- WO 2020048994 A1 [0018]