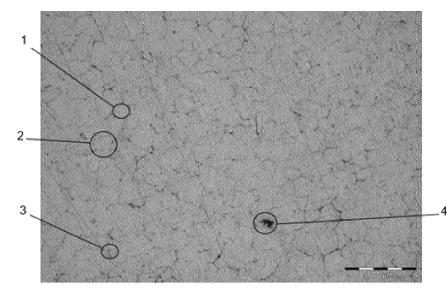


ALUMINIUM ALLOYS FOR MANUFACTURING OF ALUMINIUM CANS BY IMPACT EXTRUSION (54)

The present invention provides aluminium alloys (57) for manufacturing of aluminium cans by impact extrusion. Alloys according to the invention consist of 0.050-0.265 wt. % Si, 0.150-0.250 wt. % Fe, 0.010-0.100 wt. % Cu, 0.100-0.400 wt. % Mn, 0.080-0.200 wt. % Mg, less than

0.100 wt. %. Cr. 0.065-0.300 wt. % Ti. 0.005-0.060 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.



<u>FIG. 1</u>

Description

FIELD 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 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 AI (aluminium) content of 99.5% by weight, and EN AW 1070 having an AI 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. [0005] In the case of 3000-series aluminium alloys for cans according to the European Standard EN 573-3, the most
- ²⁵ 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 higher tonnage extrusion presses because, due to the same reason, higher tonnage machine pressures also required during the process. Also,
- presses because, due to the same reason, higher tormage 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 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 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 and requires
- ⁴⁵ 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 an undesirable reduced corrosion resistance of the alloy.
- [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</p>

alloy, compared to alloys with higher Cu amounts, and promotes the formation of AI_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 β -AI₅FeSi phase formation occurs.

[0011] EP2881477B1 discloses a heat resistant alloy for can production with good cold deformation and resistant to

- ⁵ 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. %; and 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 β -Al₅FeSi phase formation therefore inevitably occurs.
- 10 [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 % Fe, 0.05-0.2 % Si, <0.01 % Mg, <0.01 % Cu, < 0.02 % Zn, 0.0 - 0.03 % Ti, 0.01 - 0.06 % Mn, 0.05 - 0.2 % Zr. The addition of Zr into the alloy in a range of 0.05 - 0.2 wt. % allows to maintain tensile test strength and improve deformable and burst pressure. The addition of Zr increases the recrystallization threshold above 300°C,
- ¹⁵ 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
- 20 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. However,
- ²⁵ 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 processes employing recycled aluminium scraps with relatively pure aluminium. Disclosed alloys are composed at least about 97 wt.% AI, 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
- ³⁵ 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
- 40 0.15 wt.% impurities and a balance comprising one of Cu, Zn, Cr, and Ti elements. Nevertheless, these alloys with lowalloying elements content are normally more expensive than the alloys with alloy compositions that can be obtained with less pure materials.

[0016] WO2013061707A1 discloses an aluminium alloy, and its applications in the manufacture of lithium-ion battery housings to which certain mechanical properties are required, as well as the possibility of laser welding the plates of

- said alloy. Its composition is the following expressed in % by weight: 0.05 Mg, <0.1 Ti, 0.05-0.3 Si, 0.05-0.7 Fe, 0.05-0.2 Cu, 0.8-1.5 Mn, 2-20 ppm B (or 2-10 or 2-30 ppm B) with the rest aluminium and unavoidable impurities. However, this document refers to the presence of boron in the alloy in very low proportions, while this metal is understood to lend desirable characteristics to the alloy in the application of battery casing, and it also avoids the use of Ti-based grain refiners to increase the ductility of the alloy, wherein the latter may adversely affect grain refinement and fine grain</p>
- ⁵⁰ hardening, thus also negatively impacting on strength and ductility of the resulting aluminium alloy. Also, an alloy for cans with a high Mn percentage (0.8-1.5 wt.%) promotes 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 % titanium and the remeinder aluminium and entianally additional admirtures. However, a content

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, high percentages of Mn (>0.3 wt.%), were added to avoid the needle-like β-Al₅FeSi compounds, but the combination of both Mn and Fe elements increases the tooling wear, can reduce the

ductility of the alloy and increase the risk of cracking. The use of Mg as alloying element is not described, but rather appears to be present as an impurity. Thus, even though Mg is usually known in the art to provide better mechanical properties, metastable clusters and / or precipitates based on magnesium are formed (as Mg₂Si), leading to an increase in strength and thus counteracting recrystallization, so a loss of strength is caused thereby. Also, the Ti content is limited

- to 0.01 wt.% to 0.04 wt.%, wherein said amounts of Ti are known to potentially affect grain refinement in an undesirable way. While the use of titanium in an aluminium alloy may typically result in advantageous grain refinement and fine grain hardening, which may eventually increase the strength and ductility of the aluminium alloy, for a correct grain refining, higher amounts thereof are known to be usually required, thus also increasing the cost of these alloys.
 [0018] WO2020048994A1 discloses an aluminium alloy consisting of: 0.07 wt.% to 0.17 wt.% silicon, 0.25 wt.% to
- 10018 W02020048994A1 discloses an aluminium andy consisting of. 0.07 wt.% to 0.17 wt.% shicon, 0.25 wt.% to 0.45 wt.% to 0.25 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.

20 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:

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- 0.050-0.265 % by weight of silicon,
- 0.150-0.250 % by weight of iron,
- 0.010- 0.100 % by weight of copper,
- 0.100-0.400 % by weight of manganese,
- 0.080-0.200 % by weight of magnesium,
- less than 0.100% by weight of chromium,
- 0.065-0.300 % by weight of titanium,
- 0.005-0.060 % by weight of boron,
- less than 0.15% by weight of secondary alloying 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 higher temperatures, and a higher back annealing resistance is also obtained, resulting in improved container perform-

ance and mechanical properties. In particular, tensile strength is maintained or improved and deformation resistance and burst pressure is increased. **IO0231** Europerturber of intermetallic phases, strength.

[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 and other specific alloying elements can rise 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.%. Cans made from aluminium alloys of the invention achieve 5-bar higher deformation resistance

and burst pressure compared with an alloy containing 99.5 wt. % aluminium.

BRIEF DESCRIPTION OF DRAWINGS

5 [0025]

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

10 1: Small intermetallics

- 2: Globular dendrites
- 3: Fine eutectic structure
- 4: Shrinkage porosity

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

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- 1: Small intermetallics
- 2: Fine eutectic structure
- ²⁵ 3: TiB₂ 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:

- 0.050-0.265 % by weight of silicon,
- 0.150-0.250 % by weight of iron,
- 0.010- 0.100 % by weight of copper,
- 0.100-0.400 % by weight of manganese,
- 0.080-0.200 % by weight of magnesium,
 - less than 0.100% by weight of chromium,
 - 0.065-0.300 % by weight of titanium,
 - 0.005-0.060 % by weight of boron,
- less than 0.15% by weight of secondary alloying 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 from 0.100 to 0.265 wt.
 ⁴⁵ %, from 0.150 to 0.265 wt. %, from 0.200 to 0.265 wt. %, or even from 0.200 to 0.260 wt.%. Alloys of the invention including this silicon content were 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 0.150-0.240 wt.,

0.200-0.250 wt. %, or 0.210-0.230 wt. %. 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.

- 50 [0029] Furthermore, aluminium alloys of the invention, may preferably have a copper content in the range of 0.010-0.090 wt.%, in the range of 0.010-0.080 wt.%, in the range of 0.010-0.070 wt.%, or in the range of 0.010-0.065 wt.%. They may also have a copper content in the range of from 0.065 to 0.100 wt.%. Alloys of the invention, which include this copper content, advantageously allow heat treating the alloy while only producing reduced amounts of Al₂Cu precipitates. These copper contents were also found to guarantee a minimum elastic yield and ultimate tensile strength without reducing corrosion resistance of the alloy.
- [0030] Aluminium alloys of the invention may also preferably have a magnesium content in the range of 0.080-0.180 wt.% or in the range of 0.080-0.160 wt.%. They may also have a magnesium content in the range of 0.100-0.200 wt.%, or in the range of 0.150-0.200 wt.%. With this magnesium content, aluminium alloys of the invention were surprisingly

found to allow their heat treatment, while only producing reduced amounts of Mg_2Si precipitates. Besides, this magnesium content also made it possible to avoid an increase of wearing of transformation tools, and balancing the increase of yield strength increase with the minimum percentage of copper and iron to avoid adversely affecting elongation.

[0031] Aluminium alloys of the invention may preferably have a chromium content which is equal to or less than 0.090 wt.%, equal to or less than 0.080 wt.%, equal to or less than 0.070 wt.%, equal to or less than 0.060 wt.%, or equal to or less than 0.055 wt.%. Aluminium alloys of the invention may also preferably have a chromium content which is less than 0.090 wt. %, less than 0.080 wt. %, less than 0.070 wt.%, less than 0.060 wt. %, or less than 0.055 wt. %. By using these chromium amounts, it was advantageously possible to create very fine chromium precipitates and avoid the formation of beta-AlsSiFe intermetallic needles. Also, gross precipitates were created, which reduced the ductility of the alloy.

alloy. **[0032]** According to thi

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[0032] According to this first aspect of the invention, titanium content of the aluminium alloys may preferably be in the range of 0.065-0.250 wt. %, in the range of 0.065-0.200 wt. %, or in the range of 0.065-0.150 wt. %. The aluminium alloys of the invention may also preferably have 0.100-0.300% wt. % Ti, or 0.125-0.300% wt. % Ti. These titanium contents were found to surprisingly create very fine TiB₂ particles and promote a better grain refinement of the alloy,

- thus increasing the mechanical properties of the alloy, specially its ductility. As a result of this, there is no need to increase tonnage loads of extrusion presses when the aluminium alloys of the invention are used. On the other hand, when Ti amounts higher than 0.300 wt. % were used, that is, amounts higher than the ones used in the aluminium alloys of the invention, significantly more wearing on transformation tools was observed, in addition to the fact that higher titanium contents increased alloy price.
- **[0033]** Aluminium alloys of the invention may preferably have a manganese content in the range of 0.100-0.380 wt.% or in the range of 0.100-0.370 wt.%. Aluminium alloys may also have a manganese content in the range of from 0.100 to 0.200 wt.%, or from 0.150 to 0.200 wt.%. 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, boron content may preferably be in the range of 0.005-0.050 wt. %, in the range of 0.010-0.040
- wt. %, or in the range of 0.010-0.030 wt. %. Boron content may also be between 0.005 to 0.015 wt. %, between 0.015
 to 0.025 wt. %, between 0.025 to 0.040 wt. %, or between 0.040 to 0.060 wt. %. The presence of these boron amounts was found to lead to increased formation of TiB₂ particles and promote a better grain refinement of the alloy.
 [0035] 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%.
- ³⁵ **[0036]** 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%.

[0037] Phases formed with alloying elements Si, Fe, Cu, Mn, Mg, Cr, Ti and B, and secondary alloying elements, were found to strengthen the aluminium matrix by forming small polygonal intermetallic compounds.

- 40 [0038] Aluminium alloys of the invention made it possible to obtain 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 5-bar higher deformable and burst pressures compared with the 99.5 wt. % Al alloy, in the case of Alloy 1 (see examples below), and about 2-3 bar in Alloy 2 and 3 (see examples below). These alloys advantageously avoided or at least reduced the presence and size of β-Al₅FeSi due to the synergic combination of Fe and Mn in the selected amounts.
 - **[0039]** 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.

[0040] It is postulated that the desired properties were obtained due to the formation of a very fine eutectic phase, the globular shape of the dendrites, the absence of fragile β -iron needles and the presence of small TiB₂ particles that act as grain refiners in the center of the grains in the samples due to the combination of the different elements between them in the new developed alloys of the invention.

[0041] Figure 1 illustrates an exemplary aluminium alloy of the invention with the described microstructures with some porosity inherent to the slug manufacturing process (slugs were annealed at 500°C for 5 hours) at x50 augmentations.
 [0042] On the other hand, the presence of well distributed small intermetallics, fine eutectics around the grain border

⁵⁵ and TiB₂ particles in the center of the aluminium grains can be observed in Figure 2 with x500 augmentations. [0043] 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 titanium as alloying element 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 require-

- ⁵ ments, 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.
 [0044] 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
- ¹⁰ the holding furnace, where alloying of aluminium melt is performed. [0045] 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. [0046] 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 guality scraps as for the Cu. Master alloy AlTi5B1 (5% titanium;
- ¹⁵ 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 AITi3B1, AITiC or AITi10B1. 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 discernable 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
- 20 discernable increase, though there might be an increase 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.

[0047] 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.

- ²⁵ **[0048]** While not wishing to be bound by theory, it is believed that the Ti-based grain refiners allow 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.
- [0049] 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.

[0050] 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.

- [0051] 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.
- **[0052]** 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.
- **[0053]** 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
- ⁵⁰ 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.
- then to the cold rolling mill through a roller track.
 [0054] 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 aluminium 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 aluminium strip and may be used to produce impact extrusion slugs.

⁵ **[0055]** Alternatively, a block caster can be used. When a block caster is used, the molten aluminium 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.

[0056] 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.

- ¹⁰ 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.
- 15 [0057] 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. [0058] The process of strip rolling is performed by the reduction of the input narrow strip with minimal transverse
- ²⁰ deformation. Longitudinal rolling is a continuous forming operation that reduces the cross-section of the material between the counter rotating rollers.

[0059] 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.

[0060] 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. 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. Afterwards, 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

³⁵ 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 multistep 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. 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

⁴⁵ here described.

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

50 [0065] 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 where preheated at 450°C for 1 hour 15 minutes and forged, with a 22% of section reduction in the forging operation. Slugs where machined from bars and annealing thermal treatment was held at 500°C for 5 hours. After the slugs where shot blasted with white corundum f36 at 3 bar.

[0066] Several compositions where tested. In order to compare the obtained properties of the alloys according to the invention (samples hereinafter referred to as "Alloy 1", "Alloy 2" and "Alloy 3"), one of the comparative alloys was in complaining 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 Zr content 0.05 wt.% (comparative sample hereinafter referred to as "A3MnZr").

[0067] 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						
10		Alloy 1	Alloy 2	Alloy 3	A5	A3Mn	A3MnZr
	Si (% by weight)	0.210	0.259	0.254	0.088	0.080	0.090
	Fe (% by weight)	0.210	0.230	0.226	0.205	0.300	0.200
	Cu (% by weight)	0.010	0.065	0.065	0.001	0.000	0.000
15	Mn (% by weight)	0.370	0.101	0.101	0.000	0.320	0.240
	Mg (% by weight)	0.140	0.080	0.151	0.003	0.000	0.130
	Cr (% by weight)	0	0.054	0.054	0	0.030	0.000
20	Ni (% by weight)	0	0	0	0	0.010	0.000
	Ti (% by weight)	0.130	0.067	0.071	0.014	0.020	0.020
	Ag (% by weight)	0	0	0	0	0	0
	V (% by weight)	0.010	0.014	0.014	0.011	0.010	0.010
25	Zr (% by weight)	0.010	0.036	0.037	0.001	0	0.050
	B (% by weight)	0.025	0.012	0.013	0.002	0.003	0.003
	Rp0.2 (MPa)	51.00	48.50	46.50	23.00	41.00	38.00
30	Rm (MPa)	102.00	101.00	107.00	77.00	86.00	89.00
	A (%)	33.00	36.70	33.50	46.20	48.00	35.00
	Brinell Hardness (HB)	33.43	33.87	33.87	28.90	31.63	29.03

[0068] 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 15 bar. 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.

40		Table 2					
		Alloy 1	Alloy 2	Alloy 3	A5	A3Mn	A3MnZr
	Rp0.2 (MPa)	161.5	156.5	162.0	136.5	147.5	153.5
45	Rm (MPa)	179.5	175.5	173.0	145.5	156.0	168.5
45	A (%)	4.7	4.2	1.4	2.3	2.2	3.5
		1					
		I	т	able 3			
50		Alloy 1	T Alloy 2	able 3 Alloy 3	A5	A3Mn	A3MnZr
50	Rp0.2 (MPa)	Alloy 1 152.5			A5 138.0	A3Mn 141.5	A3MnZr 148.0

5.2

A (%)

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[0069] Table 4 presents the obtained results by performing the 15-bar test procedure over manufactured cans from

3.7

1.6

2.5

4.0

3.8

the different alloys. Burst test results showed an increase of more than 5 Bar in the case of alloy 1 in comparison with A5 alloy and higher values than alloys A3Mn and A3MnZr. Burst test also showed a 2-3 bar increase in the case of Alloy 2 and Alloy 3 in comparison with A5 alloy, similar in comparison with A3MnZr alloy and slightly smaller than A3Mn alloy. In the case of deformation test, there was an increase of more than 5 Bar in the case of alloy 1 in comparison with A5 alloy and higher values than alloys A3Mn and A3MnZr, and similar values in the case of Alloys 2 and 3 to those of A3Mn and A3MnZr, and similar values in the case of Alloys 2 and 3 to those of A3Mn and A3MnZr and higher than A5 alloy.

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Alloy 1 Alloy 2 Alloy 3 Α5 A3Mn A3MnZr Deformation test (Bar) 24.40 19.82 20.33 17.77 22.74 19.12 Burst test (Bar) 29.60 25.31 28.31 22.93 25.40 26.51

- Table 4
- **[0070]** With the specific defined composition of the proposed alloys with Ti and the rest of alloying elements, 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 deformation test values 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. The increase of Ti in

20 the alloy can reduce grain size, thus promoting that precipitates are smaller in size. Also, TiB₂ particles are very stable at high temperatures, improving mechanical properties of aluminium alloys at high temperatures.

Analytical methods:

- **[0071]** 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).
- [0072] 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.

[0073] 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.

strength, and elongation were calculated from obtained stress-strain diagrams.
 [0074] 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".

40 Claims

- 1. Aluminium alloy for manufacturing of aluminium cans by impact extrusion, characterized in that said alloy consists of:
- 45 0.050-0.265 % by weight of silicon,
 - 0.150-0.250 % by weight of iron,
 - 0.010- 0.100 % by weight of copper,
 - 0.100-0.400 % by weight of manganese,
 - 0.080-0.200 % by weight of magnesium,
 - less than 0.100 % by weight of chromium,
 - 0.065-0.300 % by weight of titanium,
 - 0.005-0.060 % by weight of boron,
 - less than 0.15% by weight of secondary alloying elements with less than 0.05% by weight any secondary alloying element,
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- and aluminium as the remainder.
- 2. Aluminium alloy according to claim 1, wherein the titanium content is in the range of from 0.065 to 0.200 % by weight.

- 3. Aluminium alloy according to claim 1 or 2, wherein the silicon content is in the range of from 0.100 to 0.265 % by weight.
- **4.** Aluminium alloy according to any preceding claim, wherein the silicon content is in the range of from 0.200 to 0.260 % by weight.
- Aluminium alloy according to any preceding claim, wherein the iron content is in the range of from 0.200 to 0.250 % by weight.
- 6. Aluminium alloy according to any preceding claim, wherein the iron content is in the range of from 0.210 to 0.230
 ¹⁰ % by weight.
 - Aluminium alloy according to any preceding claim, wherein the copper content is in the range of from 0.010 to 0.080 % by weight.
- Aluminium alloy according to any preceding claim, wherein the copper content is in the range of from 0.010 to 0.070 % by weight.
 - **9.** Aluminium alloy according to any preceding claim, wherein the magnesium content is in the range of from 0.080 to 0.180 % by weight.

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- **10.** Aluminium alloy according to any preceding claim, wherein the magnesium content is in the range of from 0.080 to 0.160 % by weight.
- **11.** Aluminium alloy according to any preceding claim, wherein the chromium content is less than 0.080 % by weight.

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- **12.** Aluminium alloy according to any preceding claim, wherein the chromium content is less than 0.070 % by weight.
- **13.** Aluminium alloy according to any preceding claim, wherein the manganese content is in the range of from 0.100 to 0.380 % by weight.
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- **14.** Aluminium alloy according to any preceding claim, wherein the boron content is in the range of from 0.010 to 0.0.040 % by weight.

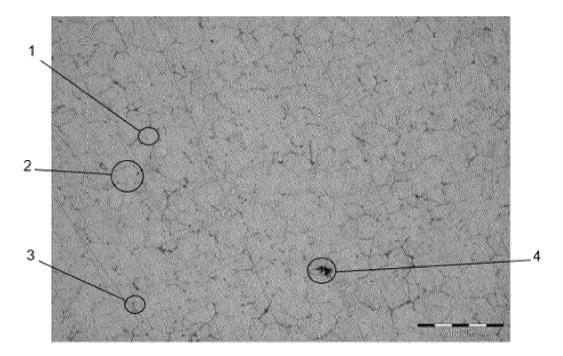
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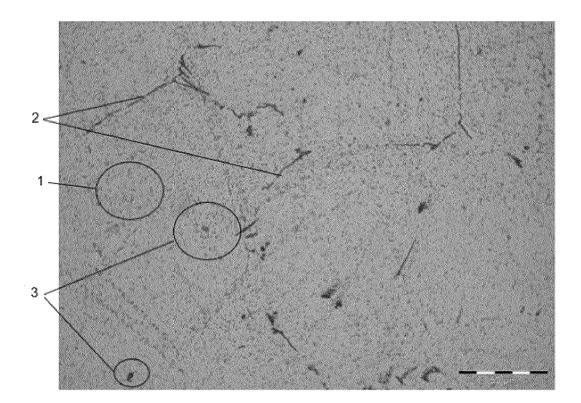
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<u>FIG. 2</u>



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