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MAS et al.(10) **Pub. No.: US 2021/0310108 A1**(43) **Pub. Date: Oct. 7, 2021**(54) **ALUMINUM-COPPER-LITHIUM ALLOY
HAVING IMPROVED COMPRESSIVE
STRENGTH AND IMPROVED TOUGHNESS****Publication Classification**(51) **Int. Cl.****C22F 1/057** (2006.01)**C22C 21/18** (2006.01)**C22C 21/16** (2006.01)**C22C 21/14** (2006.01)(52) **U.S. Cl.**CPC **C22F 1/057** (2013.01); **C22C 21/14**
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(2013.01)(71) Applicant: **CONSTELLIUM ISSOIRE**, Issoire
(FR)(72) Inventors: **Fanny MAS**, Grenoble (FR); **David
BARBIER**, Grenoble (FR); **Samuel
JUGE**, Saint Simeon De Bressieux
(FR); **Armelle DANIELOU**, Les
Echelles (FR); **Gaëlle POUGET**,
Grenoble (FR); **Nicolas
BAYONA-CARRILLO**, Coublevie
(FR)

(57)

ABSTRACT

The invention relates to a product based on an aluminium alloy comprising, as percentages by weight, 4.0 to 4.6% by weight of Cu, 0.7 to 1.2% by weight of Li, 0.5 to 0.65% by weight of Mg, 0.10 to 0.20% by weight of Zr, 0.15 to 0.30% by weight of Ag, 0.25 to 0.45% by weight of Zn, 0.05 to 0.35% by weight of Mn, at most 0.20% by weight of Fe+Si, at least one element selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being from 0.05 to 0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and 0.01 to 0.15% by weight for Ti, the other elements being at most 0.05% by weight each and 0.15% by weight in total, the remainder being aluminium. The invention also relates to a method for obtaining such a product and to the use thereof as an aircraft structural element.

(73) Assignee: **ConsTellium Isoire**, Issoire (FR)(21) Appl. No.: **17/051,659**(22) PCT Filed: **Apr. 24, 2019**(86) PCT No.: **PCT/FR2019/050965**

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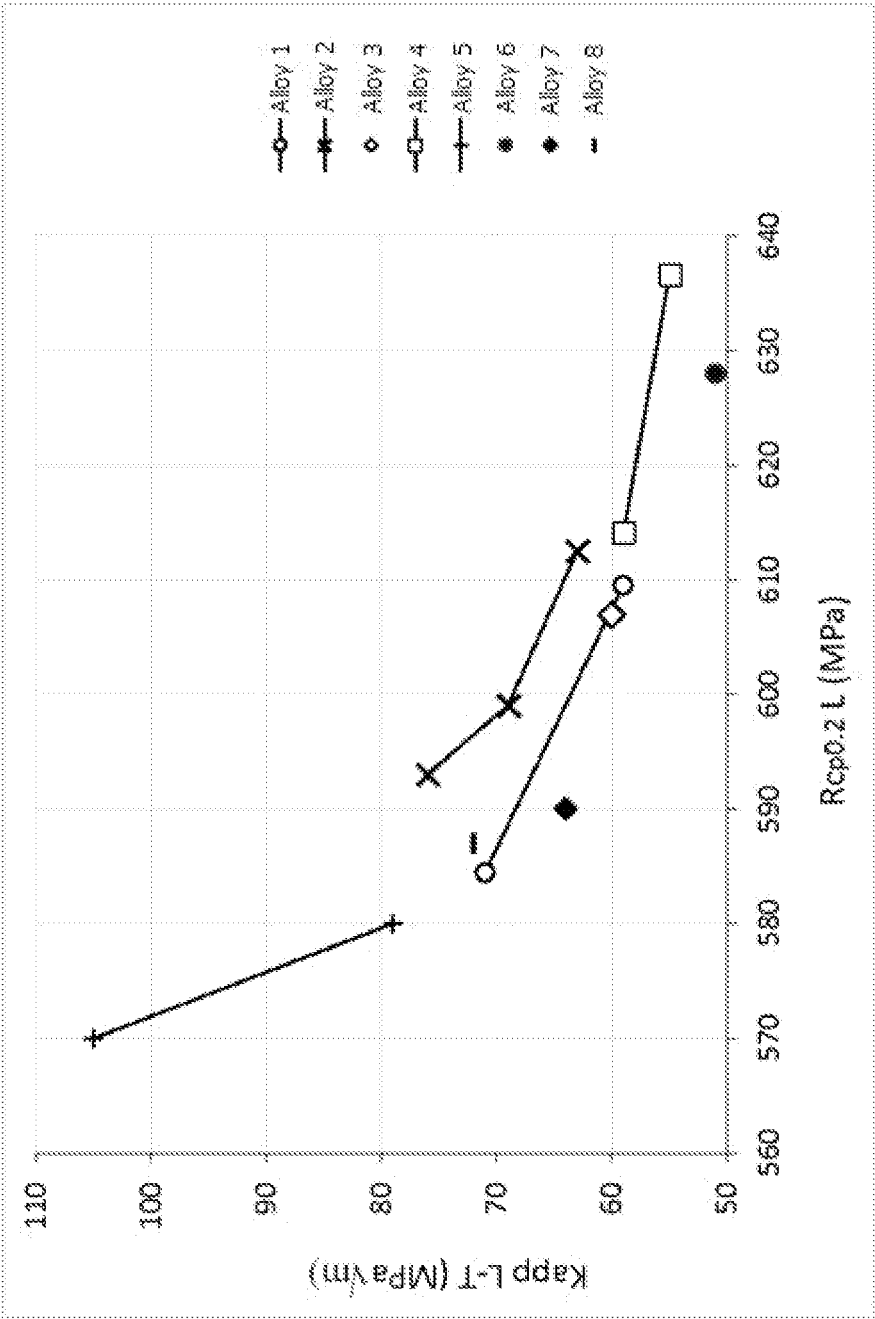


FIG 1

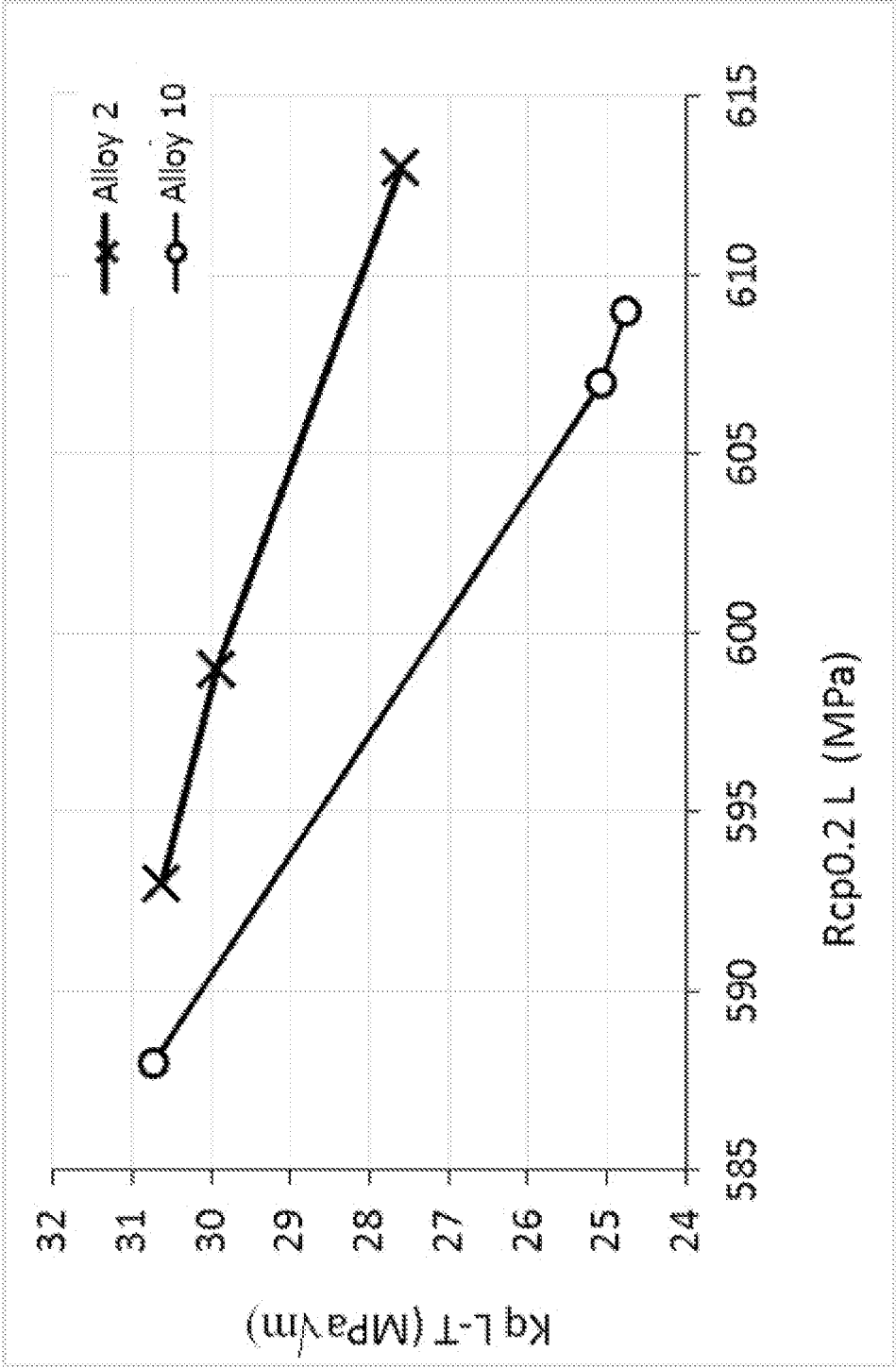


FIG 2

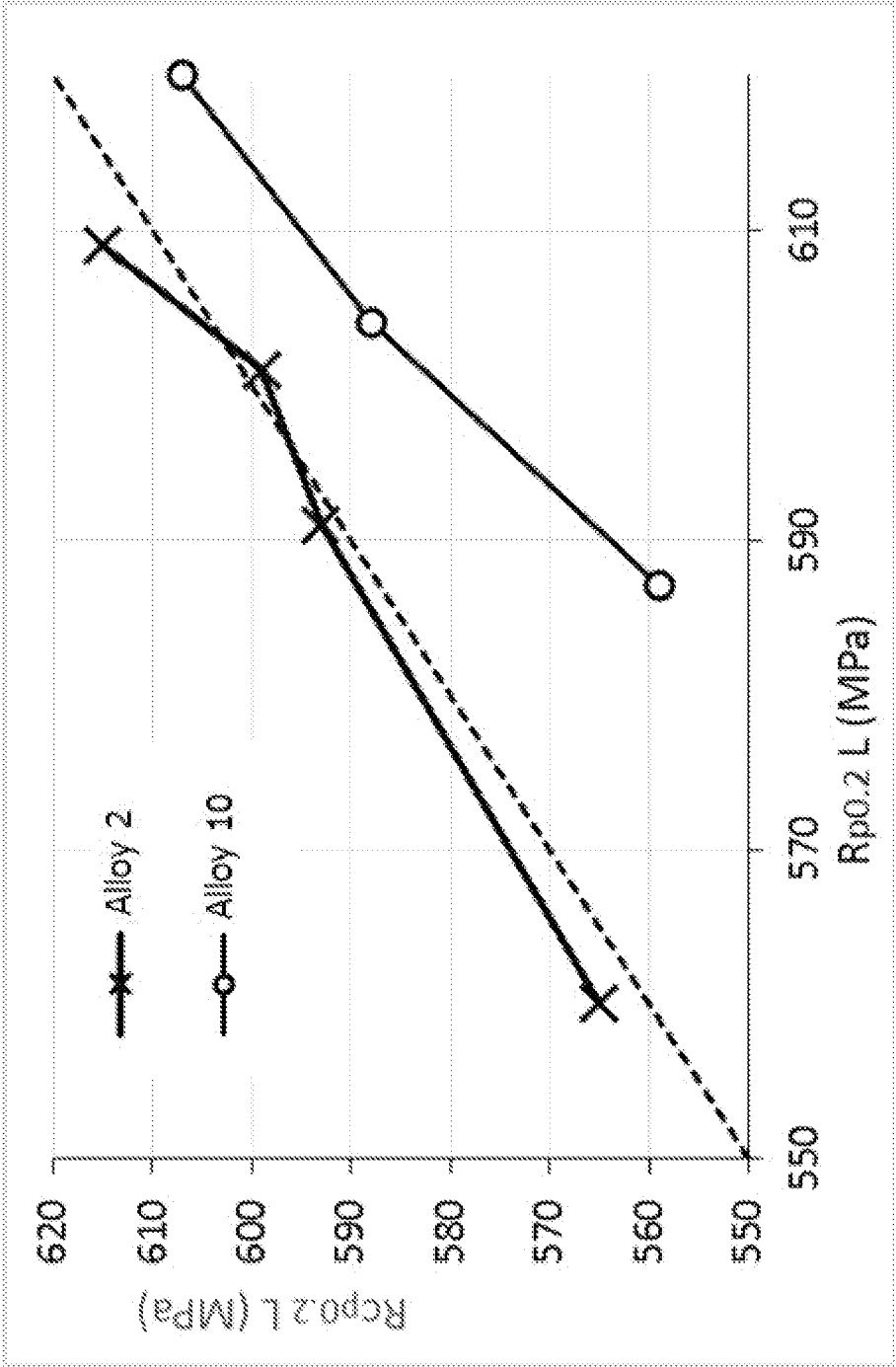


FIG 3

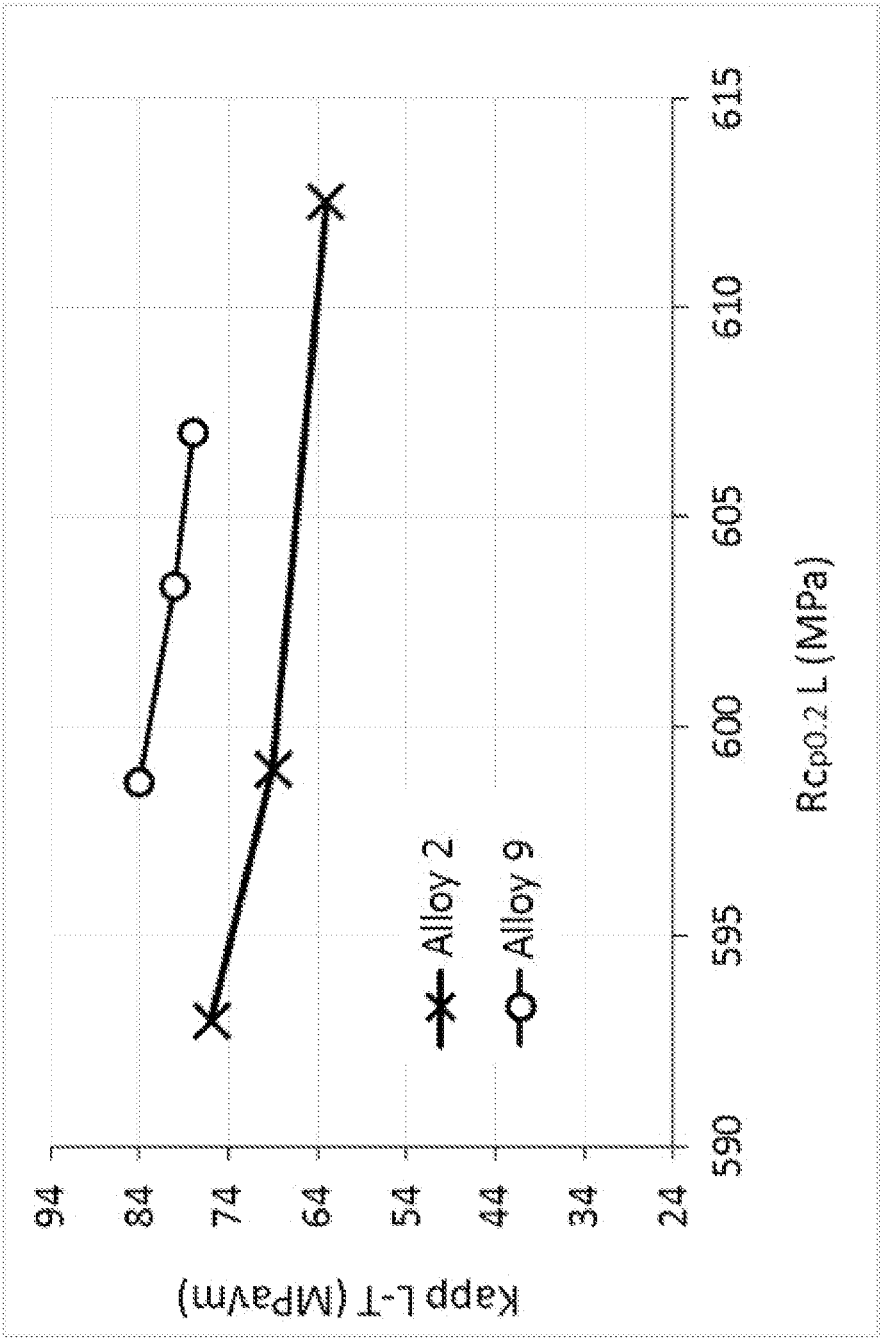


FIG 4

**ALUMINUM-COPPER-LITHIUM ALLOY
HAVING IMPROVED COMPRESSIVE
STRENGTH AND IMPROVED TOUGHNESS**

FIELD OF THE INVENTION

[0001] The invention relates to products made of aluminum-copper-lithium alloys, more particularly, such products intended for aeronautical and aerospace construction.

PRIOR ART

[0002] Aluminum alloy products are developed to produce high strength parts intended in particular for the aircraft industry and the aerospace industry.

[0003] Aluminum alloys containing lithium are of great interest in this regard, as lithium can reduce the density of aluminum by 3% and increase the modulus of elasticity by 6% for each weight percent lithium added. For these alloys to be selected in aircrafts, their performance in relation to other properties of use must reach that of commonly used alloys, in particular in terms of compromise between the properties of static mechanical strength (tensile and compressive yield strength, ultimate tensile strength) and damage tolerance properties (toughness, resistance to the fatigue crack propagation), these properties being generally mutually exclusive. For some parts such as the upper wing skin, the compressive yield strength is an essential property. These mechanical properties should moreover preferably be stable over time and have good thermal stability, that is to say not be significantly modified by aging at operating temperature.

[0004] These alloys must also have sufficient corrosion resistance, be able to be shaped according to the usual methods and have low residual stresses so that they can be fully machined. Finally, they must be able to be obtained by robust manufacturing methods, in particular, the properties must be able to be obtained on industrial tools for which it is difficult to guarantee temperature homogeneity within a few degrees for large parts.

[0005] U.S. Pat. No. 5,032,359 describes a large family of aluminum-copper-lithium alloys wherein the addition of magnesium and silver, in particular between 0.3 and 0.5 percent by weight, allows to increase the mechanical strength.

[0006] U.S. Pat. No. 5,455,003 describes a method for manufacturing Al—Cu—Li alloys which have improved mechanical strength and improved toughness at cryogenic temperature, in particular thanks to suitable work hardening and ageing. This patent recommends in particular the composition, in percentage by weight, Cu=3.0-4.5, Li=0.7-1.1, Ag=0-0.6, Mg=0.3-0.6 and Zn=0-0.75.

[0007] U.S. Pat. No. 7,438,772 describes alloys comprising, in weight percentage, Cu: 3-5, Mg: 0.5-2, Li: 0.01-0.9 and discourages the use of higher lithium content due to degradation of the compromise between toughness and mechanical strength.

[0008] U.S. Pat. No. 7,229,509 describes an alloy comprising (% by weight): (2.5-5.5) Cu, (0.1-2.5) Li, (0.2-1.0) Mg, (0.2-0.8) Ag, (0.2-0.8) Mn, 0.4 max Zr or other grain refiner agents such as Cr, Ti, Hf, Sc, V.

[0009] Patent application US 2009/142222 A1 describes alloys comprising (in % by weight), 3.4 to 4.2% of Cu, 0.9 to 1.4% of Li, 0.3 to 0.7% of Ag, 0.1 to 0.6% of Mg, 0.2 to 0.8% of Zn, 0.1 to 0.6% of Mn and 0.01 to 0.6% of at least

one element for controlling the granular structure. This application also describes a method for manufacturing extruded products.

[0010] Patent application WO2009/036953 relates to an aluminum alloy product for structural elements having a chemical composition comprising, by weight Cu from 3.4 to 5.0, Li from 0.9 to 1.7, Mg from 0.2 to 0.8, Ag from about 0.1 to 0.8, Mn from 0.1 to 0.9, Zn up to 1.5, and one or more elements selected from the group consisting of: (Zr about 0.05 to 0.3, Cr 0.05 to 0.3, Ti about 0.03 to 0.3, Sc about 0.05 to 0.4, Hf about 0.05 to 0.4), Fe<0.15, Si<0.5, normal and unavoidable impurities.

[0011] Patent application WO 2012/085359 A2 relates to a method for manufacturing rolled products made of an aluminum-based alloy comprising 4.2 to 4.6% by weight of Cu, 0.8 to 1.30% by weight of Li, 0.3 to 0.8% by weight of Mg, 0.05 to 0.18% by weight of Zr, 0.05 to 0.4% by weight of Ag, 0.0 to 0.5% by weight of Mn, at most 0.20% by weight of Fe+Si, less than 0.20% by weight of Zn, at least one element selected from Cr, Se, Hf and Ti, the amount of said element, if selected, being 0.05 to 0.3% by weight for Cr and for Se, 0.05 to 0.5% by weight for Hf and from 0.01 to 0.15% by weight for Ti, the other elements at most 0.05% by weight each and 0.15% by weight in total, the remainder being aluminum, comprising the steps of preparation, casting, homogenization, rolling with a temperature greater than 400° C., solution heat-treating, quenching, tensioning between 2 and 3.5% and ageing.

[0012] Patent application US2012/0225271 A1 relates to wrought products with a thickness of at least 12.7 mm containing from 3.00 to 3.80% by weight of Cu, from 0.05 to 0.35% by weight of Mg, from 0.975 to 1.385% by weight of Li, wherein $-0.3 \text{ Mg}-0.15\text{Cu}+1.65\leq\text{Li}\leq-0.3\text{Mg}-0.15\text{Cu}+1.85$, from 0.05 to 0.50% by weight of at least one grain structure control element, wherein the grain structure control element is selected from the group consisting of Zr, Sc, Cr, V, Hf, other rare earth elements, and combinations thereof, up to 1.0% by weight of Zn, up to 1.0% by weight of Mn, up to 0.12% by weight of Si, up to 0.15% by weight of Fe, up to 0.15% by weight of Ti, up to 0.10% by weight of other elements with a total not exceeding 0.35% by weight.

[0013] Application WO 2013/169901 describes alloys comprising, in percentage by weight, 3.5 to 4.4% of Cu, 0.65 to 1.15% of Li, 0.1 to 1.0% of Ag, 0.45 to 0.75% of Mg, 0.45 to 0.75% of Zn and 0.05 to 0.50% of at least one element for the control of granular structure. The alloys advantageously have a Zn to Mg ratio comprised between 0.60 and 1.67.

[0014] There is a need for aluminum-copper-lithium alloy products having improved properties compared to those of known products, in particular in terms of compromise between the properties of static mechanical strength, in particular the tensile and compressive yield strength and the properties of damage tolerance, in particular toughness, thermal stability, corrosion resistance and machinability, while having a low density.

[0015] In addition, there is a need for a method for manufacturing these products that is robust, reliable and economical.

OBJECT OF THE INVENTION

[0016] A first object of the invention is a product based on an aluminum alloy comprising, in percentage by weight, 4.0 to 4.6% by weight of Cu, 0.7 to 1.2% by weight of Li, 0.5

to 0.65% by weight of Mg, 0.10 to 0.20% by weight of Zr, 0.15 to 0.30% by weight of Ag, 0.25 to 0.45% by weight of Zn, 0.05 to 0.35% by weight of Mn, at most 0.20% by weight of Fe+Si, at least one element selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being 0.05 to 0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and from 0.01 to 0.15% by weight for Ti, other elements at most 0.05% by weight each and 0.15% by weight in total and the remainder being aluminum.

[0017] A second object of the invention is a method for manufacturing a product based on an aluminum alloy wherein, successively,

[0018] a) a liquid metal bath based on aluminum is prepared comprising 4.0 to 4.6% by weight of Cu; 0.7 to 1.2% by weight of Li; 0.5 to 0.65% by weight of Mg; 0.10 to 0.20% by weight of Zr; 0.15 to 0.30% by weight of Ag; 0.25 to 0.45% by weight of Zn; 0.05 to 0.35% by weight of Mn; at most 0.20% by weight of Fe+Si; at least one element selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being from 0.05 to 0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and from 0.01 to 0.15% by weight for Ti; other elements at most 0.05% by weight each and 0.15% by weight in total and the remainder being aluminum;

[0019] b) a crude form is cast from said liquid metal bath;

[0020] c) said crude form is homogenized at a temperature comprised between 450° C. and 550° C. and preferably between 480° C. and 530° C. for a period comprised between 5 and 60 hours;

[0021] d) said homogenized crude form is hot-worked, preferably by rolling;

[0022] e) the hot-worked product is solution heat-treated between 490 and 530° C. for 15 min 125 to 8 h and said solution heat-treated product is quenched;

[0023] f) said product is cold-worked with a working of 2 to 16%;

[0024] g) an ageing is carried out wherein said cold-worked product reaches a temperature comprised between 130 and 170° C. and preferably between 140 and 160° C. for 5 to 100 hours and preferably 10 to 70 hours.

[0025] Another object of the invention is an alloy product according to the invention or that can be obtained according to the method of the invention, with a thickness comprised between 8 and 50 mm having, at mid-thickness:

[0026] i) a compressive yield strength $R_{c_{p0.2}}(L) \geq 590$ MPa, preferably $R_{c_{p0.2}}(L) \geq 595$ MPa;

[0027] ii) a toughness $K_{app}(L-T) \geq 60$ MPa \sqrt{m} , preferably $K_{app}(L-T) \geq 75$ MPa \sqrt{m} , with $K_{app}(L-T)$ the value of the apparent stress intensity factor at rupture defined according to standard ASTM E561 (2015) measured on CCT test specimens of width $W=406$ mm and thickness $B=6.35$ mm;

[0028] iii) a difference between the tensile yield strength $R_{p0.2}(L)$ and the compressive yield strength $R_{c_{p0.2}}(L)$, $R_{p0.2}(L) - R_{c_{p0.2}}(L)$, less or equal to 10 MPa, preferably ≤ 5 MPa.

[0029] Yet another object is an aircraft structure member, preferably an aircraft upper wing skin element.

DESCRIPTION OF THE FIGURES

[0030] FIG. 1: Compromise between the toughness $K_{app} L-T$ and the compressive yield strength $R_{c_{p0.2}} L$ of the alloys of Example 1.

[0031] FIG. 2: Compromise between the toughness $K_q L-T$ and the compressive yield strength $R_{c_{p0.2}} L$ of the alloys of Example 2.

[0032] FIG. 3: Compromise between the compressive yield strength $R_{c_{p0.2}} L$ and the tensile yield strength $R_{p0.2} L$ for the alloys of Example 2.

[0033] FIG. 4: Compromise between the toughness $K_{app} L-T$ and the compressive yield strength $R_{c_{p0.2}} L$ of the alloys of Example 3.

DESCRIPTION OF THE INVENTION

[0034] Unless otherwise indicated, all indications relating to the chemical composition of the alloys are expressed as a percentage by weight based on the total weight of the alloy. The expression 1.4 Cu means that the copper content expressed in % by weight is multiplied by 1.4. The designation of the alloys is made in accordance with the regulations of The Aluminum Association, known to the person skilled in the art. When the concentration is expressed in ppm (parts per million), this indication also refers to a mass concentration.

[0035] Unless otherwise indicated, the definitions of metallurgical states given in European standard EN 515 (1993) apply.

[0036] The tensile static mechanical features, in other words the ultimate tensile strength R_m , the conventional yield strength at 0.2% elongation $R_{p0.2}$, and the elongation at rupture A %, are determined by a tensile test according to standard NF EN ISO 6892-1 (2016), the sampling and direction of the test being defined by standard EN 485 (2016). $R_{p0.2}(L)$ means $R_{p0.2}$ measured in the longitudinal direction.

[0037] The compressive yield strength $R_{c_{p0.2}}$ was measured at 0.2% compression according to standard ASTM E9-09 (2018). $R_{c_{p0.2}}(L)$ means $R_{c_{p0.2}}$ measured in the longitudinal direction. The stress intensity factor (K_{IC}) is determined according to standard ASTM E 399 (2012). The stress intensity factor (K_Q) is determined according to standard ASTM E 399 (2012). The standard ASTM E 399 (2012) gives the criteria that allow determining whether K_Q is a valid value of K_{IC} . For a given test specimen geometry, the values of K_Q obtained for different materials are comparable with each other provided that the yield strengths of the materials are of the same order of magnitude.

[0038] Unless otherwise indicated, the definitions of standard EN 12258 (2012) apply.

[0039] The values of the apparent stress intensity factor at rupture (K_{app}) and the stress intensity factor at rupture (K_c) are as defined in standard ASTM E561.

[0040] A curve giving the effective stress intensity factor as a function of the effective crack extension, known as the curve R, is determined according to standard ASTM E 561 (ASTM E 561-10-2).

[0041] The critical stress intensity factor K_{c_c} , in other words the intensity factor which makes the crack unstable, is calculated from the curve R. The stress intensity factor K_{CO} is also calculated by assigning the length of the initial crack at the beginning of the monotonic load, to the critical load. These two values are calculated for a test specimen of

the required shape. K_{app} represents the factor K_{CO} corresponding to the test specimen which was used to perform the test of curve R. K_{eff} represents the factor K_C corresponding to the test specimen which was used to perform the test of curve R.

[0042] A mechanical part for which the static and/or dynamic mechanical properties are particularly important for the performance of the structure, and for which a structural calculation is usually required or performed is here called “structure element” or “structural element” of a mechanical construction. These are typically elements the failure of which is likely to endanger the safety of said construction, its users, customers or others. For an airplane, these structure elements comprise in particular the elements that compose the fuselage (such as the fuselage skin), the stiffeners or stringers of the fuselage, the watertight bulkheads, the circumferential frames of the fuselage, the wings (such as the upper or lower wing skin), the stiffeners (or stringers), the ribs and spars and the empennage in particular composed of horizontal and vertical stabilizers, as well as floor beams, seat tracks and doors.

[0043] According to the present invention, a selected class of aluminum alloys containing in particular specific and critical amounts of lithium, copper, magnesium, silver, manganese and zinc allows to prepare structure elements, in particular upper wing skin sheets, having a high compressive yield strength $R_{cp,0.2}(L)$, a small difference between compressive yield strength $R_{cp,0.2}(L)$ and tensile yield strength $R_{p0.2}(L)$ and a particularly improved apparent stress intensity factor at rupture K_{app} . The selected alloy composition of the invention further allows to obtain all or part of the aforementioned advantages for a wide range of ageing times (in particular a range of at least 5 hours at a given ageing temperature). Such a composition thus allows to guarantee the robustness of the manufacturing method and therefore to guarantee the final properties of the product during industrial manufacture.

[0044] The product based on an aluminum alloy according to the invention comprises, in percentage by weight, 4.0 to 4.6% by weight of Cu; 0.7 to 1.2% by weight of Li; 0.5 to 0.65% by weight of Mg; 0.10 to 0.20% by weight of Zr; 0.15 to 0.30% by weight of Ag; 0.25 to 0.45% by weight of Zn; 0.05 to 0.35% by weight of Mn; at most 0.20% by weight of Fe+Si; at least one element selected from Cr, Sc, Hf, V and Ti; other elements at most 0.05% by weight each and 0.15% by weight in total and the remainder being aluminum.

[0045] The copper content of the products according to the invention is comprised between 4.0 and 4.6% by weight, preferably between 4.2 and 4.5% by weight and more preferably between 4.2 and 4.4% by weight. In an advantageous embodiment, the minimum copper content is 4.25% by weight.

[0046] The lithium content of the products according to the invention is comprised between 0.7 to 1.2% by weight. Advantageously, the lithium content is comprised between 0.8 and 1.0% by weight; preferably between 0.85 and 0.95% by weight.

[0047] The increase in the copper content and to a lesser extent the lithium content contributes to improving the static mechanical strength, however, copper having a detrimental effect in particular on the density, it is preferable to limit the copper content to the preferred maximum value of 4.4% by weight. The increase in the lithium content has a favorable effect on the density, however the present inventors have

observed that for the alloys according to the invention, the preferred lithium content comprised between 0.85% and 0.95% by weight allows an improvement in the compromise between mechanical strength (tensile and compressive yield strength) and toughness. A high lithium content, in particular above the preferred maximum value of 0.95% by weight, can lead to a degradation of the toughness.

[0048] The magnesium content of the products according to the invention is comprised between 0.5% and 0.65% by weight. Preferably, the magnesium content is at least 0.50% or even at least 0.55% by weight, which simultaneously improves static mechanical strength and toughness. In particular, for the selected compositions of the present invention, a magnesium content greater than 0.65% by weight can induce a degradation of the toughness.

[0049] The zinc and silver contents are respectively comprised between 0.25 and 0.45% by weight and 0.15 and 0.30% by weight. Such zinc and silver contents are necessary to guarantee a compressive yield strength having a value close to that of the tensile yield strength. In an advantageous embodiment, the products according to the invention have a difference between the tensile yield strength $R_{p0.2}(L)$ and the compressive yield strength $R_{cp,0.2}(L)$ less than or equal to 10 MPa, preferably less than or equal to 5 MPa.

[0050] The presence of silver and zinc allows to obtain a good compromise between the various desired properties. In particular, the presence of silver allows to obtain a product in a reliable and robust manner, that is to say that the desired compromise in properties is achieved for a wide range of ageing times, in particular a time range greater than 5 hours, which is compatible with the variability inherent in an industrial manufacturing method. A minimum content of 0.20% by weight of silver is advantageous. A maximum content of 0.27% by weight of silver is advantageous.

[0051] A minimum content of 0.30% by weight of zinc is advantageous. A maximum content of 0.40% by weight of zinc is advantageous. Preferably, the Zn content is comprised between 0.30 and 0.40% by weight.

[0052] Advantageously, the sum of the Zn, Mg and Ag contents comprised between 0.95 and 1.35% by weight, preferably between 1.00 and 1.30% by weight, more preferably still between 1.15 and 1.25% by weight. The present inventors have observed that the desired optimum compromise in properties, in particular for elements of the upper wing skin, was only achieved for specific and critical values of the sum of Zn, Mg and Ag.

[0053] The manganese content is comprised between 0.05 and 0.35% by weight. Advantageously, the Mn content comprised between 0.10 and 0.35% by weight. In one embodiment, the manganese content is comprised between 0.2 and 0.35% by weight and preferably between 0.25 and 0.35% by weight. In another embodiment, the manganese content is comprised between 0.1 and 0.2% by weight and preferably between 0.10 and 0.20% by weight. In particular, the addition of Mn allows to obtain high toughness. However, if the Mn content is greater than 0.35% by weight, the fatigue life can be significantly reduced.

[0054] The Zr content of the alloy is comprised between 0.10 and 0.20% by weight. In an advantageous embodiment, the Zr content is comprised between 0.10 and 0.15% by weight, preferably between 0.11 and 0.14% by weight.

[0055] The sum of the iron content and the silicon content is at most 0.20% by weight. Preferably, the iron and silicon

contents are each at most 0.08% by weight. In an advantageous embodiment of the invention the iron and silicon contents are at most 0.06% and 0.04% by weight, respectively. A controlled and limited iron and silicon content helps improve the compromise between mechanical strength and damage tolerance.

[0056] The alloy also contains at least one element which can contribute to the control of the grain size selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being from 0.05 to 0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and from 0.01 to 0.15% by weight for Ti. In an advantageous embodiment, it is selected to add between 0.01 and 0.15% by weight of titanium. In a preferred embodiment, the Ti content is comprised between 0.01 and 0.08% by weight, preferably between 0.02 and 0.06% by weight. Advantageously in the embodiments wherein it is selected to add titanium, the content of Cr, Sc, V and Hf is limited to a maximum content of 0.05% by weight, these elements possibly having an unfavorable effect, in particular on the density and being added only to further promote the production of an essentially non-recrystallized structure if necessary. In a particularly advantageous manner, the Ti is present in particular in the form of particles of TiC. Against all expectations, the present inventors have observed that, in the particular case of the present alloy, the presence of particles of TiC in the grain refining rod during casting (AlTiC refining), allows to obtain a product having an optimized compromise in properties. Advantageously the refiner has the formula $AlTi_xC_y$, which is also written AlT_xC_y , where x and y are the contents of Ti and C in % by weight for 1% by weight of Al, and $x/y > 4$. In particular, the AlTiC refinement in the alloy of the present invention allows an improvement of the compromise between the toughness K_{app} L-T and the compressive yield strength $R_{p0.2}$ L.

[0057] The content of the alloy elements can be selected to minimize the density. Preferably, the additive elements contributing to increase the density such as Cu, Zn, Mn and Ag are minimized and the elements contributing to decrease the density such as Li and Mg are maximized so as to achieve a density less than or equal to 2.73 g/cm³ and preferably less than or equal to 2.72 g/cm³.

[0058] The content of the other elements is at most 0.05% by weight each and 0.15% by weight in total. The other elements are typically unavoidable impurities.

[0059] The method for manufacturing products according to the invention comprises the steps of preparation, casting, homogenization, hot working, solution heat-treating and quenching, tensioning between 2 and 16% and ageing.

[0060] In a first step, a liquid metal bath is prepared so as to obtain an aluminum alloy of a composition according to the invention.

[0061] The liquid metal bath is then cast in the form of crude form, preferably in the shape of an ingot for rolling or an extrusion billet.

[0062] The crude form is then homogenized so as to reach a temperature comprised between 450° C. and 550° C. and preferably between 480° C. and 530° C. for a period comprised between 5 and 60 hours. The homogenization treatment can be carried out in one or more stages.

[0063] After homogenization, the crude form is generally cooled to room temperature before being preheated in order to be hot-worked. The hot working can in particular be an extrusion or a hot rolling. Preferably, this is a hot rolling step. The hot rolling is carried out to a thickness preferably comprised between 8 and 50 mm and in a preferred manner between 15 and 40 mm.

[0064] The product thus obtained is then solution heat-treated to reach a temperature comprised between 490 and 530° C. for 15 min to 8 h, then quenched typically with water at room temperature.

[0065] The product then undergoes cold working with a working of 2 to 16%. It can be a controlled tensioning with a permanent set of 2 to 5%, preferably from 2.0% to 4.0%. In an alternative advantageous embodiment, the cold working is carried out in two steps: the product is first of all cold rolled with a thickness reduction rate comprised between 8 to 12% then subsequently tensioned in a controlled manner with a permanent set comprised between 0.5 and 4%.

[0066] The product is then subjected to an ageing step carried out by heating at a temperature comprised between 130 and 170° C. and preferably between 140 and 160° C. for 5 to 100 hours and preferably 10 to 70 hours.

[0067] The present inventors have observed that, surprisingly, the specific and critical contents of the alloy of the present invention allow to achieve excellent properties, in particular a compromise between the compressive yield strength $R_{p0.2}$ (L) and toughness in plane stresses K_{app} particularly improved. Advantageously, these properties can be obtained, for the alloys of the invention, regardless of the ageing time between 15 h and 25 h at 155° C., which guarantees the robustness of the manufacturing method.

[0068] Advantageously, the granular structure of the products obtained is predominantly non-recrystallized. The rate of non-recrystallized granular mid-thickness structure is preferably at least 70% and preferably at least 80%.

[0069] The products obtained by the method according to the invention, in particular the rolled products having a thickness comprised between 8 and 50 mm, at mid-thickness, have the following features:

[0070] i) a compressive yield strength $R_{p0.2}$ (L) ≥ 590 MPa, preferably $R_{p0.2}$ (L) ≥ 595 MPa, with $R_{p0.2}$ (L) the compressive yield strength measured at 0.2% compression according to the standard ASTM E9 (2018) in the longitudinal direction;

[0071] ii) a toughness K_{app} (L-T) ≥ 60 MPa \sqrt{m} , preferably K_{app} (L-T) ≥ 75 MPa \sqrt{m} , with K_{app} (L-T) the value of the apparent stress intensity factor at rupture defined according to standard ASTM E561 (2015) measured on CCT test specimens of width W=406 mm and thickness B=6.35 mm;

[0072] iii) a difference between the tensile yield strength $R_{p0.2}$ (L) and the compressive yield strength $R_{p0.2}$ (L), $R_{p0.2}$ (L) - $R_{p0.2}$ (L), less than or equal to 10 MPa, preferably ≤ 5 MPa.

[0073] Advantageously, the features i) and ii) are obtained for a wide range of ageing time, in particular a range of at least 5 hours at a given ageing temperature. Such a composition thus allows to guarantee the robustness of the manufacturing method and therefore to guarantee the final properties of the product during industrial manufacture.

[0074] In an advantageous embodiment, the toughness is such that $K_{app} (L-T) \geq -0.48 R_{c_{p0.2}}(L) + 355.2$, with $K_{app} (L-T)$ expressed in MPa \sqrt{m} , the value of the apparent stress intensity factor at rupture defined according to standard ASTM E561 (2015) measured on CCT test specimens of width $W=406$ mm and thickness $B=6.35$ mm, and $R_{c_{p0.2}} (L)$ expressed in MPa, the compressive yield strength measured at 0.2% compression according to standard ASTM E9 (2018).

[0075] The alloy products according to the invention allow in particular the manufacture of structure elements, in particular aircraft structure elements. In an advantageous embodiment, the preferred aircraft structure element is an aircraft upper wing skin element.

[0076] These and other aspects of the invention are explained in more detail using the following illustrative and non-limiting examples.

EXAMPLES

Example 1

[0077] In this example, plates with a section of 406×1520 mm made of an alloy, the composition of which is given in Table 1, were cast.

TABLE 1

Composition in % by weight of alloys N°1 to 8										
Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr	Li	Ag
1	0.02	0.03	4.6	0.32	0.62	0.62	0.03	0.13	0.91	0.01
2	0.02	0.03	4.3	0.31	0.60	0.35	0.03	0.12	0.91	0.24
3	0.03	0.05	4.5	0.34	0.71	0.04	0.04	0.11	1.03	0.21
4	0.03	0.04	4.3	—	0.33	0.03	0.02	0.15	1.13	0.21
5	0.03	0.04	4.2	0.33	0.54	—	0.03	0.13	0.88	0.19
6	0.02	0.04	4.4	0.02	0.21	0.04	0.02	0.14	1.05	0.21
7	0.03	0.04	3.9	—	0.36	—	0.03	0.11	1.31	0.36
8	0.04	0.06	4.1	0.42	0.42	0.02	0.02	0.15	1.18	0.29

[0078] For each composition, the plate was homogenized with a 1st stage of 15 h at 500° C., followed by a second stage of 20 h at 510° C. The plate was hot rolled at a temperature above 440° C. to obtain sheets of a thickness of 25 mm for alloys 2 to 8 and 28 mm for alloy 1. The sheets were solution heat-treated at about 510° C. for 3 h, water quenched at 20° C. The sheets were then tensioned with a permanent elongation comprised between 2% and 6%.

[0079] The sheets underwent a single-stage ageing as indicated in Table 2. Samples were taken at mid-thickness to measure the static mechanical features in tension and in compression in the longitudinal direction. The toughness in plane stress was also measured at mid-thickness during tests of curve R with CCT test specimens 406 mm wide and 6.35 mm thick in the L-T direction. The results are shown in Table 2 and FIG. 1.

[0080] The structure of the obtained sheets was mostly non-recrystallized. The rate of non-recrystallized granular mid-thickness structure was 90%.

TABLE 2

Controlled tensile and ageing conditions and mechanical properties obtained for the various mid-thickness sheets.					
Alloy	Ageing	Permanent elongation during controlled tensioning	R _{p0.2} (L) Tension (Mpa)	R _{c_{p0.2}} (L) Compression (Mpa)	K _{app} (L-T) (MPa \sqrt{m})
1	15 h 155° C.	3.0	593	585	71
	20 h 155° C.	3.0	604	610	59
2	15 h 155° C.	3.0	591	593	76
	20 h 155° C.	3.0	601	599	69
3	15 h 155° C.	3.3	612	607	60
	20 h 155° C.	3.1	619	614	59
4	15 h 155° C.	3.1	636	637	55
	20 h 155° C.	3.2	574	570	105
5	15 h 155° C.	3.2	585	580	79
	20 h 155° C.	3.1	628	628	51
6	20 h 155° C.	3.1	628	628	51
7	24 h 150° C.	4.5	606	590	64
8	24 h 150° C.	4.0	594	587	72

Example 2

[0081] In this example, in addition to the alloy plate 2 of example 1, a plate with a section of 406×1520 mm, the composition of which is given in Table 3, was cast.

TABLE 3

Composition in % by weight of alloys 2 and 10,										
Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr	Li	Ag
2	0.02	0.03	4.3	0.31	0.60	0.35	0.03	0.12	0.91	0.24
10	0.04	0.02	4.3	0.31	0.64	0.33	0.03	0.14	0.90	0.35

[0082] The plates were homogenized at about 510° C. then scalped. After homogenization, the plates were hot rolled to obtain sheets having a thickness of 25 mm. The sheets were solution heat-treated for 3 hours at about 510° C., quenched in cold water and tensioned with a permanent elongation of 3%.

[0083] The structure of the sheets obtained was predominantly non-recrystallized. The rate of non-recrystallized mid-thickness granular structure was 90%.

[0084] The sheets were tempered between 15 h and 50 h at 155° C. Samples were taken at mid-thickness to measure the static mechanical features in tension, in compression in the longitudinal direction as well as the toughness K_Q in the L-T direction. The test specimens used for the toughness measurement had a width $W=40$ mm and a thickness $B=20$ mm. The results obtained are presented in Table 4 and FIGS. 2 and 3

TABLE 4

Ageing conditions and mechanical properties obtained for the sheets 2 and 10.							
Alloy	Ageing time at 155° C.	Tension properties			Com- pression properties R _{c_{p0.2}} (L) (MPa)	Tough- ness K _Q (MPa√m) L-T	Difference between R _{p0.2} (MPa) in tension and R _{p0.2} (MPa) in compression
		R _{p0.2} (L) (MPa)	R _m (L) (MPa)	A (%)			
N°2	10 h	560	598	10	565		-5
	15 h	591	617	8.3	593	30.6	-2
	20 h	601	625	8.5	599	29.9	2
	25 h				613	27.6	
	30 h	609	632	7.9	615		-6
N°10	10 h	587	620	10	559		28
	15 h	604	632	8.5	588	30.7	16
	20 h	620	644	8.2	607	25.1	13
	25 h				609	24.8	
	30 h	621	645	7.5	609		12

[0086] The plates were homogenized at about 510° C. then scalped. After homogenization, the plates were hot rolled to obtain sheets having a thickness of 25 mm. The sheets were solution heat-treated for 3 h at around 510° C., quenched in cold water and tensioned with a permanent elongation of 3%.

[0087] The sheets were tempered between 15 h and 25 h at 155° C. Samples were taken at mid-thickness to measure the static mechanical features in tension, in compression in the longitudinal direction as well as the toughness K_Q in the L-T direction. The test specimens used for the toughness measurement had a width W=40 mm and a thickness B=20 mm. The validity criteria of K_{1C} were met for some samples. Measurements of toughness in plane stress were also obtained on CCT samples 406 mm wide and 6.35 mm thick.

The results obtained are presented in Table 6 and in FIG. 4.

TABLE 6

Ageing conditions and mechanical properties obtained for sheets 2 and 9 at mid-thickness							
Tension properties					Compression properties R _{Cp0.2} (L) (MPa)	Toughness	
Alloy	Ageing time at 155° C.	Rm (L) (MPa)	in tension (MPa)	A (%)		K _Q L-T (MPa · m ^{1/2})	K _{app} L-T (MPa · m ^{1/2})
N°2	15 h	591	617	8.3	593	30.6	76
	20 h	601	625	8.5	599	29.9	69
	25 h				613	27.6	63
N°9	15 h	597	622	9.1	599	28.7	84
	20 h				603	26.8	80
	25 h	602	626	8.5	607	26.9	78

Example 3

[0085] In this example, in addition to the plate of alloy 2 of example 1, a plate with a section 406×1700 mm, the composition of which is given in Table 3 was cast using an AlTiC refining (grain refining rod containing nuclei of the TiC type).

TABLE 5

Composition in % by weight of alloys 2 and 9.											
Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr	Li	Ag	
2	0.02	0.03	4.3	0.31	0.60	0.35	0.03	0.12	0.91	0.24	
9	0.02	0.04	4.3	0.14	0.61	0.36	0.05	0.13	0.88	0.25	

1. A product based on an aluminum alloy comprising, in percentage by weight,

- 4.0 to 4.6% by weight of Cu,
- 0.7 to 1.2% by weight of Li,
- 0.5 to 0.65% by weight of Mg,
- 0.10 to 0.20% by weight of Zr,
- 0.15 to 0.30% by weight of Ag,
- 0.25 to 0.45% by weight of Zn,
- 0.05 to 0.35% by weight of Mn,
- at most 0.20% by weight of Fe+Si,

at least one element selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being from 0.05 to 0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and from 0.01 to 0.15% by weight for Ti,

other elements at most 0.05% by weight each and 0.15% by weight in total, the remainder being aluminum.

2. The product based on an aluminum alloy according to claim 1 wherein the Cu content is comprised between 4.2 and 4.5% by weight, optionally between 4.2 and 4.4% by weight.

3. The product based on an aluminum alloy according to claim 1 wherein the Li content is comprised between 0.8 and 1.0% by weight, optionally preferably between 0.85 and 0.95% by weight.

4. The product based on an aluminum alloy according to claim 1 wherein the Zn content is comprised between 0.30 and 0.40% by weight.

5. The product based on an aluminum alloy according to claim 1 wherein the Mn content comprised between 0.10 and 0.35% by weight.

6. The product based on an aluminum alloy according to claim 1 wherein the sum of the Zn, Mg and Ag contents comprised between 0.95 and 1.35% by weight, optionally between 1.00 and 1.30% by weight, optionally between 1.15 and 1.25% by weight.

7. The product based on an aluminum alloy according to claim 1 wherein the Zr content is 0.10 to 0.15% by weight, optionally between 0.11 and 0.14% by weight.

8. The product based on an aluminum alloy according to claim 1 wherein the Ti content is comprised between 0.01 to 0.15% by weight for Ti, optionally between 0.01 and 0.08% by weight, optionally between 0.02 and 0.06% by weight.

9. The product based on an aluminum alloy according to claim 8 wherein the Ti is present in the form of particles of TiC.

10. A method for manufacturing a product based on an aluminum alloy wherein, successively,

- a) a liquid metal bath based on aluminum is prepared comprising 4.0 to 4.6% by weight of Cu; 0.7 to 1.2% by weight of Li; 0.5 to 0.65% by weight of Mg; 0.10 to 0.20% by weight of Zr; 0.15 to 0.30% by weight of Ag; 0.25 to 0.45% by weight of Zn; 0.05 to 0.35% by weight of Mn; at most 0.20% by weight of Fe+Si; at least one element selected from Cr, Sc, Hf, V and Ti, the amount of said element, if selected, being from 0.05 to

0.3% by weight for Cr and for Sc, 0.05 to 0.5% by weight for Hf and for V and from 0.01 to 0.15% by weight for Ti; other elements at most 0.05% by weight each and 0.15% by weight in total and the remainder being aluminum;

- b) a crude form is cast from said liquid metal bath;
- c) said crude form is homogenized at a temperature comprised between 450° C. and 550° C. and optionally between 480° C. and 530° C. for a period comprised between 5 and 60 hours;
- d) said homogenized crude form is hot-worked, optionally by rolling;
- e) the hot-worked product is solution heat-treated between 490 and 530° C. for 15 min to 8 h and said solution heat-treated product is quenched;
- f) said product is cold-worked with a working of 2 to 16%;
- g) aging is carried out wherein said product reaches a temperature comprised between 130 and 170° C. and optionally between 140 and 160° C. for 5 to 100 hours and optionally 10 to 70 hours.

11. The product according to claim 1, with a thickness comprised between 8 and 50 mm having, at mid-thickness:

- i) a compressive yield strength $R_{p0.2}(L) \geq 590$ MPa, optionally $R_{p0.2}(L)$ 595 MPa;
- ii) a toughness $K_{app}(L-T) \geq 60$ MPa \sqrt{m} , optionally $K_{app}(L-T) \geq 75$ MPa \sqrt{m} , with $K_{app}(L-T)$ the value of the apparent stress intensity factor at rupture defined according to standard ASTM E561 (2015) measured on CCT test specimens of width $W=406$ mm and thickness $B=6.35$ mm;
- iii) a difference between the tensile yield strength $R_{p0.2}(L)$ and the compressive yield strength $R_{p0.2}(L)$, $R_{p0.2}(L) - R_{p0.2}(L)$, less than or equal to 10 MPa, optionally ≤ 5 MPa.

12. An aircraft structure element, optionally an aircraft upper wing skin element, comprising a product according to claim 1.

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