(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 670 690 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.06.2020 Bulletin 2020/26

(51) Int Cl.:
***C22C 21/10** (2006.01)* ***C22F 1/053** (2006.01)*

(21) Application number: **18214960.9**

(22) Date of filing: **20.12.2018**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

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(54) AL-ZN-CU-MG ALLOYS AND THEIR MANUFACTURING PROCESS

(57) The invention relates to a rolled aluminum-based alloy product having a thickness of at least 80 mm comprising, (in weight %) : Zn 6.85 - 7.25, Mg 1.55 - 1.95, Cu 1.90 - 2.30, Zr 0.04 - 0.10, Ti 0 - 0.15, Fe 0 - 0.15, Si 0 - 0.15, other elements ≤ 0.05 each and ≤ 0.15 total, remainder Al, wherein at mid-thickness more than 75 % of grains are recrystallized or at mid-thickness 30 to 75 % of grains are recrystallized and non-recrystallized grains have an aspect ratio in a L/ST cross section less than 3. A process for the manufacture of a rolled aluminum-based alloy product comprises the steps of: (a) casting an ingot made in an alloy according to the invention, (b) conducting an homogenization of the ingot (c) conducting hot rolling of said homogenized ingot in one or more stages by rolling, (d) conducting a solution heat treatment a quench, (e) conducting stress relieving, and, (f) conducting an artificial aging treatment. The products of the invention are suitable for aircraft construction and have advantageous fatigue crack growth properties.

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Description

Field of the Invention

[0001] The present invention relates generally to aluminum base alloys and more particularly, Al-Zn-Cu-Mg aluminum base alloys, in particular for aerospace applications.

Description of Related Art

[0002] Al-Zn-Cu-Mg aluminum base alloys have been used extensively in the aerospace industry for many years. With the evolution of airplane structures and efforts directed towards the goal of reducing both weight and cost, an optimum compromise between properties such as strength, toughness and corrosion resistance is continuously sought. Also, process improvement in casting, rolling and heat treatment can advantageously provide further control in the composition diagram of an alloy and property compromise.

[0003] Thick rolled, forged or extruded products made of Al-Zn-Cu-Mg aluminum base alloys are used in particular to produce integrally machined high strength structural parts for the aeronautic industry, for example wing elements such as wing ribs, spars, frames and the like, which are typically machined from thick wrought sections.

[0004] The performance values obtained for various properties such as static mechanical strength, fracture toughness, resistance to corrosion, quench sensitivity, fatigue resistance, and level of residual stress will determine the overall performance of the product, the ability for a structural designer to use it advantageously, as well as the ease it can be used in further processing steps such as, for example, machining.

[0005] Among the above listed properties some are often conflicting in nature and a compromise generally has to be found. Conflicting properties are, for example, static mechanical strength versus toughness and strength versus resistance to corrosion. Among corrosion or environmentally assisted cracking (EAC) properties, a distinction can be made between EAC under conditions of high stress and humid environment and EAC under conditions of standard stress corrosion cracking (SCC) tests, such as ASTM G47, where specimens are tested using alternate immersion and drying cycles with NaCl solution (ASTM G44) and typically using lower stress.

[0006] Crack deviation, crack turning or also crack branching are terms used to express propensity for crack propagation to deviate from the expected fracture plane perpendicular to the loading direction during a fatigue or toughness test. Crack deviation happens on a microscopic scale (<100 μm), on a mesoscopic scale (100-1000 μm) or on a macroscopic scale (>1 mm) but it is considered detrimental only if the crack direction remains stable after deviation (macroscopic scale). The phenomenon is a particular concern for fatigue trials in L-S direction. The term crack branching is used herein for macroscopic deviation of cracks in L-S fatigue or toughness tests from the S direction towards the L direction which occurs for rolled products with a thickness of 30 mm or higher. Crack branching may occur in relation to the rolled product composition and microstructure and to the test conditions.

[0007] Crack deviation has been considered as a major problem by aircraft manufacturers because it is difficult to take into account to design parts, using traditional design methods. This is because crack deviation invalidates conventional, mode I based, materials testing procedure and design models. The crack deviation problem has proven difficult to solve. Recently it was considered that in the absence of solution for avoiding crack deviation, efforts should be directed to predicting crack deviation behaviors. (M. J. Crill, D. J. Chellman, E. S. Balmuth, M. Philbrook, K. P. Smith, A. Cho, M. Niedzinski, R. Muzzolini and J. Feiger, Evaluation of AA 2050-T87 Al-Li Alloy Crack Turning Behavior, Materials Science Forum, Vol 519-521 (July 2006) pp 1323-1328).

[0008] The patent US 8,323,426 proposes a solution to improve crack branching for some Al-Cu-Li alloys.

[0009] However crack deviation improvement is often related to higher fatigue crack growth rate in the original cracking plane, before deviation.

[0010] US Patent 5,560,789 describes AA 7000 series alloys having high mechanical strength and a process for obtaining them. The alloys contain, by weight, 7 to 13.5% Zn, 1 to 3.8% Mg, 0.6 to 2.7% Cu, 0 to 0.5% Mn, 0 to 0.4% Cr, 0 to 0.2% Zr, others up to 0.05% each and 0.15% total, and remainder Al, corrosion properties are however not mentioned.

[0011] US Patent No 5,865,911 describes an aluminum alloy consisting essentially of (in weight %) about 5.9 to 6.7% zinc, 1.8 to 2.4% copper, 1.6 to 1.86% magnesium, 0.08 to 0.15% zirconium balance aluminum and incidental elements and impurities. The '911 patent particularly mentions the compromise between static mechanical strength and toughness.

[0012] US Patent application N° US20050167016A1 discloses in particular an Al-Zn-Cu-Mg product comprising (in weight %) : 5.8-6.8% Zn, 1.5-2.5% Cu , 1.5-2.5% Mg, 0.04-0.09% Zr remainder aluminum and incidental impurities, wherein said product possesses a recrystallization rate greater than about 35% at a quarter thickness location, with improved fatigue crack growth resistance.

[0013] US Patent No 6,027,582 describes a rolled, forged or extruded Al-Zn-Mg-Cu aluminum base alloy products greater than 60 mm thick with a composition of (in weight %), Zn : 5.7-8.7, Mg : 1.7-2.5, Cu : 1.2-2.2, Fe : 0.07-0.14, Zr :

0.05-0.15 with Cu + Mg < 4.1 and Mg>Cu. The '582 patent also describes improvements in quench sensitivity.

[0014] US Patent No 6,972,110 teaches an alloy, which contains preferably (in weight %) Zn : 7-9.5, Mg : 1.3-1.68 and Cu 1.3-1.9 and encourages keeping Mg +Cu ≤ 3.5. The '110 patent discloses using a three step aging treatment in order to improve resistance to stress corrosion cracking. A three step aging is long and difficult to master and it would be desirable to obtain high corrosion resistance without necessarily requiring such a thermal treatment.

[0015] PCT Patent application No WO2004090183 discloses an alloy comprising essentially (in weight percent): Zn: 6.0 - 9.5, Cu: 1.3 - 2.4, Mg: 1.5 - 2.6, Mn and Zr < 0.25 but preferably in a range between 0.05 and 0.15 for higher Zn contents, other elements each less than 0.05 and less than 0.25 in total, balance aluminium, wherein (in weight percent): 0.1[Cu] + 1.3 < [Mg] < 0.2[Cu] + 2.15, preferably 0.2[Cu] + 1.3 < [Mg] < 0.1[Cu] + 2.15.

[0016] US Patent application No 2005/006010 a method for producing a high strength Al-Zn-Cu-Mg alloy with an improved fatigue crack growth resistance and a high damage tolerance, comprising the steps of casting an ingot with the following composition (in weight percent) Zn 5.5-9.5, Cu 1.5-3.5, Mg 1.5-3.5, Mn<0.25, Zr<0.25, Cr<0.10, Fe<0.25, Si<0.25, Ti<0.10, Hf and/or V<0.25, other elements each less than 0.05 and less than 0.15 in total, balance aluminum, homogenizing and/or pre-heating the ingot after casting, hot rolling the ingot and optionally cold rolling into a worked product of more than 50 mm thickness, solution heat treating, quenching the heat treated product, and artificially ageing the worked and heat-treated product, wherein the ageing step comprises a first heat treatment at a temperature in a range of 105 ° C to 135 ° C for more than 2 hours and less than 8 hours and a second heat treatment at a higher temperature than 135 ° C but below 170 ° C for more than 5 hours and less than 15 hours. Again, such three step aging is long and difficult to master.

[0017] EP Patent 1 544 315 discloses a product, especially rolled, extruded or forged, made of an AlZnCuMg alloy with constituents having the following percentage weights: Zn 6.7 - 7.3; Cu 1.9 - 2.5; Mg 1.0 - 2.0; Zr 0.07 - 0.13; Fe less than 0.15; Si less than 0.15; other elements not more than 0.05 to at most 0.15 per cent in total; and aluminum the remainder. The product is preferably treated by solution heat treatment, quenching, cold rolling and artificial aging.

[0018] US Patent No 8,277,580 teaches a rolled or forged Al-Zn-Cu-Mg aluminum-based alloy wrought product having a thickness from 2 to 10 inches. The product has been treated by solution heat-treatment, quenching and aging, and the product comprises (in weight-%): Zn 6.2-7.2, Mg 1.5-2.4, Cu 1.7-2.1. Fe 0-0.13, Si 0-0.10, Ti 0-0.06, Zr 0.06-0.13, Cr 0-0.04, Mn 0-0.04, impurities and other incidental elements <=0.05 each.

[0019] US Patent No 8,673,209 discloses aluminum alloy products about 4 inches thick or less that possesses the ability to achieve, when solution heat treated, quenched, and artificially aged, and in parts made from the products, an improved combination of strength, fracture toughness and corrosion resistance, the alloy consisting essentially of: about 6.8 to about 8.5 wt. % Zn, about 1.5 to about 2.00 wt. % Mg, about 1.75 to about 2.3 wt. % Cu; about 0.05 to about 0.3 wt. % Zr, less than about 0.1 wt. % Mn, less than about 0.05 wt. % Cr, the balance Al, incidental elements and impurities and a method for making same.

[0020] None of the documents, which describe high strength 7xxx alloy products, describe alloy products without a tendency to crack deviation and low fatigue crack growth rate and having simultaneously high strength, high toughness properties and high corrosion resistance.

[0021] A problem that the present invention addresses is to obtain thick rolled products of the 7XXX alloy series with improved fatigue crack growth rate without increased tendency of crack deviation, while maintaining a good balance between mechanical strength, fracture toughness, resistance to corrosion, quench sensitivity, fatigue resistance, and level of residual stress. By thick rolled products it is meant products with a thickness of at least 80 mm or even of at least 100 mm.

SUMMARY OF THE INVENTION

[0022] An object of the invention was to provide an Al-Zn-Cu-Mg alloy having a specific composition range and manufacturing process that enables, for thick rolled products, an improved fatigue crack growth rate without increased tendency of crack deviation.

[0023] Another object of the invention was the provision of a manufacturing process of wrought aluminum products which enables an improved compromise improved fatigue crack growth rate without increased tendency of crack deviation.

[0024] To achieve these and other objects, the present invention is directed to a rolled product having a thickness of at least 80 mm comprising (in weight %) :

Zn 6.85 - 7.25,
Mg 1.55 - 1.95,
Cu 1.90 - 2.30,
Zr 0.04 - 0.10,
Ti 0 - 0.15,

Fe 0 - 0.15,
Si 0 - 0.15,

other elements ≤ 0.05 each and ≤ 0.15 total, remainder Al, wherein at mid-thickness more than 75 % of grains are recrystallized or at mid-thickness 30 to 75 % of grains are recrystallized and non-recrystallized grains have an aspect ratio in a L/ST cross section less than 3.

[0025] To achieve these and other objects, the present invention is directed the present invention is directed to a process for the manufacture of a rolled aluminum-based alloy product comprising the steps of:

a) casting an ingot comprising, (in weight-%)

Zn 6.85 - 7.25,
Mg 1.55 - 1.95,
Cu 1.90 - 2.30,
Zr 0.04 - 0.10,
Ti 0 - 0.15,
Fe 0 - 0.15,
Si 0 - 0.15,

other elements ≤ 0.05 each and ≤ 0.15 total, remainder Al;

b) homogenizing the ingot;

c) hot rolling said homogenized ingot to a rolled product with a final thickness of at least 80 mm;

d) solution heat treating and quenching the product;

e) stress-relieving the solution heat-treated an quenched the product;

f) artificially aging the stress-relieved product;

wherein the hot rolling starting temperature is controlled to obtain after step f at mid-thickness more than 75 % of recrystallized grains or at mid-thickness 30 to 75 % of recrystallized grains and non-recrystallized grains with an aspect ratio in a L/ST cross section less than 3.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026]

Figure 1 shows the C(T) specimen used for the Fatigue Crack Growth Rate testing. A cone of ±20° which origin is at the intersection of a line passing through the holes centers and the specimen axis of symmetry used for the criteria of crack deviation is represented as a bold line.

Figure 2a is a schematic of the C(T) specimen showing before the fatigue test and the for the criteria of crack deviation. Figure 2b shows a cracked specimen without a tendency to crack deviation: the cracks remains within the cone. Figure 2c shows a specimen with a tendency of crack deviation.

Figure 3 shows specimen of alloy A after Fatigue Crack Growth Rate testing.

Figure 4 shows specimen of alloy B after Fatigue Crack Growth Rate testing.

DETAILED DESCRIPTION

[0027] Unless otherwise indicated, all the indications relating to the chemical composition of the alloys are expressed as a mass percentage by weight based on the total weight of the alloy. In the expression Cu/Mg, Cu means the Cu content in weight % and Mg means the Mg content in weight %. Alloy designation is in accordance with the regulations of The Aluminium Association, known to those skilled in the art. The definitions of tempers are laid down in EN 515 (1993).

[0028] Unless mentioned otherwise, static mechanical characteristics, *i.e.*, the ultimate tensile strength UTS, the tensile yield stress TYS and the elongation at fracture E, are determined by a tensile test according to standard NF EN ISO 6892-1 (2016), the location at which the pieces are taken and their direction being defined in standard EN 485 (2016).

[0029] Unless otherwise specified, the definitions of standard EN 12258 apply.

[0030] The symbol * is used for "multiplied by".

[0031] The fracture toughness K_{1C} is determined according to ASTM standard E399 (2012).

[0032] Except if mentioned otherwise, EAC under conditions of high stress and humid environment was tested under a constant strain on a tensile sample at mid-thickness as described in standard ASTM G47 and using a load of about 80% of ST direction TYS, under 85% relative humidity, and at a temperature of 70°C. The minimum life without failure after Environmentally Assisted Cracking (EAC) corresponds to the minimum number of days to failure from 3 specimens for each plate.

[0033] The tendency to crack deviation is observed using a L-S Compact Tension C(T) fatigue specimen as defined in ASTM E647. The term "deviation" in is not meant herein as described in ASTM E647-15 (which definition is focused on the precision of measurement of fatigue crack growth rate), but is meant as the crack remaining within a cone of ±20°and preferably of ±15°, which origin is at the intersection of a line passing through the holes centers and a specimen axis of symmetry, illustrated by the line A-A in Figure 1. The C(T) specimen has a width W = 40 mm and a thickness B = 10 mm. A representation of the specimen used is shown in Figure 1 which also illustrates with a bold line the cone of ±20°. For the test specimen used L = 48 mm, W = 40 mm, Z = 50 mm, C = 22 mm, B = 10 mm. The method to evaluate crack deviation is illustrated by Figure 2. Figure 2a shows schematically the CT specimen before the fatigue test. Figure 2b shows a cracked specimen without a tendency to crack deviation: the cracks remains with the cone illustrated by bolded lines. Figure 2c shows a specimen with a tendency of crack deviation.

[0034] The term "structural member" is a term well known in the art and refers to a component used in mechanical construction for which the static and/or dynamic mechanical characteristics are of particular importance with respect to structure performance, and for which a structure calculation is usually prescribed or undertaken. These are typically components the rupture of which may seriously endanger the safety of the mechanical construction, its users or third parties. In the case of an aircraft, structural members comprise members of the fuselage (such as fuselage skin), stringers, bulkheads, circumferential frames, wing components (such as wing skin, stringers or stiffeners, ribs, spars), empennage (such as horizontal and vertical stabilizers), floor beams, seat tracks, and doors.

[0035] The alloy of the invention has a specific composition and microstructure which makes possible to obtain products which have a very low fatigue crack growth rate and do not have a tendency to crack deviation.

[0036] A minimum Zn content of 6.85 and preferably 6.90 or even 6.90 is needed to obtain sufficient strength. However the Zn content should not exceed 7.25 and preferably 7.20 or even 7.15 to obtain the sought balance of properties, in particular toughness and elongation.

[0037] A minimum Mg content of 1.55 and preferably 1.60 or even 1.65 is needed to obtain sufficient strength. However, the Mg content should not exceed 1.95 and preferably 1.90 or even 1.85 to obtain the sought balance of properties in particular toughness and elongation and avoid quench sensitivity.

[0038] A minimum Cu content of 1.90 and preferably 1.95 or 2.00, or even 2.05 is needed to obtain sufficient strength and also to obtain sufficient EAC performance. However the Cu content should not exceed 2.30 and preferably 2.25 in particular to avoid quench sensitivity. In an embodiment the Cu maximum content is 2.20.

[0039] In order to obtain products with low sensitivity to EAC under conditions of high stress and humid environment and avoid quench sensitivity, the sum Cu + Mg is preferably controlled between 3.8 and 4.2.

[0040] The alloys of the present invention further contains 0.04 to 0.10 wt.% zirconium, which is typically used for grain size control. The control of the zirconium content in combination with the hot rolling conditions is important to obtain the desired microstructural properties of the invention which are at mid-thickness more than 75 % of recrystallized grains or at mid-thickness 30 to 75 % of recrystallized grains and non-recrystallized grains with an aspect ratio in a L/ST cross section less than 3.

[0041] The Zr content should preferably comprise at least about 0.05 wt. %, but should advantageously remain below about 0.08 or even 0.07 wt.%.

[0042] Titanium, associated with incidental elements such as boron or carbon can usually be added if desired during casting in order to limit the as-cast grain size. The present invention may typically accommodate up to about 0.15 wt. % and preferably up to about 0.06 wt.% Ti. In a preferred embodiment of the invention, the Ti content is about 0.02 wt.% to about 0.06 wt.% and preferentially about 0.03 wt.% to about 0.05 wt.%.

[0043] The present alloy can further contain other elements to a lesser extent and in some embodiments, on a less preferred basis. Iron and silicon typically affect fracture toughness properties. Iron and silicon content should generally be kept low, with a content of at most 0.15 wt.%, and preferably not exceeding about 0.13 wt.% or preferentially about 0.10 wt.% for iron and preferably not exceeding about 0.10 wt.% or preferentially about 0.08 wt.% for silicon. In one embodiment of the present invention, iron and silicon content are ≤ 0.07 wt.%.

[0044] Other elements are impurities or incidental elements which should have a maximum content of 0.05 wt.% each and ≤ 0.15 wt.% total, preferably a maximum content of 0.03 wt.% each and ≤ 0.10 wt. total.

[0045] A suitable process for producing rolled products according to the present invention comprises: (a) casting an ingot made in an alloy according to the invention, (b) conducting an homogenization of the ingot preferably with at least one step at a temperature from about 460 to about 510 °C or preferentially from about 470 to about 500 °C typically for 5 to 30 hours, (c) conducting hot rolling of said homogenized ingot in one or more stages by rolling, with an entry temperature preferably comprised from about 280 to about 420 °C, to a rolled product with a final thickness of at least 80 mm, (d) conducting a solution heat treatment preferably at a temperature from 460 to about 510 °C or preferentially from about 470 to about 500 °C typically for 1 to 10 hours depending on thickness and conducting a quench, preferentially with room temperature water, (e) conducting stress relieving by controlled stretching or compression with a permanent set of preferably less than 5% and preferentially from 1 to 4%, and, (f) conducting an artificial aging treatment.

[0046] The hot rolling entry temperature is controlled in order to obtain the desired microstructural properties of the invention which are at mid-thickness more than 75 % of recrystallized grains or at mid-thickness 30 to 75 % of recrystallized grains and non-recrystallized grains with an aspect ratio in a L/ST cross section less than 3. Advantageously the hot rolling starting temperature is at least $145*Zr^{-0.313} - 20$ and preferably at least $145*Zr^{-0.313} - 10$. Preferably the hot rolling starting temperature is at most $145*Zr^{-0.313} + 20$ and preferably at least $145 *Zr^{-0.313} + 10$. Zr is the weight percent concentration of Zirconium in the alloy.

[0047] The present invention finds particular utility in thick gauges of greater than about 80 mm. In a preferred embodiment, a rolled product of the present invention is a plate having a thickness from 80 to 200 mm, or advantageously from 100 to 180 mm comprising an alloy according to the present invention. "Over-aged" tempers ("T7 type") are advantageously used in order to improve corrosion behavior in the present invention. Tempers that can suitably be used for the products according to the invention, include, for example T6, T651, T73, T74, T76, T77, T7351, T7451, T7452, T7651, T7652 or T7751, the tempers T7351, T7451 and T7651 being preferred. Aging treatment is advantageously carried out in two steps, with a first step at a temperature comprised between 110 and 130 °C for 3 to 20 hours and preferably for 4 or 5 to 12 hours and a second step at a temperature comprised between 140 and 170 °C and preferably between 150 and 165 °C for 5 to 30 hours.

[0048] In an advantageous embodiment, the equivalent aging time t(eq) at 155°C is comprised between 8 and 35 or 30 hours and preferentially between 12 and 25 hours.

[0049] The equivalent time t(eq) at 155°C being defined by the formula :

$$t(eq) = \frac{\int \exp(-16000 \ / \ T)\, dt}{\exp(-16000 \ / \ T_{ref})}$$

where T is the instantaneous temperature in °K during annealing and T_{ref} is a reference temperature selected at 155 °C (428 °K). t(eq) is expressed in hours.

[0050] With the narrow composition range of the invention it is possible to obtain a product with a low tendency to crack deviation and with a very low fatigue crack growth rate. Thus, for the product of the invention, during a fatigue crack growth rate test according to standard ASTM E647, the crack remains within a cone of $\pm 20°$, as illustrated by Figure 2b, and preferably of $\pm 15°$, which origin is at intersection of a line passing through specimen holes centers and a specimen axis of symmetry and da/dN at $\Delta K = 15$ MPa√m is less than 2.0 10^{-4} mm/cycle, preferably less than 1.0 10^{-4} mm/cycle and more preferably less than 0.9 10^{-5} mm/cycle, on a L-S C(T) fatigue specimen at mid-thickness with W = 40 mm and B = 10 mm.

[0051] The narrow composition range of the alloy from the invention, selected mainly for a strength versus toughness compromise provided rolled products with unexpectedly high EAC performance under conditions of high stress and humid environment.

[0052] A product according to the invention also preferably has preferably one, more preferably two and most preferably three of the following properties:

a) a minimum life without failure after Environmentally Assisted Cracking (EAC) under conditions of high stress, at a short transverse (ST) stress level of 80% of the product tensile yield strength in ST direction, and humid environment with 85% relative humidity at a temperature of 70°C, of at least 20 days and preferably of at least 30 days,

b) a conventional tensile yield strength measured in the L direction at quarter thickness of at least 515 - 0.279 * t MPa and preferably of 525 - 0.279 * t MPa and even more preferably of 535 - 0.279 * t MPa (t being the thickness of the product in mm),

c) a K_{1C} toughness in the L-T direction measured at quarter thickness of at least 32 - 0.1*t MPa√m and preferably 34 - 0.1*t MPa√m and even more preferably 36 - 0.1*t MPa√m (t being the thickness of the product in mm).

[0053] Rolled products according to the present invention are advantageously used as or incorporated in structural members for the construction of aircraft.

[0054] In an advantageous embodiment, the products according to the invention are used in wing ribs, spars and frames. In embodiments of the invention, the rolled products according to the present invention are welded with other rolled products to form wing ribs, spars and frames.

[0055] These, as well as other aspects of the present invention, are explained in more detail with regard to the following illustrative and non-limiting examples.

EXAMPLE

[0056] Two ingots were cast, one of a product according to the invention (A), and one reference example (B) with the following composition (Table 1) :

Table 1 : composition (wt. %) of a cast according to the invention and a reference cast.

Alloy	**Si**	**Fe**	**Cu**	**Mg**	**Zn**	**Ti**	**Zr**
A	0.03	0.04	2.13	1.75	7.05	0.04	0.06
B	0.05	0.09	1.64	2.25	6.10	0.02	0.11

[0057] The ingots were then scalped and homogenized at about 475 °C. The ingots were hot rolled to a plate of thickness of 102 mm (alloy A) or 110 mm (alloys B). Hot rolling entry temperature was 350 °C for alloy A and 440 °C for alloy B. The plates were solution heat treated with a soak temperature of about 475 °C. The plates were quenched and stretched with a permanent elongation comprised between 2.0 and 2.5 %.

[0058] The reference plates were submitted to a two-step aging of 4 hours at 120 °C followed by approximately 15 hours at 155°C for a total equivalent time at 155 °C of 17 hours, to obtain a T7651 temper.

[0059] The plates made of alloy A had at mid-thickness more than 75 % of recrystallized grains and the plates of alloy B were substantially unrecrystallized, with a volume fraction of recrystallized grains lower than 35% at mid-thickness.

[0060] The samples were mechanically tested, at quarter-thickness for L and LT directions and at mid-thickness for ST direction to determine their static mechanical properties as well as their fracture toughness. Tensile yield strength, ultimate strength and elongation at fracture are provided in Table 2.

Table 2: Static mechanical properties of the samples

Alloy	L Direction			LT Direction			ST Direction		
	UTS (MPa)	TYS (MPa)	E (%)	UTS (MPa)	TYS (MPa)	E (%)	UTS (MPa)	TYS (MPa)	E (%)
A	548	518	8,4	550	502	6,5	525	473	4,8
B	502	448	12,1	514	443	7,5	495	428	5,8

[0061] Results of the fracture toughness testing are provided in Table 3.

Table 3: Fracture toughness properties of the samples

Alloy	K_{1C}		
	L-T (MPa√m)	T-L (MPa√m)	S-L (MPa√m)
A	26.9	25.1	28.6
B	35.1	29.5	29.3

[0062] EAC under conditions of high stress and humid environment was measured with ST direction tensile specimens which are described in ASTM G47. Testing stress and environment were different from ASTM G47 and used a load of about 80% of ST direction TYS at t/2, under 85% relative humidity, and at a temperature of 70°C. The number of days to failure is provided for 3 specimens for each plate,
The results are provided in Table 4

Table 4 Results of EAC under conditions of high stress and humid environment

Alloy	ST TYS t/2 (MPa)	EAC Stress (MPa)	Test Method	Number of Days to Failure		
				Sample 1	Sample 2	Sample 3
A	473	402	Constant Strain	30	43	60

[0063] The plate made of alloy A resisted in average 33 days under a stress of 350 MPa for SCC testing under ASTM G47.

[0064] The L-S fatigue crack growth rate was measured according to standard ASTM E647 at mid-thickness and quarter thickness in the L-S direction on CT specimen (CT10W40 thickness 10 mm, width 40 mm) under a load of 4 KN. The results are presented in Table 5.

Table 5. Results of the L-S fatigue crack growth rate test (da/dN at ΔK = 15 MPa$\sqrt{m}$)

	Alloy A				Alloy B		
	1/2 thickness		1/4 thickness		1/2 thickness	1/4 thickness	
da/dN (mm/cycle)	7,9E-05	6,8E-05	8,2E-05	8,5E-05	2,5E-04	2,0E-04	2,1E-04

[0065] The L-S fatigue crack growth rate is reduced up to a factor at least 3 on CT specimens for the invention alloy A vs alloy B.

[0066] Images of the cracked specimen of alloy A are shown in Figure 3. None of the cracked specimen exhibited a tendency to crack deviation, and the cracks remained within a cone of ±15°. The cracked specimen of alloy B are shown in Figure 4 and the cracks remained within a cone of ±20° but not however within a cone of ±15°.

[0067] All documents referred to herein are specifically incorporated herein by reference in their entireties.

[0068] As used herein and in the following claims, articles such as "the", "a" and "an" can connote the singular or plural.

[0069] In the present description and in the following claims, to the extent a numerical value is enumerated, such value is intended to refer to the exact value and values close to that value that would amount to an insubstantial change from the listed value.

Claims

1. A rolled aluminum-based alloy product having a thickness of at least 80 mm comprising, (in weight %) :

Zn 6.85 - 7.25,
Mg 1.55 - 1.95,
Cu 1.90 - 2.30,
Zr 0.04 - 0.10,
Ti 0 - 0.15,
Fe 0 - 0.15,
Si 0 - 0.15,

other elements ≤ 0.05 each and ≤ 0.15 total, remainder Al,
wherein at mid-thickness more than 75 % of grains are recrystallized or at mid-thickness 30 to 75 % of grains are recrystallized and non-recrystallized grains have an aspect ratio in a L/ST cross section less than 3.

2. A product according to claim 1 wherein Cu 1.95 - 2.25 and preferably Cu : 2.00 -2.20.

3. A product according to claim 1 or claim 2 wherein during a fatigue crack growth rate test according to standard ASTM E647 the crack remains within a cone of ±20° and preferably of ±15°, which origin is at intersection of a line passing through specimen holes centers and a specimen axis of symmetry and da/dN at ΔK = 15 MPa$\sqrt{m}$ is less than 2.0 10^{-4} mm/cycle, preferably less than 1.0 10^{-4} mm/cycle and more preferably less than 0.9 10^{-5} mm/cycle, on a L-S C(T) fatigue specimen at mid-thickness with W = 40 mm and B = 10 mm .

4. A product according to any of claims 1 to 3, wherein said product has at least one of the following properties:

a) a minimum life without failure after Environmentally Assisted Cracking (EAC) under conditions of high stress, at a short transverse (ST) stress level of 80% of the product tensile yield strength in ST direction, and humid environment with 85% relative humidity at a temperature of 70°C, of at least 30 days and preferably of at least 40 days,
b) a conventional tensile yield strength measured in the L direction at quarter thickness of at least 515 - 0.279 * t MPa and preferably of 525 - 0.279 * t MPa and even more preferably of 535 - 0.279 * t MPa, t being the thickness of the product in mm,
c) a K_{1C} toughness in the L-T direction measured at quarter thickness of at least 32 - 0.1*t MPa√m and preferably 34 - 0.1*t MPa√m and even more preferably 36 - 0.1*t MPa√m, t being the thickness of the product in mm.

5. A product according to any of claims 1 to 4 wherein the thickness thereof is from 80 to 200 mm, or advantageously from 100 to 180 mm.

6. A structural member suitable for aircraft construction wherein said structural member is used in wing ribs, spars and frames, comprising a product according to any of claims 1 to 5.

7. A process for the manufacture of a rolled aluminum-based alloy product comprising the steps of:

a) casting an ingot comprising, (in weight-%)

Zn 6.85 - 7.25,
Mg 1.55 - 1.95,
Cu 1.90 - 2.30,
Zr 0.04 - 0.10,
Ti 0 - 0.15,
Fe 0 - 0.15,
Si 0 - 0.15,

other elements ≤ 0.05 each and ≤ 0.15 total, remainder Al;
b) homogenizing the ingot;
c) hot rolling said homogenized ingot to a rolled product with a final thickness of at least 80 mm ;
d) solution heat treating and quenching the product;
e) stress-relieving the solution heat treated and quenched product;
f) artificially aging the stress-relieved product;

wherein the hot rolling starting temperature is controlled to obtain after step f at mid-thickness more than 75 % of recrystallized grains or at mid-thickness 30 to 75 % of recrystallized grains and non-recrystallized grains with an aspect ratio in a L/ST cross section less than 3.

8. A process according to claim 7 wherein the hot rolling starting temperature is at least $145*Zr^{-0.313} - 20$ and preferably at least $145*Zr^{-0.313} - 10$.

9. A process according to claim 7 or claim 8 wherein the hot rolling starting temperature is at most $145*Zr^{-0.313} + 20$ and preferably at least $145*Zr^{-0.313} + 10$.

10. A process according to anyone of claims 7 to 9 wherein the equivalent aging time t(eq) is comprised between 8 and 30 hours and preferentially between 12 and 25 hours, the equivalent time t(eq) at 155°C being defined by the formula :

$$t(eq) = \frac{\int \exp(-16000 \ / \ T)\, dt}{\exp(-16000 \ / \ T_{ref})}$$

where T is the instantaneous temperature in °K during annealing and T_{ref} is a reference temperature selected at 155 °C (428 °K). t(eq) is expressed in hours.

11. A process according anyone of claims 7 to 10 wherein the solution heat treatment temperature is from 460 to about 510 °C or preferentially from about 470 to about 500 °C.

Figure 1

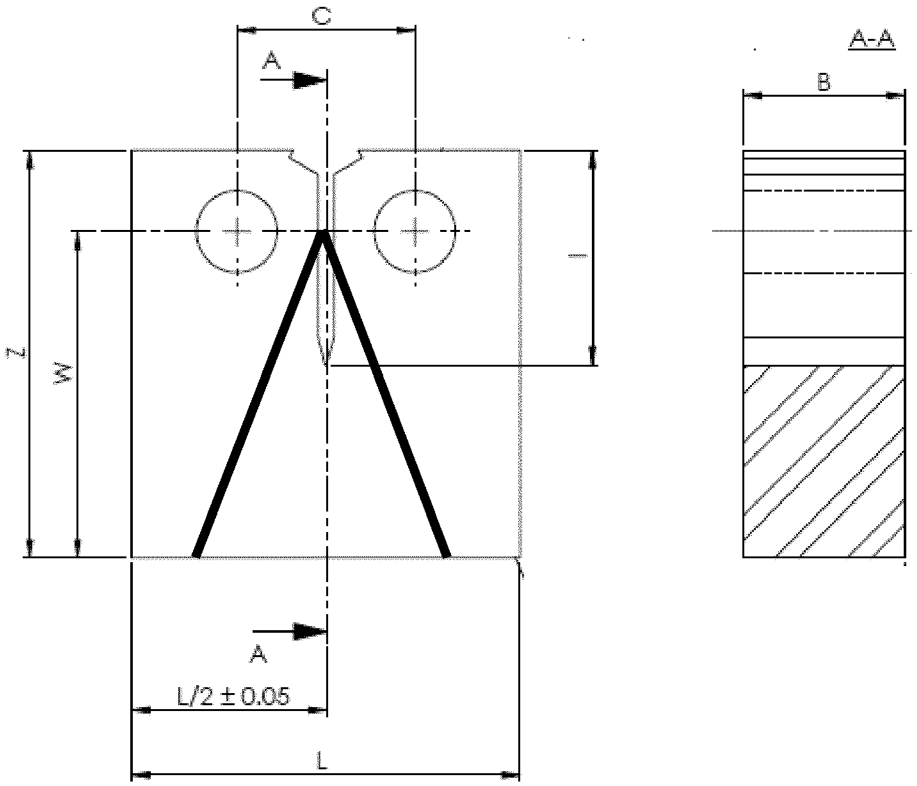


Figure 2a

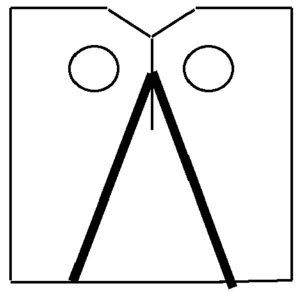


Figure 2b

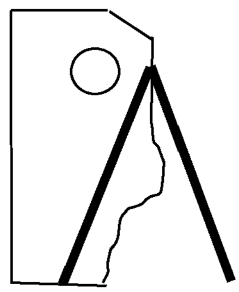


Figure 2c

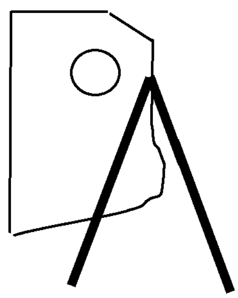


Figure 3

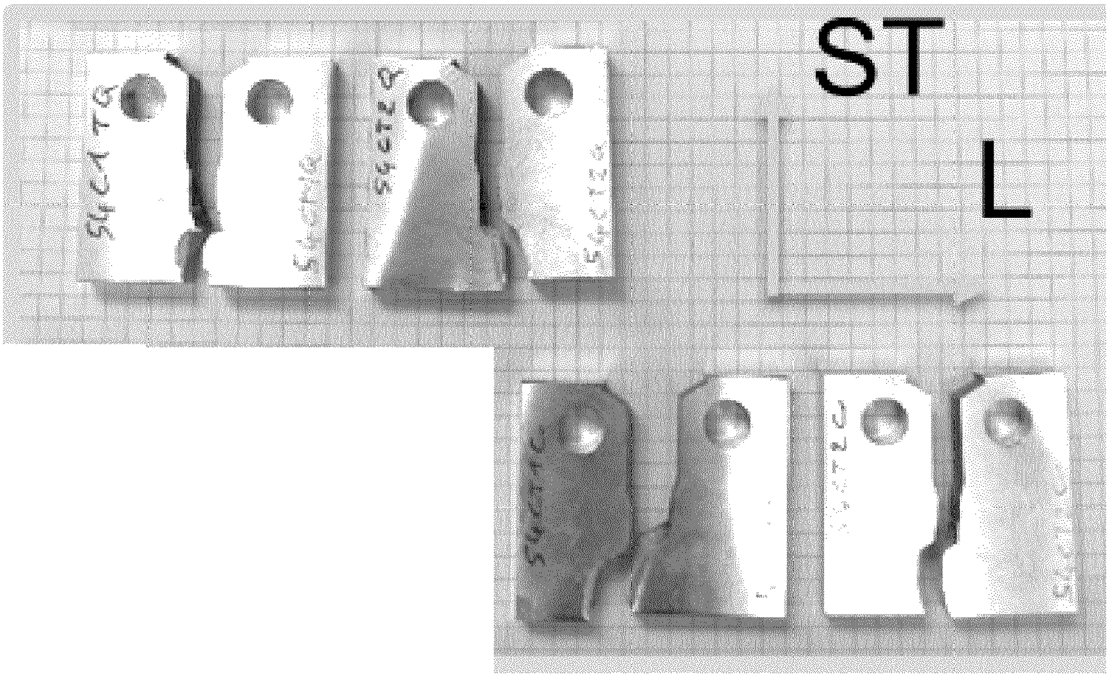
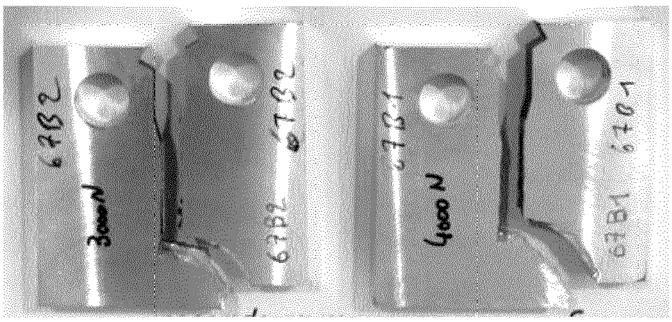


Figure 4



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EUROPEAN SEARCH REPORT

Application Number
EP 18 21 4960

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A	CONNOLY B J ET AL: "Environmentally assisted crack growth rates of high-strength aluminum alloys", JOM: JOURNAL OF METALS, SPRINGER NEW YORK LLC, UNITED STATES, vol. 55, 1 January 2003 (2003-01-01), pages 49-52, XP001249177, ISSN: 1047-4838, DOI: 10.1007/S11837-003-0195-7 * abstract; tables I,II * -----	1-11	INV. C22C21/10 C22F1/053
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A	US 5 865 911 A (MIYASATO SHELLY M [US] ET AL) 2 February 1999 (1999-02-02) * claim 1; example 1; table 2 * -----	1-11	
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			C22C C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	14 June 2019	González Junquera, J

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