METALLURGICAL PRODUCT AND STRUCTURE MEMBER FOR AIRCRAFT MADE OF AL-ZN-CU-MG ALLOY

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(57) ABSTRACT

The present invention relates to a work-hardened product, and particularly a rolled, extruded and/or forged product made of an alloy with composition (% by weight):

Zn 6.7-7.3% Cu 1.9-2.5% Mg 1.0-2.0%

other elements ≤0.05 each and ≤0.15 total, remainder aluminium and wherein Mg/Cu<1. The product is preferable treated by solution heat treatment, quenching, cold working and artificial aging. Cold working may be achieved by controlled tension and/or cold transformation, for example rolling or drawing. The product may be used, for example, as an aircraft structural member.
METALLURGICAL PRODUCT AND STRUCTURE MEMBER FOR AIRCRAFT MADE OF AL-ZN-CU-MG ALLOY

CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Ser. No. 60/529,594 filed Dec. 16, 2003, the content of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to rolled, extruded and/or forged products made of Al—Zn—Cu—Mg alloy treated by solution heat treatment, quenching, cold working and artificial aging, and particularly structural members made from such products and designed for use such as in aircraft construction.

2. Description of Related Art

It is generally known that when manufacturing semi-finished products and structural members for aeronautical construction, certain various required properties are difficult to optimize at the same time independently of each other. When the chemical composition of the alloy or the parameters of production processes are modified, several critical mechanical properties can tend to vary in opposite directions. This is sometimes the case with respect to properties collectively known in the art as “static mechanical strength” (particularly the ultimate tensile strength Rm (or UTS) and the tensile yield strength Rp0.2 (or TYS)). Other properties also at issue are commonly referred to under the term “damage tolerance” properties (particularly toughness and resistance to crack propagation). Some frequently employed properties such as fatigue strength, corrosion resistance, formability and elongation at failure are related to these mechanical properties (or “characteristics”) in a complicated and frequently unpredictable manner. Therefore, optimization of all properties of a material for aeronautical construction very frequently means making a compromise between several key parameters.

Typically, 7xxx type alloys are used for wing structural members (except for undersurface wing members).

U.S. Pat. No. 5,865,911 (Aluminum Company of America) discloses an Al—Zn—Cu—Mg type alloy with composition:

Zn 5.9-6.7, Mg 1.6-1.86, Cu 1.8-2.4, Zr 0.08-0.15

for making structural members for aircraft. These structural members are optimized to have high mechanical strength, toughness and fatigue strength.

Patent application WO 02/052053 describes three Al—Zn—Cu—Mg type alloys with composition (a) Zn 7.3+Cu 1.6, (b) Zn 6.7+Cu 1.9; (c) Zn 7.4 Cu 1.9; each of these three alloys also containing Mg 1.5+Zr 0.11. This WO publication also describes appropriate thermomechanical treatments for making structural members for aircraft.

Furthermore, a 7040 alloy with the following standardized chemical composition is known:

<table>
<thead>
<tr>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7-6.7</td>
<td>1.7-2.4</td>
<td>1.5-2.3</td>
<td>0.05-0.12</td>
</tr>
<tr>
<td>Si ≤ 0.10</td>
<td>Fe ≤ 0.13</td>
<td>Ti ≤ 0.06</td>
<td>Mn ≤ 0.04</td>
</tr>
</tbody>
</table>

other elements ≤ 0.05 each and ≤ 0.15 total.

A 7475 alloy with the following standardized chemical composition is also known:

<table>
<thead>
<tr>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2-6.2</td>
<td>1.9-2.6</td>
<td>1.2-2.9</td>
<td>0.18-0.25</td>
</tr>
<tr>
<td>Si ≤ 0.10</td>
<td>Fe ≤ 0.12</td>
<td>Ti ≤ 0.06</td>
<td>Mn ≤ 0.06</td>
</tr>
</tbody>
</table>

other elements ≤ 0.05 each and ≤ 0.15 total.

Alloys in the 2xxx series are routinely used, for example the 2324 alloy, for some structural members of civil aircraft wings such as under wing members.

Alloys conventionally used for fuselage structural members typically belong to the 2xxx series, for example the 2024 alloy.

SUMMARY OF THE INVENTION

A purpose of the present invention was to obtain aircraft structural members, and particularly fuselage members made of Al—Zn—Cu—Mg alloy, with a higher mechanical strength than is possible in prior alloys, with comparable damage tolerance and sufficient formability.

Another purpose was to obtain aircraft structural members, and particularly members for the under surface wings of aircraft, or for machining integral structures made of Al—Zn—Cu—Mg alloy, with a better compromise between mechanical strength, toughness and fatigue strength properties, than is possible to achieve with prior materials.

In accordance with these and other objects there is provided a work-hardened product, (preferably a rolled, extruded and/or forged product) of an alloy comprising (% by weight):

Zn 6.7-7.3% Cu 1.9-2.5% Mg 1.0-2.0%

Zr 0.04-0.15% Fe ≤ 0.15 Si ≤ 0.15

other elements ≤ 0.05 each and ≤ 0.15 total, the remainder being aluminium, wherein Mg/Cu<1. The product is preferably treated by solution heat treatment, quenching, cold working and artificial aging. Cold working may be achieved by controlled stretching and/or cold transformation, for example by rolling or drawing.

In further accordance with the present invention there is provided a structural member suitable for aeronautical construction, and particularly for an aircraft fuselage, or for members of the under surface of an aircraft wing, or an integral structural member for an aircraft, made from such a work hardened product, and particularly from such a rolled or extruded product.

Additional objects, features and advantages of the invention will be set forth in the description which follows,
and in part, will be obvious from the description, or may be learned by practice of the invention. The objects, features and advantages of the invention may be realized and obtained by means of the instrumentalities and combination particularly pointed out in the appended claims.

**DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT**

[0025] Unless mentioned otherwise, all information about the chemical composition of alloys is expressed in percent by mass. Consequently, in a mathematical expression “0.4 Zn” means 0.4 times the zinc content expressed in percent by mass; the same applies by analogy to other chemical elements. Alloys are named in accordance with the rules of The Aluminium Association, known to those skilled in the art. The metallurgical tempers are defined in European standard EN 515. The chemical composition of normalized aluminum alloys is defined for example in standard EN 573-3. Unless mentioned otherwise, static mechanical characteristics, in other words the ultimate tensile strength Rm, the tensile yield strength R0.2 and the elongation at fracture A, are determined by a tensile test according to standard EN 10002-1, the location at which the pieces are taken and their direction being defined in standard EN 485-1. The fatigue strength is determined by a test according to ASTM E 466, and the fatigue crack propagation rate (using the da/dn test) according to ASTM E 647. The R curve is determined according to ASTM standard 561. The critical strength intensity factor Kc, in other words the intensity factor that makes the crack unstable, is calculated starting from the R curve. The stress intensity factor Kc is also calculated by assigning the initial crack length to the critical load, at the beginning of the monotonic load. These two values are calculated for a test piece of the required shape. Kc denotes the Kc factor corresponding to the test piece that was used to make the R curve test. Unless otherwise mentioned, the crack size at the end of the fatigue precracking stage is W/4 for test pieces of the M(T) type, and W/2 for test pieces of the CT type, wherein W is the width of the test piece as defined in standard ASTM E561.

[0026] The term “extruded product” includes so-called “drawn” products, in other words, products produced by extrusion followed by drawing.

[0027] Unless mentioned otherwise, the definitions in European standard EN 12258-1 are applicable.

[0028] The term “structural member” in this specification refers to a mechanical part used in mechanical construction, for which failure could endanger the safety of the said construction and/or its users, or others. For an aircraft, these structure members include particularly members making up the fuselage (such as the fuselage skin, fuselage stiffeners or stringers, bulkheads, fuselage circumferential frames, wings (such as wing skin), stringers or stiffeners, ribs and spars and the tail fin composed particularly of horizontal and vertical stabilizers, and floor beams, seat tracks and doors.

[0029] For the purposes of this description, “integral structure” means the structure of part of an aircraft that was designed to achieve material continuity over the largest possible size in order to reduce the number of mechanical assembly points. An integral structure may be made either by in-depth machining, or by the use of shaped parts for example obtained by extrusion, forging or casting, or by welding of structural members made of weldable alloys. Thus, the result is large single-piece structure members, with no mechanical assembly or with a small number of mechanical assembly points compared with an assembled structure in which the thin or thick plates depending on the destination of the structure member (for example fuselage member or wing member) are fixed, usually by riveting, onto stiffeners and/or frames (that can be made by machining from extruded or rolled products).

[0030] The present invention can advantageously be applied to an aluminum alloy containing from about 6.7% to about 7.3% of zinc. The zinc content should preferably be high enough to achieve good mechanical properties, but if too high, the sensitivity of the alloy to quenching may increase, which in particular introduces a risk for thick products of degrading the compromise between target properties. In one advantageous embodiment of the instant invention, the product is a plate thinner than about 20 mm. In another advantageous embodiment of the invention, the product is a thick plate, thicker than about 20 mm.

[0031] The chemical composition of the Al—Zn—Cu—Mg alloy was chosen such that the Mg/Cu ratio of the alloy according to the invention is preferably below about 1. Preferably, this ratio is kept at a value less than 0.9. A value less than 0.85, or even about 0.8 is preferred.

[0032] An advantageous compromise was found when the copper content was kept at from about 1.9 to about 2.5%, and preferably from about 2.0 to about 2.3%, while the content of magnesium is fixed at from about 1 to about 2% and preferably from about 1.5 to about 1.8%.

[0033] The inventors have observed that a zirconium content from about 0.07 to about 0.13 made it possible to achieve a better compromise between Rpe, toughness (at ambient temperature or when cold) and fatigue strength (particularly the propagation rate of fatigue cracks), for this composition of major elements Al—Zn—Cu—Mg. If the content of Zr exceeds about 0.12%, there may be a significant risk of primary Al2Zr type phases being formed, unless cooling is fast enough; in the case of semi-continuous casting, such a sufficient rate can be achieved particularly when billets are being cast.

[0034] The Zr content for rolled products is preferably less than about 0.12%, and advantageous results have been obtained with a content of from about 0.07 to about 0.09%. A zirconium content of up to about 0.13% can be suitable for billets in some embodiments.

[0035] In all cases, silicon and iron contents should preferably each be kept below about 0.15% and particularly preferably below about 0.10% to have good toughness. In one particularly preferred embodiment of the present invention, the iron content preferably does not exceed about 0.07%, and the silicon content preferably does not exceed about 0.06%.

[0036] An alloy according to the instant invention can be cast according to one of the techniques known to those skilled in the art to obtain unwrought products such as an extrusion billet, or a rolling ingot. This unwrought product, possibly after scalping, is then homogenized, typically for a duration of 15 to 16 hours at a temperature of preferably from about 470 to about 485°C.
0037 The unwrought product is then transformed hot into extruded products (particularly bars, tubes or sections), hot rolled plates or forged parts. In one preferred embodiment of the invention, the inventors have discovered that surprisingly, thick products according to the invention could be hot rolled at a temperature of about 350°C, which is much lower than the temperature usually used for this type of product (which is about 415 to 440°C) without affecting the required compromise between properties for thick products used in aircraft structures.

0038 Hot transformation may possibly be followed by cold transformation. For example, extruded and drawn tubes can be manufactured. In the case of rolled products, one or several cold rolling passes may also be performed. This may be necessary if the desired final thickness is below about 3 mm.

0039 Products obtained are then preferably solution heat treated. This solution heat treatment may be made in any appropriate furnace such as an air furnace (horizontal or vertical) or a salt bath furnace. In one preferred embodiment of the invention leading to thick products (>10 mm), this solution heat treatment is carried out at a temperature from about 470 to 480°C and preferably from about 475 to about 480°C, preferably for at least 4 hours. In another preferred embodiment, leading to thin products (<10 mm), the solution heat treatment is carried out at preferably from about 470°C to about 475°C, and the duration of the solution heat treatment, for which the optimum value depends on the product thickness, is typically at least about one hour.

0040 The products are then quenched, preferably in a liquid medium such as water, the liquid preferably being at a temperature of not more than about 40°C.

0041 The products are then usually subjected to controlled stretching with a permanent set of the order of preferably from about 1 to 5%, and particularly preferably from about 1.5 to 3%.

0042 Finally, the products are subjected to an artificial aging treatment that has a large influence on the final properties of the product. Depending on the required compromise, a two-step artificial aging or a single step artificial aging may be preferred.

0043 Products according to the invention result in new products with particularly attractive characteristics for aeronautical construction. These products may be in any desired form such as in the form of sheet or plates, particularly fuselage sheet, thick plates for undersurface structural members or for integral structures, or in the form of extruded sections, or in the form of forged parts. Rolled products according to the present invention may be thick or thin and have a tensile yield strength $R_{p0.2, L}$ equal to at least about 500 MPa and preferably at least about 520 MPa and even at least about 530 MPa, for a $K_{app}(T)$ measured according to ASTM 561 on a (CT) type test piece with $W=127$ mm and thickness $B=5.5$ mm equal to at least 100 Mpa/v, or possibly even more than 110 Mpa/v.

0044 In one advantageous embodiment of the present invention, sheet and plate with a thickness from about 1 to about 10 mm has a $K_{app}(T)$ value, measured on a test piece with $W=760$ mm, of at least about 130 Mpa/v, and/or a $K_{app}(T)$ value, measured on a test piece with $W=760$ mm, of at least about 160 Mpa/v.

0045 In another advantageous embodiment of the invention, the thickness of the sheet or plates obtained is more than or equal to about 20 mm, and the sheet or plate has a yield strength $R_{p0.2, L}$ of at least about 520 MPa, a $K_{app}(T)$ measured according to ASTM E 561 on a (CT) type test piece with $W=406$ mm and thickness $B=6.35$ mm equal to at least about 130 Mpa/v, and $K_{app}(T)$ measured on a (CT) type test piece with $W=406$ mm and thickness $B=6.35$ mm equal to at least about 185 Mpa/v.

0046 Another important advantage of products according to the present invention is that surprisingly, the value of $K_{app}(T)$ as determined above is the same as or even higher when cold than its value at ambient temperature. More precisely, this value evaluated at $-54^\circ$C is slightly greater than its value at ambient temperature. This is particularly attractive, since $-54^\circ$C is approximately the typical temperature of structural members during the flight of a civil jet aircraft. It is known that the toughness decreases with the temperature in some alloys in the 7xxx series. For example, it has been described that the toughness of plates made of 7475 T7651 reduces by 25% (determined from R curves on panels with thickness B=6 mm in the L-T direction) between about 20°C and about $-50^\circ$C (see P. R. Abelski et al., Proceedings of “Fatigue at Low Temperatures”, Louisville, Ky., May 10, 1983, pages 257-273 (published by ASTM)). Under the same conditions, thick plates made of 7050 T7451 have a reduction in $K_C$ or $K_I$ in the L-T or T-L direction equal to at least 5% (see W. F. Brown et al., Aerospace Materials Handbook, published by CINDAS (USAF CRDA Handbook Operation, Purdue University, 1997)). The inventors have also observed a reduction in $K_C$ for thick plates made of 7075 T7351, 7475 T7351, 7475 T7651, and under-aged 7475; this reduction is of the order of 2% to 10%. Thus, if it is known that the static mechanical characteristics $R_{p0.2, L}$ and $R_{m}$ of alloys in the 7xxx series tend to increase when the temperature drops from about 20°C to about $-50^\circ$C, which improves safety for the structure at this temperature, the drop in toughness of alloys in the 7xxx series according to the state of the art has to be taken into account when sizing structural members. A product according to the instant invention does not have a significant reduction (in other words more than 2%) of the toughness at low temperature, and in some cases the toughness at low temperature is even slightly higher, i.e. up to about 2% higher or even up to about 5% higher.

0047 As structural members for wing lower structures of aircrafts, products according to the present invention advantageously replace structural members made of alloys known as 2x24 alloys, for example a 2024 or 2324 alloy. For example, rolled products according to the present invention may be thinner than about 10 mm and thus be used, for example, as a fuselage skin. They may also be thicker than about 10 mm and thus be used as structural members such as for lower wing structures. Rolled products more than about 40 mm thick may be used, for example, for the manufacture of structural members by integral machining as described below. Rolled products with a thickness of more than about 60 mm can be used, for example, for manufacturing stiffeners or frames, particularly for large capacity aircraft.

0048 Products according to the present invention may be clad on at least one face thereof if desired for any reason using methods and with alloys conventionally used to clad
products made of Al—Zn—Cu—Mg type alloys. This is particularly attractive for plates used for manufacturing aircraft fuselage members that have to resist corrosion. One exemplary cladding alloy that can be used is 7072.

One particularly advantageous use of products according to the instant invention is related to the concept of the integral structure in aeronautical construction. A large proportion of aircraft structures are sized as a function of a compromise between damage tolerance and resistance to static loads. Requirements for damage tolerance are, for example specified in the article “Damage Tolerance Certification of Commercial Aircraft” by T. Swift, ASM Handbook vol. 19 (1996), pp 566-576. Sizing under static loads is explained for example in the book “Airframe Stress Analysis and Sizing” by M. Niu, Hong Kong Committ Press Ltd, 1999, particularly pages 607 to 654. From the material point of view, it is known that the damage tolerance of alloys in the 7xxx series, and particularly their toughness, generally decreases when their yield strength increases. This phenomenon leads to specialization of alloys with high damage tolerance—particularly alloys in the 2xxx series—for parts with very high tension stresses, knowing that the tolerance certification requires the acceptance of the presence of cracks, and conversely alloys with a high yield strength—particularly alloys in the 7xxx series, for parts with very high compression stresses. In reality, parts with very high compression stresses such as wing upper surfaces and fuselage lower structures, are also subjected to tension loads, which although they are not as high, make it necessary for the material to have a certain damage tolerance. Conversely, parts such as wing undersurfaces and fuselage upper structures, in which tension stresses are very high, require a certain minimum compression strength. Thus, it frequently happens that damage tolerance is a controlling parameter for a part that is stressed essentially in compression, and vice versa. Thus for example, an increase in toughness of \( x \) % for a constant yield strength as with the alloy according to the present invention may result in a corresponding weight saving, or even better if the fact that allowing a high load on the part considered also makes it possible to reduce the weight of other components. Similarly, an increase in the yield strength equal to \( x \) %, for constant damage tolerance, can result in a weight saving of the order of \( x/5 \) to \( x \)%.

In an integral structure, continuity between the stiffeners and the skin means that damage tolerance becomes more critical than in a component assembled by riveting. At a given stress, the stress intensity factor increases strongly when a crack passes through the stiffener, since it must be assumed that this stiffener will be necessarily cracked. The present inventors have found that high toughness products, for a given yield strength, are particularly suitable for manufacturing of integral structures. In one particularly advantageous embodiment of this aspect of the present invention, fuselage lower structure panels and wing skins are made by integral machining of products according to one of the previous embodiments. Such products, and particularly thin plates, to be machined are advantageously at least 40 mm thick; this value also depends on the type of aircraft and particularly its size. According to the observations made by the inventors, a weight saving of the same order of magnitude as the improvement in toughness, namely about 10%, can be achieved compared with an integral structure made from a type AA7475 alloy according to the state of the art. More precisely, a product according to the invention, with a yield strength \( \sigma_{y,21/2} \), at mid-thickness equal to at least about 540 MPa and a toughness \( K_{IC,21/2} \), measured on an M(T) type specimen with a width \( W \) of 16 inches (about 406 mm) equal to at least about 140 MPa√m, can be used to make structural members for aircraft such as a wing skin member with a weight saving equal to at least 10% compared with the same part with the same shape and size made from a 7475 alloy according to the state of the art and typically having an \( \sigma_{y,21/2} \) at mid-thickness equal to 475 MPa, and an \( K_{IC,21/2} \) measured on an M(T) type specimen with a width \( W \) of 16 inches (about 406 mm) equal to 125 MPa√m.

The inventors have observed that refining the grain to a lower level than is accepted in normal practice during casting can give a particularly attractive compromise between properties, particularly for toughness. The use of a refining agent made of TiC (for example addition of an Al3% Ti0.15% C wire) in controlled doses is particularly beneficial, the solidification germ obtained with this approach having a different compromise between germination and growth than is possible with germs obtained for example by refining with Al15% Ti1% B (in other words a TiB type germ). The level of this refining may be quantified by the quantity of C added, since it indirectly corresponds to the quantity of added solidification germs and the quantity of free Ti (not combined with C) into the alloy. Although the stoichiometry of the germ is not definitively quantified, it can be considered that the germ comprises TiC, each C atom combining with a Ti atom to form the said germs.

There are different types of refining agents Al-x% Ti-y% C, in general excess Ti being added compared with C. The quantity of added germs is preferably proportional to the quantity of refining agent (in kilograms) added per ton of liquid metal multiplied by y/0.3, in other words proportional to A(number of kilograms of refining agent added per ton of metal) x y%.

Thus, for example, for the addition of 2 kg/t of Al3%-Ti0.15% C, the addition of germs can be quantified by specifying 3 g/t of added C (2x0.0015 kg/t).

There are other means of adding Al3%-Ti0.15% C to arrive at the addition of the same quantity of germs, for example by adding twice as much refining agent with half the concentration of C.

In one advantageous embodiment of this invention, a refining agent comprising titanium and carbon is also added such that the added carbon quantity is preferably between 0.43 and 3 g/t of carbon, more preferably between 0.6 and 2 g/t and such that the total content of Ti in the final product is between 50 and 500 ppm (by weight) and preferably between 150 and 300 ppm.

Other advantageous embodiments are described by the claims.

In the following example, advantageous embodiments of the invention are described for illustration purposes. These examples are in no way limiting.

**EXAMPLE 1**

An alloy N was made for which the chemical composition complies with the invention. The liquid metal
was treated firstly in a holding furnace by injecting gas using an IRMA® type of rotor, and then in an Alpur® type of ladle, these two trademarks belonging to the inventors. Refining was done in line, in other words in the channel between the holding furnace and the Alpur® ladle, with 1.1 kg/tonne of Al-3% Ti-0.15% C wire (9.5 mm diameter). An industrial sized rolling ingot was cast. It was relaxed for 10 h at 350°C.

[0059] The product thus cast was homogenised after scalping for 15 hours at a temperature between 471°C and 482°C (between 880°F and 900°F) and then hot rolled to a thickness of 5 mm (0.2 inches). The rolling start temperature was 450°C (840°F) and the rolling end temperature was 349°C (660°F). Plates with width 178 mm (7 inches) and length 508 mm (20 inches) were sampled. These coupons were solution heat treated in a salt bath furnace for 1 hour at 472°C and then quenched in water and tensioned to obtain a permanent deformation of 2%. The coupons thus obtained were then subjected to a two-step artificial aging treatment, the first step being 6 hours at 105°C, the second step being 18 hours at 155°C, in order to reach the peak of mechanical properties.

[0060] Using a similar process, sheet with a thickness of 6 mm and 3.2 mm in alloy Y was elaborated.

[0061] Plates made of 2xxx type alloys (references E and F outside the scope of the invention) were also produced according to the following process:

[0062] The alloy was cast firstly by treating the liquid metal in a holding furnace by injecting gas using an IRMA® type of rotor, and then in an Alpur® type of ladle. Refining was done in line, in other words in the channel between the holding furnace and the Alpur® ladle, with 0.7 kg/tonne of ATS5B wire (9.5 mm diameter). The cast rolling ingots were stress relieved for 10 hours at 350°C. These rolling ingots were then homogenised for 12 hours at 500°C, then hot rolled (end of rolling temperature between 230 and 255°C) to a thickness of 6 mm. A solution heat treatment was then carried out in a salt bath furnace for 1 hour at 500°C on the 600 mm by 200 mm coupons. This operation was followed by quenching in cold water at about 20°C and stretching with a permanent set of 2% (temper T351).

[0063] Rolling ingots made of a 7xxx alloy according to prior art were also cast (reference G), in the same foundry device as plates made with 2xxx alloy described above. The resulting rolling ingot was homogenised for 24 hours at 470°C and then 24 hours at 495°C, then hot rolled (end of rolling temperature between 230 and 255°C) to a thickness of 6 mm. A solution heat treatment of 1 hour was then carried out at 450°C in a salt bath furnace on a 600 mm by 200 mm coupon. This operation was followed by quenching in water and stretched with a permanent set of 2%. The coupon was then subjected to artificial aging treatment for 5 hours at 100°C, then 6 hours at 155°C, in order to achieve the peak mechanical properties (temper T6).

[0064] A rolling ingot made of an AA7475 alloy was also cast (reference H) according to conventional processes according to prior art. The rolling ingot thus obtained was homogenised for 9 hours at 480°C, and then hot co-rolled at a temperature of about 270°C with a 7072 cladding plate, until a sheet with a thickness of 4.5 mm was obtained. The 7072 cladding accounts for about 2% of the final thickness.

The product thus obtained was solution heat treated in a salt bath furnace for 45 minutes at 478°C, then quenched in water at a temperature of about 20°C, and then stretched with a permanent set of 2%. It was then subjected to a two-step artificial aging operation for 4 hours at 120°C, then 24 hours at 162°C. (temper T76).

[0065] The chemical compositions of the N, Y, E, F, G and H alloys measured on a spectrometry slug taken from the casting run, are given in table 1:

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Zr</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (invention)</td>
<td>0.05</td>
<td>0.06</td>
<td>2.05</td>
<td>—</td>
<td>1.64</td>
<td>7.08</td>
<td>0.08</td>
<td>—</td>
</tr>
<tr>
<td>Y (invention)</td>
<td>0.04</td>
<td>0.05</td>
<td>2.16</td>
<td>—</td>
<td>1.80</td>
<td>6.76</td>
<td>0.09</td>
<td>—</td>
</tr>
<tr>
<td>E (7024A)</td>
<td>0.06</td>
<td>0.06</td>
<td>4.12</td>
<td>0.4</td>
<td>3.37</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>G</td>
<td>0.05</td>
<td>0.08</td>
<td>1.47</td>
<td>—</td>
<td>1.56</td>
<td>4.27</td>
<td>0.11</td>
<td>—</td>
</tr>
<tr>
<td>H (7475)</td>
<td>0.03</td>
<td>0.06</td>
<td>1.5</td>
<td>—</td>
<td>2.22</td>
<td>5.73</td>
<td>—</td>
<td>0.21</td>
</tr>
<tr>
<td>Cladding (7072)</td>
<td>0.15</td>
<td>0.35</td>
<td>&lt;0.02</td>
<td>&lt;0.05</td>
<td>&lt;0.30</td>
<td>1.05</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

[0066] The ultimate tensile strength $R_m$ (in MPa), the tensile yield strength at 0.2% elongation $R_{y0.2}$ (in MPa) and the elongation at failure $\varepsilon$ (in %) were measured using a tensile test according to EN 10002-1.

[0067] The results of measurements of the static mechanical characteristics for temper T6 for plates N and Y according to the invention, and for temper T351 for plates E, F and G according to prior art, are shown in table 2:

<table>
<thead>
<tr>
<th>Static mechanical characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Plate</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>Y</td>
</tr>
<tr>
<td>E</td>
</tr>
<tr>
<td>G</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>

[0068] It can be seen that the ultimate tensile strength and tensile yield strength of the plate according to the invention in both measured directions is very much higher than the corresponding values for plates made of a 2xxx alloy. The elongation of the plate according to the invention is lower than that of plate E, but is sufficient for the target applications. Compared with 7xxx alloys according to prior art G and H, the alloy according to the invention has a significantly improved ultimate strength and yield strength for a comparable elongation.

[0069] Plates N, E, F, G and H were evaluated to determine the toughness measured by determination of the stress intensity factors $K_{IC}$ or $K_{IIC}$ according to standard ASTM 561; this determination was made in the TL direction, on C(T) test pieces with W=127 mm (5 inches) and B=5.5 mm.
The results are shown in Table 3 below.

<table>
<thead>
<tr>
<th>Measurements of $K_{app}$</th>
<th>$K_{app}$ [MPa m$^{1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (Invention)</td>
<td>107</td>
</tr>
<tr>
<td>E (2024 A)</td>
<td>105</td>
</tr>
<tr>
<td>G</td>
<td>97</td>
</tr>
<tr>
<td>H (7475 cladded)</td>
<td>87</td>
</tr>
</tbody>
</table>

Sheet Y in thickness 6 mm had a fracture toughness $K_{app}$ of 150 MPa m$^{1/2}$ (for $W=760$ mm) or 134 MPa m$^{1/2}$ (for $W=406$ mm) in the L-T direction, and of 128 MPa m$^{1/2}$ (for $W=760$ mm) or 110 MPa m$^{1/2}$ (for $W=406$ mm) in the T-L direction.

The value of $K_{app}$ for the plate according to the invention is much greater than the value for plates made of 7475 alloy according to prior art, and is of the same order of magnitude as for plates made of 2XXX alloy.

The fatigue behaviour was also tested according to ASTM standard E 647, measuring the crack propagation rate in plate N in comparison to plates E, F and G. The test pieces used were of the C(T) type, where $W$ is 76.2 mm (3 inches).

The crack propagation rate results $dA/dN$ for $AK$ equal to 10 MPa m$^{1/2}$, then 30 MPa m$^{1/2}$ were measured; the value of $dA$ for a propagation rate of 100 $\mu$m/ cycle (or 0.24 mm/cycle) was measured. The comparative results are given in Table 4. Sheet Y had a thickness of 6 mm.

The plate according to the invention behaves just as well in fatigue as plates according to prior art.

Another sheet Y with a thickness of 3.2 mm had the following properties: $dA/dN(10)$=1.71$10^{-4}$ mm/cycles, $dA/dN(30)$=30 $10^{-4}$ mm/cycles, $AH$ at 100 $\mu$m/cycle=28.3 MPa m$^{1/2}$.

Example 2

An alloy M with chemical composition complying with the invention was produced.

For comparison, a plate made of 2324 alloy according to prior art (reference 1) was produced according to a conventional casting process.

The chemical compositions of alloys M and I measured on a spectrometry slug taken from the casting runner, are given in the following table:

<table>
<thead>
<tr>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>M</td>
</tr>
<tr>
<td>I (AA2324)</td>
</tr>
</tbody>
</table>

After scalping, rolling ingots made of alloy M were homogenised for 15 hours at 749°C, and then slowly cooled to 420-440°C and rolled to a thickness of 25.4 mm. The outlet temperature from the hot rolling mill was 354°C, which is significantly lower than the value normally used for this type of product.

The plates thus obtained were then subjected to a solution heat treatment at 749°C for 4 hours (total time, about 1/3 of which is spent in the temperature increase), and were then quenched and tensioned such that the resulting permanent deformation is 2%. The plates were then subjected to an artificial aging treatment for 8 hours at 100°C.

The ultimate tensile strength $R_m$ (in MPa) the tensile yield strength at 0.2% elongation $R_p0.2$, (in MPa) and the elongation at fracture A (in %) were measured using a tensile test according to EN 10002-1 for the plate according to the invention, and for the plate according to prior art. The corresponding results are shown in Table 6 below.

Alloy I (AA2324) was subjected to a conventional procedure to obtain a plate made of AA2324 alloy, 25.4 mm thick in the T39 temper, in other words a homogenisation step followed by a hot rolling step, then solution heat treatment and quenching, followed by cold working of about 9%, and controlled stretch with a permanent set of between 1.5 and 3%.

It was observed that the ultimate strength and the yield strength of the plate according to the invention are significantly higher than the corresponding values of plate I usually used for these applications, and for quite comparable elongations.

The toughness was also evaluated for plates M and I, measured by determining the critical stress intensity factors $K_C$ and $K_{CO}$ or $K_{app}$ according to the ASTM standard 561; this determination was made at ambient temperature in the L-T direction on M(T) test pieces with $B=6.35$ mm (0.25 inches) and $W=406.4$ mm (16 inches), and on C(T) test pieces with $B=7.6$ mm (0.3 inches) and $W=127$ mm (5 inches). $K_{app}$ was also determined on a C(T) test piece with $B=7.6$ mm and $W=127$ mm in the L-T direction at a temperature of -54°C. The results are given in table 7 below.
It was found that the alloy according to the invention had better toughness than the conventional alloy I under all conditions. And also surprisingly, the alloy according to the invention had a value of $K_{\text{app(L-T)}}$ that was of the same order at $-54^\circ$ C. as it is at ambient temperature.

Plates M and I were also tested for fatigue strength along the L direction, using the following two protocols taken from ASTM standard E 466:

1) A notched test piece 5 mm thick, 38.1 mm wide and 254 mm long was used with two circular notches with radius 43.2 mm machined symmetrically about the centre of the test piece at a distance of 12.7 mm from the centre. The test is made according to ASTM standard E 466, by applying a cyclic stress such that the maximum stress is equal to 270 MPa and the minimum stress is equal to 27 MPa (R=0.1), at a frequency of 15 Hz.

2) A “double hole” test piece 2.54 mm thick, 25.4 mm wide and 209 mm long, was used, with two circular holes with diameter 4.8 mm located on the median line of the test piece, at equal distance from the centre of the test piece, and with centres at a spacing of 19 mm. The test is made according to ASTM standard E 466, by applying a cyclic stress such that the maximum stress is equal to 140 MPa, and the minimum stress is equal to 14 MPa (R=0.1), at a frequency of 15 Hz.

This test was carried out on five test pieces for each protocol, and the logarithmic average of 5 tests was calculated.

The results of these two test protocols on two plates M and I are given in Table 8 below:

Finally, the exfoliation corrosion behaviour of plates in this test was evaluated according to ASTM Standard G34; this test was done on the surface and at mid-thickness under conditions adapted to 7xxx alloys for plate M according to the invention, and under conditions adapted to 2xxx alloys for plate I. Sample M according to the invention was classified EA, both at the surface and at mid-thickness, while sample I according to prior art was classified EA at the surface and EB at mid-thickness. Therefore, the performance of the plate according to the invention in terms of exfoliation corrosion is at least as good, if not better, than the plate according to prior art.

It is observed that plate M is better for static mechanical characteristics, $K_{\text{app}}$, fatigue resistance and for the crack propagation rates.

EXAMPLE 3

An alloy P similar to alloy M in example 2 was produced. A manufacturing procedure similar to that for example 2 was used to make thick integrally hot rolled plates from this alloy (input temperature 420-440° C.), with a thickness of 75 mm.

After solution heat treatment and quenching as indicated in example 2, the plates were subjected to annealing processes with the following two steps:

First step: temperature increase at 30° C./hour up to 120° C. and hold for 6 hours at this temperature of 120° C.

Second step: temperature increase at 15° C./hour up to 160° C. and hold for 5 hours (process A), 10 hours (process B) or 15 hours (process C) at this temperature of 160° C.

The values of $K_{\text{app(L-T)}}$ were determined on type C(T) test pieces with W=127 mm and B=7.6 mm.
Table 10 summarises the main mechanical characteristics obtained:

<table>
<thead>
<tr>
<th>Process</th>
<th>$R_{p0.2\langle L\rangle}$ (MPa)</th>
<th>$R_{m\langle L\rangle}$ (MPa)</th>
<th>$A\langle L\rangle$ [%]</th>
<th>$K_{IC\langle C\langle T\rangle\rangle}$ (MPa√m)</th>
<th>$K_{app\langle C\langle T\rangle\rangle}$ (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>542</td>
<td>561</td>
<td>9.7</td>
<td>30.1</td>
<td>57.1</td>
</tr>
<tr>
<td>B</td>
<td>525</td>
<td>549</td>
<td>10.2</td>
<td>32.8</td>
<td>63.2</td>
</tr>
<tr>
<td>C</td>
<td>507</td>
<td>537</td>
<td>11.3</td>
<td>34.6</td>
<td>72.5</td>
</tr>
</tbody>
</table>

Additional advantages, features and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, and representative devices, shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

Units listed herein and in the following claims can be expanded to cover close values so long as one or more inventive concepts described herein are maintained.

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

As used herein and in the following claims, articles such as “the”, “a” and “an” can connote the singular or plural.

1. A work-hardened product comprising an alloy having a composition (% by weight):
   - Zn 6.7-7.3%
   - Cu 1.9-2.5%
   - Mg 1.0-2.0%
   - Zr 0.04-0.15%
   - Fe ≤0.15%
   - Si ≤0.15%
   - other elements ≤0.05 each and ≤0.15 total, remainder aluminium, wherein Mg/Cu<1.
   - said product being treated by solution heat treatment, quenching, cold working and artificial aging.

2. A product according to claim 1, wherein Zr ≤0.12%.

3. A product according to claim 1, wherein Zr content is from about 0.07 to about 0.09%.

4. A product according to claim 1, wherein the Cu content is from about 2.0 to about 2.3%.

5. A product according to claim 1, wherein the Mg content is from about 1.5 to about 1.8%.

6. A product according to claim 1, wherein Mg/Cu ≥0.80.

7. A product according to claim 1 having a thickness of at most about 20 mm, wherein
   - (a) $K_{IC\langle C\langle T\rangle\rangle}$ (measured at ambient temperature on a C(T) type test piece with W=127 mm and B=5.5 mm)>100 MPa√m
   - (b) $R_{p0.2\langle L\rangle}$>500 MPa

8. A product according to claim 1, wherein $R_{p0.2\langle L\rangle}$>500 MPa.

9. A product according to claim 1, wherein $R_{p0.2\langle L\rangle}$>460 MPa.

10. A plate with a thickness of at most about 20 mm comprising a product according to claim 2, having at least one selected from the group consisting of:
   - (a) $R_{m\langle L\rangle}$>520 MPa and $R_{p0.2\langle L\rangle}$>515 MPa
   - (b) $R_{p0.2\langle L\rangle}$>500 MPa and $R_{p0.2\langle L\rangle}$>480 MPa and (c) $R_{p0.2\langle L\rangle}$>500 MPa and $K_{app\langle C\langle T\rangle\rangle}$>100 MPa√m (measured at ambient temperature on a C(T) type test piece with W=127 mm and B=5.5 mm).

11. A plate according to claim 10, wherein da/dn in the T-L direction is at least about 28x10⁻⁴ mm/cycles, determined at $\Delta K$=30 MPa√m.

12. A sheet or plate with a thickness from about 1 to about 10 mm comprising a product according to claim 1, wherein $K_{IC\langle C\langle T\rangle\rangle}$ measured on a test piece with W=760 mm, is at least about 130 MPa√m, and/or wherein $K_{IC\langle C\langle T\rangle\rangle}$ measured on a test piece with W=760 mm, is at least about 160 MPa√m.

13. A plate according to claim 10, wherein said plate has been hot rolled only.

14. A plate with thickness of at least about 10 mm comprising a product according to claim 2, wherein said plate has been heat treated for at least 4 hours at a temperature of from about 470 to about 480°C.

15. A plate with thickness of at most about 10 mm comprising a product according to claim 2 wherein said plate has been solution heat treated for at least 1 hour at a temperature of from about 470 to about 480°C.

16. A plate with a thickness of at least about 20 mm comprising a product according to claim 2 having at least two characteristics selected from the group consisting of:
   - (a) $R_{m\langle L\rangle}$>540 MPa
   - (b) $R_{p0.2\langle L\rangle}$>535 MPa
   - (c) $K_{IC\langle C\langle T\rangle\rangle}$>100 MPa√m (measured at ambient temperature on a C(T) type test piece with W=127 mm and B=7.6 mm)
   - (d) $\Delta K$ at a crack propagation rate of 2.54 mm/cycle>28 MPa√m;
   - (e) $K_{IC\langle C\langle T\rangle\rangle}$>28 MPa√m.

17. A plate with a thickness of at least 20 mm comprising a product according to claim 2, having at least two characteristics selected from the group consisting of:
   - (a) yield strength $R_{p0.2\langle L\rangle}$ equal to at least 520 MPa;
   - (b) $K_{IC\langle C\langle T\rangle\rangle}$ (measured at ambient temperature according to ASTM 561 on a C(T) type test piece with W=406 mm and thickness B=6.35 mm) equal to at least 130 MPa√m;
   - (c) $K_{IC\langle C\langle T\rangle\rangle}$ (measured at ambient temperature on a C(T) type test piece with W=406 mm and thickness B=6.35 mm) equal to at least 185 MPa√m.

18. A plate comprising a product of claim 1 that is clad on at least one face thereof.

19. A product according to claim 1 wherein said product has been produced from a liquid metal to which a refining agent containing titanium and carbon has been added, such that the carbon quantity added to said liquid metal is from about 0.4 to about 3 g/t of carbon, and such that the total content of Ti in the product is from about 50 to about 500 ppm (by weight).

20. A structural member suitable for aircraft comprising at least one product according to claim 1.

21. An integral structure suitable for aircraft comprising at least one product according to claim 1.

22. A fuselage skin comprising a rolled product comprising a product according to claim 2 and having a thickness of at most about 10 mm.
23. A method for machining aircraft structural members comprising using a product according to claim 1 having a thickness of at least about 40 mm.

24. A method for making aircraft stiffeners or frames comprising using a product according to claim 1 with a thickness of at least about 60 mm.

25. A product wherein the value of $K_{app(LT)}$ measured according to ASTM 561 on a C(T) type test piece with $W=406$ mm and thickness $B=6.35$ mm when measured at $-54^\circ$ C. is not more than about 2% less than said value at ambient temperature.

26. A product of claim 25, wherein said value at $-54^\circ$ C is the same or slightly greater than said value at ambient temperature.

27. A product with a yield strength $R_{p0.2(LT)}$ at mid-thickness equal to at least about 540 MPa and a toughness $K_{app(LT)}$ measured on an $M(T)$ type specimen with a width $W$ of 16 inches (about 406 mm) equal to at least about 140 Mpa/$\text{m}^2$, said product comprising a structural member for aircraft and having a weight at least 10% less than a structural member with the same yield strength and toughness comprising a 7475 alloy.

28. A product of claim 27 wherein said product comprises an alloy having a composition (\% by weight) of:

\[
\begin{align*}
\text{Zn} & \quad 6.7-7.3\% \\
\text{Cu} & \quad 1.9-2.5\% \\
\text{Mg} & \quad 1.0-2.0\% \\
\text{Zr} & \quad 0.04-0.15\% \\
\text{Fe} & \quad \leq 0.15\% \\
\text{Si} & \quad \leq 0.15\%
\end{align*}
\]

other elements $\leq 0.05$ each and $\leq 0.15$ total, remainder aluminium, wherein $\text{Mg/Cu}<1$.

29. An integral structure comprising a plate according to claim 16.

30. An integral structure of claim 29 that is at least about 40 mm in thickness.

31. An integral structure comprising a plate according to claim 17.

32. An integral structure according to claim 31 that is at least about 40 mm in thickness.

33. A structural member comprising a product of claim 2.

34. A structural member of claim 33 that is at least about 10 mm in thickness.

35. A structural member comprising a product of claim 3.

36. A structural member of claim 35 that is at least about 10 mm in thickness.

37. A structural member comprising a plate according to claim 14.

* * * * *