(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 March 2009 (26.03.2009)

PCT

(10) International Publication Number
WO 2009/036953 A1

(51) International Patent Classification:
C22C 21/12 (2006.01) *C22C 21/18* (2006.01)
C22C 21/16 (2006.01) *C22F 1/057* (2006.01)

(21) International Application Number: PCT/EP2008/007731

(22) International Filing Date: 16 September 2008 (16.09.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
07018595.4 21 September 2007 (21.09.2007) EP

(71) Applicant *(for all designated States except US)*: **ALERIS ALUMINUM KOBLENZ GMBH** [DE/DE]; Carl-Spaeter-Str. 10, 56070 Koblenz (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **TELIOUI, Nadia** [NL/NL]; Evertsenstraat 10, NL-1970 CA Ijmuiden (NL). **NORMAN, Andrew** [GB/NL]; Dennenstraat 44, NL-1943 LS Beverwijk (NL). **BÜRGER, Achim** [DE/DE]; Jacques-Remy-Strasse 5, 56203 Höhr Grenzhausen (DE). **SPANGEL, Sabine, Maria** [DE/DE]; Rheinzollstrasse 12, 56068 Koblenz (DE).

(74) Agent: **MÜLLER SCHUPFNER & PARTNER**; Bavariaring 11, 80336 München (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

WO 2009/036953 A1

(54) **Title:** AL-CU-LI ALLOY PRODUCT SUITABLE FOR AEROSPACE APPLICATION

(57) **Abstract:** The present invention relates to an aluminium alloy product for structural members having a chemical composition comprising, in wt.%: Cu 3.4 to 5.0, Li 0.9 to 1.7, Mg about 0.2 to 0.8, Ag about 0.1 to 0.8, Mn about 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 about 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 and balance aluminium.

Al-Cu-Li ALLOY PRODUCT SUITABLE FOR AEROSPACE APPLICATION

FIELD OF THE INVENTION

The invention relates to an aluminium alloy, in particular an Al-Cu-Li type alloy product, more in particular an Al-Cu-Li-Mg-Ag-Mn alloy product, for structural members, the aluminium alloy product combining a high strength with high toughness. Products made from this aluminium alloy product are very suitable for aerospace applications, but not limited to that. The alloy can be processed to various product forms, e.g. sheet, thin plate, thick plate, extruded or forged products.

BACKGROUND TO THE INVENTION

As will be appreciated herein below, except as otherwise indicated, alloy designations and temper designations refer to the Aluminum Association designations in Aluminum Standards and Data and the Registration Records, as published by the Aluminum Association in 2007.

For any description of alloy compositions or preferred alloy compositions, all references to percentages are by weight percent unless otherwise indicated.

As used herein, the term "about" when used to describe a compositional range or amount of an alloying addition means that the actual amount of the alloying addition may vary from the nominal intended amount due to factors such as standard processing variations as understood by those skilled in the art.

The term "substantially free" means having no significant amount of that component purposely added to the alloy composition, it being understood that trace amounts of incidental elements and/or impurities may find their way into a desired end product.

It is generally well known in the aerospace industry that one of the most effective ways to reduce the weight of an aircraft is to reduce the density of aluminium alloys used in aircraft construction. This desire led to the addition of lithium, the lowest density metal element, to aluminium alloys. Aluminum Association alloys, such as AA2090 and AA2091 contain about 2.0 wt.% lithium, which translates into about a 7% weight savings over alloys containing no lithium. Aluminum alloys AA2094 and AA095 contain about 1.2 wt.% lithium. Another aluminium alloy, AA8090 contains about 2.5 wt.% lithium, which translates into an almost 10% weight savings over alloys without lithium.

However, casting of such conventional alloys containing relatively high amounts of lithium is difficult. Furthermore, the combined strength and fracture toughness of such alloys is not optimal. A trade-off exists with conventional aluminium-lithium alloys in which fracture toughness decreases with increasing strength. Another important characteristic of aerospace aluminium alloys is fatigue crack growth resistance. For example, in damage tolerant applications in aircraft, increased fatigue crack growth resistance is desirable. Better fatigue crack growth resistance means that cracks will grow slower, thus making airplanes much safer because small cracks can be detected before they achieve critical size for catastrophic propagation. Furthermore, slower crack growth can have an economic benefit due to the fact that longer inspection intervals can be utilized.

Some other prior art documents are:

US-2004/0071586 discloses a broad ranges for an aluminium alloy comprising, in wt.%, 3 to 5% of Cu, 0.5 to 2% of Mg, and 0.01 to 0.9% of Li. It is disclosed that the Li content should remain at a low level in combination with having controlled amounts of Cu and Mg to provide the desired levels of fracture toughness and strength. Preferably the Cu and Mg are present in the alloy in a total amount below a solubility limit of the alloy.

WO-2004/106570 discloses another Al-Cu-Li-Mg-Ag-Mn-Zr alloy for use as a structural member. The alloy comprises, in wt.%, 2.5 to 5.5% Cu, 0.1 to 2.5% Li, 0.2 to 1% Mg, 0.2 to 0.8% Ag, 0.2 to 0.8% Mn, and up to 0.3% Zr, balance aluminium.

US-2007/0181229 discloses an alumunium alloy comprising, in wt.%, 2.1 to 2.8% Cu, 1.1 to 1.7% Li, 0.1 to 0.8% Ag, 0.2 to 0.6% Mg, 0.2 to 0.6% Mn, a content of Fe and Si less or equal to 0.1% each, balance impurities and aluminium, and wherein the alloy is substantially zirconium free. The low Zr content is reported to increase the toughness.

A need therefore exists for an aluminium alloy that is useful in aircraft application which has high fracture toughness, high strength and excellent fatigue crack growth resistance.

DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide AlCuLi-type alloy product, ideally for structural members, having a balance of high strength and high toughness.

It is yet another object of the present invention to provide a method of manufacturing such an aluminium alloy product.

These and other objects and further advantages are met or exceeded by the present invention in which there is provided an aluminium alloy product for structural members having a chemical composition comprising, in wt.%: Cu 3.4 to 5.0, Li 0.9 to 1.7, Mg about 0.2 to 0.8, Ag about 0.1 to 0.8, Mn about 0.1 to 0.9, Zn maximum 1.5, one or more elements selected from the group consisting of: (Zr about 0.05 to 0.3, Cr about 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 and balance aluminium.

The alloy product can contain normal and/or inevitable elements and impurities, typically each <0.05% and the total <0.2%, and the balance is made by aluminium.

Optionally the alloy product may contain 0 to 1%, and preferably 0 to 0.1%, of a grain refiner elements selected from the group consisting of B, TiB_2, Ce, Nb, Er, and V.

Copper is one of the main alloying elements in the alloy products and is added to increase the strength of the alloy product. Care must be taken, however, to not add too much copper since the corrosion resistance can be reduced. Also, copper additions beyond maximum solubility will lead to low fracture toughness and low damage tolerance. A preferred upper-limit for the Cu-content is for that reason about 4.4%, and more preferably about 4.2%. A preferred lower-limit is about 3.6%, and more preferably about 3.75%, and most preferably about 3.9%.

Magnesium is another main alloying element in the alloy product and is added to increase strength and reduce density. Care should be taken, however, to not add too much magnesium in combination with copper since additions beyond maximum solubility will lead to low fracture toughness and low damage tolerance. A more preferred lower-limit for the Mg addition is 0.3%, and a more preferred upper-limit is 0.65%. It has been found that at a level of above about 0.8% the further addition of Mg may result in a decrease in toughness of the alloy product.

Lithium is another important alloying element in the product of this invention and to added together with the copper to obtain an improved combination of fracture toughness and strength. This means the present alloy either posses higher fracture toughness and equivalent or higher strength, or possess higher strength and equivalent or higher fracture toughness, in at least one temper in comparison with similar alloys having no lithium or greater amounts of lithium. A preferred lower-limit for the Li addition is 1.0%. A preferred upper-limit for the Li addition is about 1.4%, and more preferably 1.25%. A too high Li content has adverse effect on the damage tolerance properties of the alloy product in particular with the relatively high Cu levels in the alloy product of this invention.

The silver addition is to further increase strength and should not exceed about 0.8%, and a preferred lower limit is about 0.1%. A preferred range for the Ag addition is about 0.2 to 0.6%, and more preferably of about 0.25 to 0.50%.

The manganese addition is to control the grain structure by providing a more uniform distribution of the main precipitating phases and thereby further increases strength in particular. The Mn addition should not exceed about 0.9% and should be at least about 0.1%. A preferred lower-limit for the manganese addition is at least about 0.2%, and more preferably at least about 0.3%, and more preferably at least 0.35%. A preferred upper-limit for the Mn addition is about 0.7%.

In addition to aluminium, copper, magnesium, lithium, silver, manganese, and preferably also zinc, the alloy of the present invention contains at least one element selected from the group of Zr, Cr, Ti, Sc, Hf.

If added zirconium should be present in a range of 0.05 to 0.3%, and preferably in a range of 0.07 to 0.2%. A too low Zr addition has an adverse on the unit propagation energy of the alloy product.

The Cr addition can be made to increase in particular the unit propagation energy (UPE) of the alloy product. The UPE is typically measured in the Kahn-tear test and is the energy needed for crack growth. It is commonly believed that the higher the UPE, the more difficult to grow the crack, which is a desired feature of the material. The Cr addition should be in a range of 0.05 to 0.3%, and preferably in a range of 0.05 to 0.16%. The purposive addition of Cr to lithium containing aluminium alloy products has been reported previously as having adverse effect on engineering properties.

The effect of the Cr addition on the UPE is significantly enhanced with a combined addition of Cr and Ti. The Ti should be in a range of 0.05 to 0.3% also, and preferably in a range of 0.05 to 0.16%. The combined addition of Cr and Ti has also a positive effect of the intergranular corrosion resistance of the alloy product.

The scandium addition can be made to significantly increase in particular the unit propagation energy (UPE) of the alloy product. The Sc addition should be in a range of 0.05 to 0.4%, and preferably in a range of 0.05 to 0.25%.

The scandium can be replaced in part or in whole by the addition of hafnium. The Hf addition should be made in similar compositional ranges as the scandium.

In a preferred embodiment of the alloy product of this invention there are combined additions of at least Cr, Ti, and Sc.

And in a more preferred embodiment of the alloy product of this invention there is combined addition of Zr, Cr, Ti, and Sc.

The Si content in the alloy product should be less than 0.5% and can be present as a purposive alloying element. In another embodiment silicon is present as an impurity element and should be present at the lower-end of this range, e.g. less than about 0.10%, and more preferably less than 0.07%, to maintain fracture toughness properties at desired levels.

The Fe content in the alloy product should be less than 0.15%. When the alloy product is used for aerospace application the lower-end of this range is preferred, e.g. less than about 0.1%, and more preferably less than about 0.07% to maintain in particular the toughness at a sufficiently high level. Where the alloy product is used for commercial applications, such as tooling plate, a higher Fe content can be tolerated.

In a further embodiment of the alloy product the zinc is present as an impurity element which can be tolerated to a level of at most 0.1%, and preferably at most about 0.05%, e.g. at about 0.02% or less. Thus the alloy product may be substantially free from Zn.

In another preferred embodiment of the alloy product the zinc is purposively added to improve strength and it has a small effect on the damage tolerance properties of the alloy product. In this embodiment the zinc is typically present in a range of about 0.1 to 1.5%, and more preferably in a range of about 0.2 to 1.0%. As a particular example, zinc in an amount of about 0.5% is being added.

In the embodiment of the alloy product having the purposive addition of zinc also one or more alloying elements selected from the group consisting of (Zr, Cr, Ti, Sc, Hf) is added. In a more preferred embodiment only one of the elements of this group is being added, while still having a desirable balance in strength and toughness. For example the alloy product may contain Ti in a range of 0.03 to 0.3%, whereas it is substantially free from each of Zr, Cr, Sc, and Hf. In another example the alloy product may contain Zr in a range of 0.05 to 0.3%, preferably in a range of 0.05 to 0.25%, whereas it is further substantially free from each of Cr, Ti, Sc, and Hf. In yet another example the alloy product may contain Cr in a range of 0.05 to 0.3%, whereas it is further substantially free from each of Zr, Ti, Sc, and Hf.

In an embodiment of the alloy product the product is in the form of a rolled, extruded or forged product, and more preferably the product is in the form of a sheet, plate, forging or extrusion as part of an aircraft structural part. In a more preferred embodiment the alloy product is provided in the form of an extruded product.

When used as part of an aircraft structural part the part can be for example a fuselage sheet, upper wing plate, lower wing plate, thick plate for machined parts, forging or thin sheet for stringers.

Resistance to intergranular corrosion of the products of the present invention is generally high, for example, typically only pitting is detected when the metal is submitted to corrosion testing. However, the sheet and light gauge plate may also be clad, with preferred cladding thickness of from about 1% to about 8% of the thickness of the sheet or plate. The cladding is typically a low composition aluminium alloy.

In a further aspect of the invention it relates to a method of manufacturing a wrought aluminium alloy product of an Al-Cu-Li alloy, the method comprising the steps of:

a. casting stock of an ingot of an AlCuLi-alloy according to this invention,

b. preheating and/or homogenizing the cast stock;

c. hot working the stock by one or more methods selected from the group consisting of rolling, extrusion, and forging;

d. optionally cold working the hot worked stock;

e. solution heat treating ("SHT") of the hot worked and/or optionally cold worked stock, the SHT is carried out at a temperature and time sufficient to place into solid solution the soluble constituents in the aluminium alloy;

f. cooling the SHT stock, preferably by one of spray quenching or immersion quenching in water or other quenching media;

g. optionally stretching or compressing the cooled SHT stock or otherwise cold working the cooled SHT stock to relieve stresses, for example levelling or drawing or cold rolling of the cooled SHT stock; and

h. ageing, preferably artificial ageing, of the cooled and optionally stretched or compressed or otherwise cold worked SHT stock to achieve a desired temper.

The aluminium alloy can be provided as an ingot or slab or billet for fabrication into a suitable wrought product by casting techniques regular in the art for cast products, e.g. DC-casting, EMC-casting, EMS-casting. Slabs resulting from continuous casting, e.g. belt casters or roll casters, also may be used, which in particular may be advantageous when producing thinner gauge end products. Grain refiners such as those containing titanium and boron, or titanium and carbon, may also be used as is known in the art. After casting the alloy stock, the ingot is commonly scalped to remove segregation zones near the cast surface of the ingot.

Homogenisation treatment is typically carried out in one or multiple steps, each step having a temperature in the range of about 475°C to 535°C. The pre-heat temperature involves heating the hot working stock to the hot-working entry temperature, which is typically in a temperature range of about 440°C to 490°C.

Following the preheat and/or homogenisation practice the stock can be hot worked by one or more methods selected from the group consisting of rolling, extrusion, and forging, preferably using regular industry practice. The method of hot rolling is preferred for the present invention.

The hot working, and hot rolling in particular, may be performed to a final gauge, e.g. 3 mm or less or alternatively thick gauge products. Alternatively, the hot working step can be performed to provide stock at intermediate gauge, typical sheet or thin plate. Thereafter, this stock at intermediate gauge can be cold worked, e.g. by means of rolling, to a final gauge. Depending on the alloy composition and the amount of cold work an intermediate anneal may be used before or during the cold working operation.

Solution heat-treatment ("SHT") is typically carried out within the same temperature range as used for homogenisation, although the soaking times that are chosen can be somewhat shorter. A typical SHT is carried out at a temperature of 480°C to 525°C for 15 min to about 5 hours. Lower SHT temperatures generally favour high fracture toughness. Following the SHT the stock is rapidly cooled or quenched, preferably by one of spray quenching or immersion quenching in water or other quenching media.

The SHT and quenched stock may be further cold worked, for example, by stretching in the range of about 0.5 to 15% of its original length to relieve residual stresses therein and to improve the flatness of the product. Preferably the stretching is in the range of about 0.5 to 6%, more preferably of about 0.5 to 5%.

After cooling the stock is aged, typically at ambient temperatures, and/or alternatively the stock can be artificially aged.

The alloy product according to this invention is preferably provided in a slightly under-aged T8 condition to provide the best balance in strength and damage tolerance properties.

A desired structural shape is then machined from these heat treated plate sections, more often generally after artificial ageing, for example, an integral wing spar. SHT, quench, optional stress relief operations and artificial ageing are also followed in the manufacture of thick sections made by extrusion and/or forged processing steps.

In one embodiment of the present invention comprising a welding step, the ageing step can be divided into two steps: a pre-ageing step prior to a welding operation, and a final heat treatment to form a welded structural member.

The AlCuLi-alloy product according to this invention can be used amongst others as in the thickness range of at most 0.5 inch (12.5 mm) the properties will be excellent for fuselage sheet. In the thin plate thickness range of 0.7 to 3 inch (17.7 to 76 mm) the properties will be excellent for wing plate, e.g. lower wing plate. The thin plate thickness range can be used also for stringers or to form an integral wing panel and stringer for use in an aircraft wing structure. When processed to thicker gauges of more than 2.5 inch (63 mm) to about 11 inch (280 mm) excellent properties have been obtained for integral part machined from plates, or to form an integral spar for use in an aircraft wing structure, or in the form of a rib for use in an aircraft wing structure. The thicker gauge products can be used also as tooling plate, e.g. moulds for manufacturing formed plastic products, for example via die-casting or injection moulding. The alloy products according to the invention can also be provided in the form of a stepped extrusion or extruded spar or extruded stiffeners for use in an aircraft structure, or in the form of a forged spar for use in an aircraft wing structure.

When applied in the form of a sheet product the yield strength or proof strength of the product should be at least 460 MPa, and preferably at least 480 MPa. When applied in the form of an extruded product, e.g. as a stringer, or in the form of a plate product the yield strength or proof strength of the product should be at least 480 MPa, and more preferably at least 500 MPa. These strength levels can be obtained by a selecting the alloy composition within the claimed ranges, and preferably within the preferred narrower ranges, in combination with the artificial ageing practice.

In the following, the invention will be explained by the following non-limitative example.

Example.

On an laboratory scale eight aluminium alloys were cast to prove the principle of the current invention and processed into 2 mm sheet. The alloy compositions are in listed Table 1, and wherein alloy no. 2 is a comparative alloy due to a lower Li-content. For all ingots the balance were inevitable impurities and aluminium. Rolling blocks of approximately 80 by 80 by 100 mm (height x width x length) were sawn from round lab cast ingots of about 12kg. The ingots were homogenised at 520±5°C for about 24 hours and consequently slowly air cooled to mimic an industrial homogenisation process. The rolling ingots were pre-heated for about 4 hours at 450±5°C and hot rolled to a gauge of 8 mm and subsequently cold rolled to a final gauge of 2 mm. The hot-rolled product were solution heat treated (SHT) for 30 min at 520±5°C and quenched in water. The quenched products were cold stretched for about 1.5%. On the SHT and quenched sheet two ageing practices were carried out: (1) an under-aged condition by ageing for 20 hours at 170°C, and only for alloys 1, 7, and 8: (2) a peak-aged condition by ageing for 48 hours at 170°C.

Following the ageing the tensile properties have been determined according to EN10.002, and whereby "Rp" represents the yield strength in MPa, "Rm" represents the tensile strength in MPa and "Ag" the uniform elongation in % in the L- and LT-direction. For all alloys also the tear-strength have been determined according to ASTM B871-96, and the test direction of the results are for the T-L and L-T direction. The so-called notch-toughness can be obtained by dividing the tear-strength, obtained by the Kahn-tear test, by the tensile yield strength ("TS/Rp"). This typical result from the Kahn-tear test is known in the art to be a good indicator for true fracture toughness. The mechanical properties as tested are shown in Table 2 and 3. If the tensile strength is given in the L-direction then the corresponding direction for the notch-toughness is the L-T direction, and if the tensile strength is given in the LT-direction then the corresponding direction for the notch-toughness is the T-L direction.

Table 1. Chemical composition of the aluminium alloys tested. All alloying additions are by wt.%, the balance is made by unavoidable impurities and aluminium. For all alloys Fe 0.03%, Si 0.03%.

Alloy No.	Alloying element									
	Li	Cu	Mg	Ag	Mn	Zr	Cr	Ti	Sc	Zn
1	1.1	3.9	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
2	0.6	3.9	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
3	1.3	3.9	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
4	1.1	3.6	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
5	1.1	4.4	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
6	1.6	3.6	0.5	0.4	0.5	0.11	0.11	0.10	0.15	-
7	1.1	3.9	0.5	0.4	0.5	-	-	0.10	-	0.5
8	1.1	3.9	0.5	0.4	0.5	0.11	-	-	-	1.0

Table 2. Mechanical properties of the rolled alloy product after aging for 16 hours at 170°C.

Alloy No.	L-direction					LT-direction				
	Rp	Rm	Ag	TS	TS/ Rp	Rp	Rm	Ag	TS	TS/ Rp
1	502	536	6.1	654	1.30	442	509	6.8	580	1.31
2	346	443	9.3	668	1.93	362	449	8.4	611	1.69
3	527	565	5.6	598	1.13	471	542	5.6	454	0.96
4	479	518	7.0	678	1.42	414	482	8.5	621	1.50
5	508	549	6.5	578	1.14	477	541	7.7	505	1.06
6	456	516	6.8	565	1.24	-	-	-	-	-
7	574	611	5.5	571	0.99	542	600	5.9	479	0.88
8	570	606	5.4	483	0.85	514	550	3.4	451	0.88

Table 3. Mechanical properties of the rolled alloy products after aging for 24 hours at 170°C.

Alloy No.	L-direction					LT-direction				
	Rp	Rm	Ag	TS	TS/ Rp	Rp	Rm	Ag	TS	TS/ Rp
1	510	543	5.9	647	1.27	461	535	7.2	546	1.18
7	582	617	4.9	-	-	547	603	4.3	-	-
8	564	604	4.9	-	-	536	592	5.0	-	-

From the results of Table 2 it can ben seen from a comparison between Alloy no. 1 (according to the invention) and Alloy no. 2 (comparative) that lowering the Li-content has a significant adverse effect on the yield strength and the tensile strength. For that reason the lower-limit for the Li-content in the alloy product according to this invention is at least 0.9%, and more preferably at least 1.0%.

From a comparison between Alloy no. 1 and Alloy no. 3 it can be seen from Table 2 that raising the Li-content increases the strength levels, but has an adverse effect on the toughness of the alloy product. In order to obtain a good balance in strength and toughness in the alloy product according to this invention, the Li-content should not exceed 1.7%, and preferable not more than 1.4%, and more preferably should not exceed 1.25%.

From a comparison between Alloy no. 1 and Alloy no. 4 it can be seen from Table 2 that lowering the Cu-content has an adverse effect on the strength levels. For that reason the Cu-content in the alloy product according to this invention should not be less than 3.4%, and preferably not be less than 3.6% in order to maintain sufficient strength levels. Whereas from a comparison between Alloy No. 1 and Alloy no. 5 it can be seen that increasing the Cu-content results only in a small increase of the strength levels, but has a significant adverse effect on the toughness of the alloy product. In order to obtain a good balance in strength and toughness in the alloy product according to this invention, the Cu-content should preferably not exceed 4.4%, and more preferable should not exceed 4.2%.

From a comparison between Alloy no. 1 and Alloy no. 6 it can be seen that significantly increasing the Li content while reducing the Cu content results in a decrease in strength while significantly reducing the toughness in the alloy product according to this invention.

From a comparison between Alloy no. 1 and Alloy no. 7 it can be seen that adding only about 0.5% of zinc significantly increases the strength of the alloy product. This strength increase is obtained in this example even in the absense of the purposive combined addition of Zr, Cr, and Sc.

From a comparison between Alloy no. 7 and Alloy no. 8 it can be seen that increasing the Zn-content does not necessarily lead to a further increase of strength or toughness and may have an adverse effect on other enginnering properties. For that reason a preferred upper-limit of the Zn content is about 1.0%. The alloy products having a purposive addition of zinc represent a preferred embodiment of the alloy product according to this invention.

From the results in Table 2 for Alloy no. 7 and Alloy no. 8 it can be seen that high strength levels are obtained while purposively adding only one element selected from the group of (Zr, Cr, Ti, Sc, and Hf).

From the results of Table 2 and Table 3 it can be seen that depending on the artificial ageing practice a further increase in strength can be obtained.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the spirit or scope of the invention as herein described.

CLAIMS

1. An aluminium alloy product for structural members having a chemical composition comprising, in wt.%:

Cu	3.4 to 5.0
Li	0.9 to 1.7
Mg	0.2 to 0.8
Ag	0.1 to 0.8
Mn	0.1 to 0.9
Zn	max. 1.5,

one or more elements selected from the group consisting of:

Zr	0.05 to 0.3
Cr	0.05 to 0.3
Ti	0.03 to 0.3
Sc	0.05 to 0.4
Hf	0.05 to 0.4,

Fe	< 0.15
Si	< 0.5,

unavoidable impurities and balance aluminium.

2. An aluminium alloy product according to claim 1, wherein the Cu content is in a range of 3.6 to 4.4%, preferably in a range of 3.75 to 4.4%, and more preferably in a range of 3.75 to 4.2%.

3. An aluminium alloy product according to claim 1 or 2, wherein the Li content is in a range of 1.0 to 1.4%, and preferably in a range of 1.0 to 1.25%.

4. An aluminium alloy product according to any one of claims 1 to 3, wherein the product contains Zr in a range of 0.05 to 0.25%.

5. An aluminium alloy product according to any one of claims, 1 to 4, wherein the product comprises Zn in a range of 0.1 to 1.5%, and preferably in a range of 0.2 to 1.0%.

6. An aluminium alloy product according to any one of claims 1 to 5, wherein the product contains Ag in a range of 0.2 to 0.6%, and preferably of 0.25 to 0.50%.

7. An aluminium alloy product according to any one of claims 1 to 6, wherein the product contains Mn in a range of 0.2 to 0.7%.

8. An aluminium alloy product according to any one of claims 1 to 7, wherein the product is in the form of a rolled, extruded or forged product.

9. An aluminium alloy product according to claim 8, wherein the product is in the form of an extruded product.

10. An aluminium alloy product according to any one of claims 1 to 9, wherein the product is in the form of a sheet, plate, forging or extrusion as part of an aircraft structural part.

11. An aluminium alloy product according to any one claims 8 to 10, wherein said product has been treated with a hot deformation operation, a solution heat-treatment, quenching, and ageing.

12. An aluminium alloy product according to any one of claims 8 to 11, wherein said product has been treated with a solution heat-treatment, quenching and cold strain-hardening, and possesses a permanent deformation between 0.5 and 15%, and preferably between 0.5 and 5%.

13. Method of manufacturing an aluminium alloy product according to any of claims 1 to 12, comprising the steps of:
   a. casting stock of an ingot of an AlCuLi-alloy according to any one of claims 1 to 7,
   b. preheating and/or homogenizing the cast stock;
   c. hot working the stock by one or more methods selected from the group consisting of rolling, extrusion, and forging;
   d. optionally cold working the hot worked stock;
   e. solution heat treating (SHT) of the hot worked and/or optionally cold worked stock, the SHT is carried out at a temperature and time sufficient to place into solid solution the soluble constituents in the aluminium alloy;
   f. cooling the SHT stock;
   g. optionally stretching or compressing the cooled SHT stock or otherwise cold working the cooled SHT stock to relieve stresses, for example levelling or drawing or cold rolling of the cooled SHT stock; and

h. ageing, preferably artificial ageing, of the cooled and optionally stretched or compressed or otherwise cold worked SHT stock to achieve a desired temper.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/007731

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C21/12 C22C21/16 C22C21/18 C22F1/057

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/106570 A (PECHINEY ROLLED PRODUCTS [US]; CHO ALEX [US]) 9 December 2004 (2004-12-09) cited in the application page 6, line 13 - page 11, line 2; examples A1,A2; tables 1,3 claims	1-13
X	RU 2 237 098 C1 (AVIATION MATERIALS RES INST) 27 September 2004 (2004-09-27) page 5; example 3; table 1 -& DATABASE WPI Thomson Scientific, London, GB; AN 2004-755565 XP002461605 & RU 2 237 098 C (AVIATION MATERIALS RES INT) 27 September 2004 (2004-09-27) abstract	1-13

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 November 2008	12/11/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Patton, Guy

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 03 107440 A (SHOWA ALUMINUM CORP) 7 May 1991 (1991-05-07) abstract page 3; examples 1,3,4,6; table 1	1-13
X	WO 92/20830 A (REYNOLDS METALS CO [US]; MARTIN MARIETTA CORP [US]) 26 November 1992 (1992-11-26) page 9, line 21 - page 13, line 30 page 17, line 17 - page 21, line 23; example F; table I claims	1-13
X	US 5 389 165 A (CHO ALEX [US]) 14 February 1995 (1995-02-14) column 4, line 47 - column 5, line 48 column 6, line 44 - column 9, line 51; examples D,E,F; table I claims	1-13
X	US 5 211 910 A (PICKENS JOSEPH R [US] ET AL) 18 May 1993 (1993-05-18) column 10, line 34 - column 11, line 20; examples Broad,Pref.,MorePref.,MostPref.; table I column 12, line 4 - line 8 column 12, line 35 - column 13, line 55; examples I-V,VII-XI; table II column 15, line 61 - line 68 claims	1-13
X	US 2004/071586 A1 (RIOJA ROBERTO J [US] ET AL) 15 April 2004 (2004-04-15) cited in the application paragraph [0046] - paragraph [0050]; example 5; table 2 claims	1-13
A	US 5 393 357 A (CHO ALEX [US]) 28 February 1995 (1995-02-28) the whole document	1-13
A	WO 02/063059 A (MCCOOK METALS L L C [US]) 15 August 2002 (2002-08-15) the whole document	1-13
A	WO 89/01531 A (MARTIN MARIETTA CORP [US]) 23 February 1989 (1989-02-23) the whole document	1-13
A	US 2007/181229 A1 (BES BERNARD [FR] ET AL) 9 August 2007 (2007-08-09) cited in the application the whole document	1-13

International application No
PCT/EP2008/007731

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 2004106570	A	09-12-2004	DE	04753337	T1	08-11-2007
			EP	1641953	A1	05-04-2006
RU 2237098	C1	27-09-2004	NONE			
RU 2237098	C	27-09-2004	NONE			
JP 3107440	A	07-05-1991	NONE			
WO 9220830	A	26-11-1992	DE	69212602	D1	05-09-1996
			DE	69212602	T2	16-01-1997
			EP	0584271	A1	02-03-1994
			ES	2093837	T3	01-01-1997
			JP	6508401	T	22-09-1994
			JP	3314783	B2	12-08-2002
			KR	100245632	B1	02-03-2000
			RU	2109835	C1	27-04-1998
			US	5198045	A	30-03-1993
			US	5389165	A	14-02-1995
US 5389165	A	14-02-1995	DE	69212602	D1	05-09-1996
			DE	69212602	T2	16-01-1997
			EP	0584271	A1	02-03-1994
			ES	2093837	T3	01-01-1997
			JP	6508401	T	22-09-1994
			JP	3314783	B2	12-08-2002
			KR	100245632	B1	02-03-2000
			RU	2109835	C1	27-04-1998
			WO	9220830	A1	26-11-1992
			US	5198045	A	30-03-1993
US 5211910	A	18-05-1993	AU	7243491	A	21-08-1991
			CA	2071555	A1	27-07-1991
			DE	69117494	D1	04-04-1996
			DE	69117494	T2	11-07-1996
			EP	0512056	A1	11-11-1992
			ES	2084154	T3	01-05-1996
			IL	96809	A	29-06-1995
			JP	3197274	B2	13-08-2001
			JP	5503737	T	17-06-1993
			NO	922877	A	20-07-1992
			NZ	236886	A	28-04-1993
			PT	96582	A	15-10-1991
			WO	9111540	A1	08-08-1991
US 2004071586	A1	15-04-2004	NONE			
US 5393357	A	28-02-1995	CA	2145293	A1	14-04-1994
			DE	69330679	D1	04-10-2001
			DE	69330679	T2	27-06-2002
			EP	0665901	A1	09-08-1995
			ES	2161721	T3	16-12-2001
			WO	9408060	A1	14-04-1994
			US	5439536	A	08-08-1995
WO 02063059	A	15-08-2002	DE	01998021	T1	10-02-2005
			EP	1409759	A1	21-04-2004

International application No
PCT/EP2008/007731

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 8901531	A	23-02-1989	AU	615946	B2	17-10-1991
			AU	2314988	A	09-03-1989
			BR	8807653	A	12-06-1990
			CA	1335697	C	30-05-1995
			DE	3884957	D1	18-11-1993
			DE	3884957	T2	03-02-1994
			EP	0377640	A1	18-07-1990
			IL	87229	A	01-12-1992
			JP	2504531	T	20-12-1990
			JP	2892666	B2	17-05-1999
			NO	900587	A	07-02-1990
			NZ	225563	A	21-12-1990
US 2007181229	A1	09-08-2007	NONE			