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METHOD FOR PRODUCING SUCH AN
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WASHINGTON, DC 20036 (US)(21) Appl. No.: **10/819,130**(22) Filed: **Apr. 7, 2004****Related U.S. Application Data**(60) Provisional application No. 60/463,723, filed on Apr.
18, 2003.(30) **Foreign Application Priority Data**

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Publication Classification(51) **Int. Cl.⁷** **C22C 21/10**(52) **U.S. Cl.** **148/552**; 148/417; 420/532(57) **ABSTRACT**

The present invention relates to a high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness, the alloy including 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. The invention also relates to a method to produce these alloy products, and to some preferred applications thereof such as upper wing applications in aerospace.

HIGH STRENGTH AL-ZN ALLOY AND METHOD FOR PRODUCING SUCH AN ALLOY PRODUCT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This claims priority from U.S. provisional patent application Ser. No. 60/463,723 filed Apr. 18, 2003 and European patent application No. 03076049.0 filed Apr. 10, 2003, both incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a wrought high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness, a method for producing a wrought high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness and a plate product of such alloy, optionally produced in accordance with the method. More specifically, the present invention relates to a wrought high strength Al—Zn alloy designated by the 7000-series of the international nomenclature of the Aluminium Association for structural aeronautical applications. Even more specifically, the present invention relates to a new chemistry window for an Al—Zn alloy product having improved combinations of strength, toughness and corrosion resistance, which does not need specific ageing or temper treatments.

BACKGROUND OF THE INVENTION

[0003] It is known in the art to use heat treatable aluminium alloys in a number of applications involving relatively high strength, high toughness and corrosion resistance such as aircraft fuselages, vehicular members and other applications. Aluminium alloys AA7050 and AA7150 exhibit high strength in T6-type tempers, see e.g. U.S. Pat. No. 6,315,842. Also precipitation-hardened AA7x75, AA7x55 alloy products exhibit high strength values in the T6 temper. The T6 temper is known to enhance the strength of the alloy, wherein the aforementioned AA7x50, AA7x75 and AA7x55 alloy products which contain high amounts of zinc, copper and magnesium are known for their high strength-to-weight ratios and, therefore, find application in particular in the aircraft industry. However, these applications result in exposure to a wide variety of climatic conditions necessitating careful control of working and ageing conditions to provide adequate strength and resistance to corrosion, including both stress corrosion and exfoliation.

[0004] In order to enhance resistance against stress corrosion and exfoliation as well as fracture toughness it is known to artificially over-age these AA7000-series alloys. When artificially aged to a T79, T76, T74 or T73-type temper their resistance to stress corrosion, exfoliation corrosion and fracture toughness improve in the order stated (T73 being best and T79 being close to T6) but at cost to strength compared to the T6 temper condition. An acceptable temper condition is the T74-type temper which is a limited over-aged condition, between T73 and T76, in order to obtain an acceptable level of tensile strength, stress corrosion resistance, exfoliation corrosion resistance and fracture toughness. Such T74 temper is performed by over-ageing the aluminium alloy product at temperatures of 121° C. for 6 to 24 hours and 171° C. for about 14 hours.

[0005] Depending on the design criteria for a particular airplane component even small improvements in strength,

toughness or corrosion resistance result in weight savings, which translate to fuel economy over the life time of the aircraft. To meet these demands several other 7000-series type alloys have been developed:

[0006] EP-0377779 discloses an improved process for producing a 7055 alloy for sheet or thin plate applications in the field of aerospace such as upper-wing members with high toughness and good corrosion properties which comprises the steps of working a body having a composition consisting of, in wt. %:

[0007] Zn: 7.6-8.4

[0008] Cu: 2.2-2.6

[0009] Mg: 1.8-2.1,

[0010] one or more elements selected from

[0011] Zr: 0.5-0.2

[0012] Mn: 0.05-0.4

[0013] V: 0.03-0.2

[0014] Hf: 0.03-0.5,

[0015] the total of said elements not exceeding 0.6 wt. %, the balance aluminium plus incidental impurities, solution heat treating and quenching the product and artificially ageing the product by either heating the product three times in a row to one or more temperatures from 79° C. to 163° C. or heating such product first to one or more temperatures from 79° C. to 141° C. for two hours or more or heating the product to one or more temperatures from 148° C. to 174° C. These products show an improved exfoliation corrosion resistance of "EB" or better with about 15% greater yield strength than similar sized AA7x50 counterparts in the T76-temper condition. They still have at least about 5% greater strength than their similarly-sized 7x50-T77 counterpart (M7150-T77 will be used hereinbelow as a reference alloy).

[0016] U.S. Pat. No. 5,312,498 discloses another method for producing an aluminium-based alloy product having improved exfoliation resistance and fracture toughness with balanced zinc, copper and magnesium levels such that there is no excess of copper and magnesium. The method of producing the aluminium-based alloy product utilizes either a one- or two-step ageing process in conjunction with the stoichiometric balancing of copper, magnesium and zinc. A two-step ageing sequence is disclosed wherein the alloy is first aged at approx. 121° C. for about 9 hours followed by a second ageing step at about 157° C. for about 10 to 16 hours followed by air-cooling. Such ageing method is directed to thin plate or sheet products which are used for lower-wing skin applications or fuselage skin.

[0017] U.S. Pat. No. 4,954,188 discloses a method for providing a high strength aluminium alloy characterised by improved resistance to exfoliation using an alloy consisting of the following alloying elements, in wt. %:

[0018] Zn: 5.9-8.2

[0019] Cu: 1.5-3.0

[0020] Mg: 1.5-4.0

[0021] Cr: <0.04,

[0022] other elements such as zirconium, manganese, iron, silicon and titanium in total less than 0.5, the balance aluminium, working the alloy into a product of a pre-determined shape, solution heat treating the reshaped product, quenching, and ageing the heat treated and quenched product to a temperature of from 132° C. to 140° C. for a period of from 6 to 30 hours. The desired properties of having high strength, high toughness and high corrosion resistance were achieved in this alloy by lowering the ageing temperature rather than raising the temperature as taught previously from e.g. U.S. Pat. No. 3,881,966 or U.S. Pat. No. 3,794,531.

[0023] It has been reported that the known precipitation-hardened aluminium alloys AA7075 and other M7000-series alloys, in the T6 temper condition, have not given sufficient resistance to corrosion under certain conditions. The T7-type tempers which improve the resistance of the alloys to stress-corrosion cracking however decrease strength significantly vis-a-vis the T6 condition.

[0024] U.S. Pat. No. 5,221,377 therefore discloses an alloy product consisting essentially of about 7.6 to 8.4 wt. % Zn, about 1.8 to 2.2 wt. % Mg and about 2.0 to 2.6 wt. % Cu. Such alloy product exhibits a yield strength which is about 10% greater than its 7x50-T6 counterpart with good toughness and corrosion resistance. The yield strength was reported to be over 579 MPa with an exfoliation resistance (EXCO) level of "EC" or better.

[0025] U.S. Pat. No. 5,496,426 discloses an alloy as disclosed in U.S. Pat. No. 5,221,377 and a process including hot rolling, annealing and cold rolling within a preferred cold reduction range of 20% to 70% which, in turn, is preferably followed by controlled annealing thereby displaying characteristics which are better than AA7075-T6 characteristics. While the AA7075-T6 failed the stress corrosion resistance test (SCC resistance 40 days in the 35% NaCl alternate immersion test) at 138 MPa the disclosed processed alloy had a SCC resistance of 241 MPa.

[0026] U.S. Pat. No. 5,108,520 and U.S. Pat. No. 4,477,292 disclose an ageing process for solution-heat-treated, precipitation hardening metal alloy including three steps of ageing, comprising (1) ageing the alloy at one or more temperatures substantially above room temperature but below 163° C. to substantially below peak yield strength, (2) subsequently ageing the alloy at one or more temperatures at about 190° C. for increasing the resistance of the alloy to corrosion and thereafter, (3) ageing the alloy at one or more temperatures substantially above room temperature but below about 163° C. for increasing yield strength. The resultant product displayed good strength properties and a good corrosion performance. However, the three step ageing procedure is cumbersome and difficult to perform so that the costs for producing such alloy increase.

SUMMARY OF THE INVENTION

[0027] It is therefore the object of the present invention to provide an improved Al—Zn alloy preferably for plate products with high strength and an improved balance of toughness and corrosion performance. More specifically, it is the object of the present invention to provide an alloy which can be used for upper wing applications in aerospace with an improved compression yield strength with properties

which are better than the properties of a conventional AA7055-alloy in the T77 temper.

[0028] It is another object of the invention to obtain an AA7000-series aluminium alloy which exhibits strength in the range of T6-type tempers and toughness and corrosion resistance properties in the range of T73-type tempers.

[0029] It is furthermore an object of the present invention to provide an alloy that can be used in an age-creep forming process, which is an alloy which does not need a complicated or cumbersome ageing process.

[0030] The present invention has a number of preferred objects.

[0031] As will be appreciated herein below, except otherwise indicated, alloy designations and temper designations refer to the Aluminum Association designations in Aluminum Standards and Data and the Registration Records, all published by the US Aluminum Association. All percentages are in weight percents, unless otherwise indicated.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0032] The above mentioned objects of the invention are achieved by using a high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness, the alloy comprising essentially (in wt. %):

[0033] Zn about 6.0 to 9.5

[0034] Cu about 1.3 to 2.4

[0035] Mg about 1.5 to 2.6

[0036] Mn<0.12

[0037] Zr<0.20, and preferably 0.05-0.15

[0038] Cr<0.10

[0039] Fe<0.25, and preferably <0.12

[0040] Si<0.25, and preferably <0.12

[0041] Ti<0.10

[0042] Hf and/or V<0.25, and

[0043] optionally Ce and/or Sc<0.20, especially in a range of 0.05 to 0.15, other elements each less than 0.05 and less than 0.25 in total, balance aluminium, wherein (in weight percent):

[0044] $0.1[\text{Cu}] + 1.3 < [\text{Mg}] < 0.2[\text{Cu}] + 2.15$,

[0045] and preferably $0.2[\text{Cu}] + 1.3 < [\text{Mg}] < 0.1[\text{Cu}] + 2.15$.

[0046] Such chemistry window for an AA7000-series alloy exhibits excellent properties when produced to thin plate products which is preferably useable in aerospace upper-wing applications. In the present specification all percentages are weight percents unless otherwise indicated.

[0047] The above defined chemistry has properties which are comparable or better than existing alloys of the AA7x50 or AA7x55 series in the T77-temper, without using the above described cumbersome and complicated T77 ageing cycles. The chemistry leads to an aluminium product which is not only superior with regard to the question of costs but also simpler to produce since less processing steps are

necessary. Additionally, the chemistry allows new manufacturing techniques like age creep forming which is not feasible when a T77-temper alloy is applied. Even better, the chemistry as defined above can also be aged to the T77-temper wherein the corrosion resistance further improves as compared to the two-step ageing procedure which is described hereinbelow, wherein especially the exfoliation corrosion performance is enhanced.

[0048] By way of this invention it has been found that a selected range of elements, using a higher amount of Zn and a specific combination of a particular range of Mg and Cu, exhibit substantially better combinations of strength, toughness and corrosion performance such as exfoliation corrosion resistance and stress corrosion cracking resistance.

[0049] While it has been reported that copper contents should be maintained higher, preferably above about 2.2 wt. % in order to improve the exfoliation and stress corrosion cracking performance, better combinations of strength and density were reported to be achievable with relatively low zinc contents.

[0050] In this invention, however, it has been found that elevated amounts of zinc together with an optimised relation of magnesium to copper results in better strength while maintaining a good corrosion performance and a toughness which is better than conventional T77-temper alloys. It is therefore advantageous to have a combined zinc, magnesium and copper content in a range of between about 11.50 and 12.50 (in wt. %) without any manganese and below 11.00 in the presence of manganese which is preferably between 0.06 and 0.12 (in wt. %).

[0051] A preferred amount of magnesium is in a range of $0.2[\text{Cu}] + 1.3 < [\text{Mg}] < 0.1[\text{Cu}] + 2.15$, most preferably in a range of $0.2[\text{Cu}] + 1.4 < [\text{Mg}] < 0.1[\text{Cu}] + 1.9$. Copper is in a range of about 1.5 to 2.1, more preferably in a range of 1.5 to less than 2.0. The balance of magnesium and copper is important for the inventive chemistry.

[0052] Copper and magnesium are important elements for adding strength to the alloy. Too low amounts of magnesium and copper result in a decrease of strength while too high amounts of magnesium and copper result in a lower corrosion performance and problems with the weldability of the alloy product. Prior art techniques used special ageing procedures to ameliorate the strength and low amounts of magnesium and copper are used in order to achieve a good corrosion performance. In order to achieve a compromise in strength, toughness and corrosion performance copper and magnesium amounts (in wt. %) of between about 1.5 and 2.3 have been found to give a good balance for thick alloy products. However, the corrosion performance is the vital parameter for thin alloy products so that less amounts of copper and magnesium must be used, thereby resulting in a lower strength. Throughout the claimed chemistry of the present invention it is now possible to achieve strength levels in the region of a T6-temper alloy while maintaining corrosion performance characteristics similar to those of T74-temper alloys.

[0053] Apart from the amounts of magnesium and copper the invention discloses a balance of magnesium and copper amounts to zinc, especially the balance of magnesium to zinc, which gives the alloy these performance characteristics. The improved corrosion resistance of the alloy accord-

ing to the invention has exfoliation resistance properties ("EXCO") of EB or better, preferably EA or better.

[0054] These exfoliation properties are measured in accordance with the standards for resistance to stress corrosion cracking ("SCC") and exfoliation resistance ("EXCO") currently required for AA7075, AA7050 and AA7150-products aged to the T73, T74 and T76, along with typical performance of T6, tempers. To determine whether commercial alloys meet the SCC standards, a given test specimen is subjected to predefined test conditions. Bar-shaped specimens are exposed to cycles of immersing in a 3.5% NaCl aqueous solution for 10 minutes, followed by 50 minutes of air drying while being pulled from both ends under a constant strain (stress level). Such testing is usually carried out for a minimum of 20 days (or for less time should the specimen fail or crack before 20 days have passed). This test is the ASTM standard G47 (G47-98) test.

[0055] Another preferred SCC-test, conducted in accordance with ASTM standard G47, (G38-73) is used for extruded alloy products that include thin plate products. This test consists of compressing the opposite ends of a C-shaped ring using constant strain levels and alternate immersion conditions substantially similar to those as described above. While an M7075, M7050 or M7150-T6 tempered alloy fails the SCC test in less than 20 days and while the exfoliation properties are EC or ED, the corrosion resistance performance increases with tempers T76-, T74-, T73. The exfoliation properties of T73 are EA or better. Specific examples are described hereinbelow.

[0056] The inventive alloy has a chemistry with a preferred amount of magnesium and copper of about 1.93 when the amount (in wt. %) of zinc is about 8.1. However, the amount (in wt. %) of zinc is in a range of 6.1 to 8.3, more preferably in a range of 6.1 to 7.0 if manganese is lower than 0.05, and preferably lower than 0.02. Some preferred embodiments of the present invention are described within the examples hereinbelow.

[0057] The amount of manganese (in wt. %) is preferably in a range of about 0.06 to 0.12 when the amount of zinc is above 7.6. Manganese contributes to or aids in grain size control during operations that can cause the alloy microstructure to recrystallize. The preferred levels of manganese are lower than in conventional AA7000-series alloys but may be raised when zinc is raised.

[0058] The amount of the additional alloying elements Ce and/or Sc is smaller than 0.20, preferably in a range of 0.05 to 0.15, most preferably around 0.10.

[0059] A preferred method for producing a wrought high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness comprises the steps of

[0060] a) casting an ingot with the following composition (in weight percent):

[0061] Zn about 6.0 to 9.5

[0062] Cu about 1.3 to 2.4

[0063] Mg about 1.5 to 2.6

[0064] Mn < 0.12

[0065] Zr < 0.20, preferably 0.05-0.15

[0066] Cr<0.10

[0067] Fe<0.25

[0068] Si<0.25

[0069] Ti<0.10

[0070] Hf and/or V<0.25, optionally Ce and/or Sc<0.20, other elements each less than 0.05 and less than 0.25 in total, balance aluminium, and wherein (in weight percent):

[0071] $0.1[\text{Cu}] + 1.3 < [\text{Mg}] < 0.2[\text{Cu}] + 2.15$,

[0072] b) homogenising and/or pre-heating the ingot after casting,

[0073] c) hot working the ingot and optionally cold working into a worked product,

[0074] d) solution heat treating at a temperature and time sufficient to place into solid solution essentially all soluble constituents in the alloy, and

[0075] e) quenching the solution heat treated product by one of spray quenching or immersion quenching in water or other quenching media.

[0076] The properties of the invention may be further achieved throughout a preferred method which includes artificially ageing the worked and solution heat-treated product, wherein the ageing step comprises a first heat treatment at a temperature in a range of 105° C. to 135° C., preferably around 120° C. for 2 to 20 hours, preferably around 8 hours, and a second heat treatment at a higher temperature than 135° C. but below 210° C., preferably around 155° C. for 4 to 12 hours, preferably 8 to 10 hours.

[0077] Throughout such two-step aging treatment a corrosion performance is achieved which is similar to the corrosion performance of a T76-temper alloy. However, it is also possible to artificially ageing the worked and heat treated product wherein the ageing step comprises a third heat treatment at a temperature in a range of 105° C. to 135° C. for more than 20 hours and less than 30 hours. This T77-temper ageing procedure is known and even increases the performance characteristics as compared to the two-step ageing procedure. However, the two-step ageing procedure results in thin aluminium alloy products which are partially comparable and partially better than T77-temper products.

[0078] It is furthermore possible to artificially ageing the worked and heat treated product with a two-step ageing procedure to a T79- or T76-temper. After homogenizing and/or pre-heating the ingot after casting it is preferably advisable to hot working the ingot and optionally cold working the hot worked products into a worked product of 15 mm to 45 mm, thereby obtaining a thin plate.

[0079] Such plate product of high strength Al—Zn alloy may be obtained by an alloy having a composition as described above or being produced in accordance with a method as described above. Such plate product is preferably useable as thin aircraft member, more preferably as an elongated structural shape member. Even more preferred is a plate product for use as an upper-wing member, preferably a thin skin member of an upper-wing or of a stringer of an aircraft.

[0080] The foregoing and other features and advantages of the alloys according to the invention will become readily apparent from the following detailed description of preferred embodiments.

EXAMPLE 1

[0081] Tests were performed comparing the performance of the alloy according to the present invention and AA7150-T77 alloys. It has been found that the examples of the alloy of the present invention show an improvement over conventional AA7150-T77-temper alloys.

[0082] On an industrial scale four different aluminium alloys have been cast into ingots, homogenized, preheated for more than 6 hours at 410° C. and hot rolled to 30 mm plates. Thereafter, the plates were solution heat treated at 475° C. and water quenched. Thereafter, the quenched product was aged by a two-step T79-T76 ageing procedure. The chemical compositions are set out in Table 1.

TABLE 1

| Chemical composition of thin plate alloys, in wt. %, balance aluminium and inevitable impurities, Alloys 1 to 4 with Mn \leq 0.02: | | | | | | | | | |
|--|------|------|------|------|------|------|------|------|------|
| | Si | Fe | Cu | Mn | Mg | Cr | Zn | Ti | Zr |
| Alloy 1 (7050) | 0.03 | 0.06 | 2.23 | 0.00 | 2.08 | 0.00 | 6.24 | 0.03 | 0.10 |
| Alloy 2 | 0.05 | 0.08 | 2.05 | 0.01 | 2.04 | 0.01 | 6.18 | 0.04 | 0.11 |
| Alloy 3 | 0.05 | 0.09 | 2.20 | 0.01 | 2.30 | 0.01 | 7.03 | 0.04 | 0.10 |
| Alloy 4 | 0.04 | 0.07 | 1.91 | 0.02 | 2.13 | 0.00 | 6.94 | 0.03 | 0.11 |

[0083] The aged alloys were thereafter tested in accordance with the following test conditions:

[0084] Tensile yield strength was measured according to EN 10.002, exfoliation resistance properties ("EXCO") were measured according to ASTM G-34-97, stress corrosion cracking ("SCC") was measured according to ASTM G-47-98, all in ST-direction, Kahn-Tear (toughness) was measured according to ASTM E-399 and the compression yield strength ("CYS") was measured according to ASTM E-9.

[0085] The results of the T79-T76 aged plate products of the four alloys as shown in Table 1 are shown in Table 2a when compared with conventional M7150-T77 tempered alloys, and in Table 2b when compared with conventional M7150-T76/T74/T6 tempered alloys:

TABLE 2a

| Overview of strength and toughness of the alloys of Table 1 (30 mm plates) compared to three reference alloys (AA7150-T77); alloys 1 to 4 aged to T79-T76: | | | | |
|--|------------|--------------|------|-----------------------------|
| | Rp-L (MPa) | CYS-LT (MPa) | EXCO | K _{1C} -LT (MPa√m) |
| Alloy 1 | 555 | 565 | EC | 35.1 |
| Alloy 2 | 561 | 604 | EA/B | 34.5 |
| Alloy 3 | 565 | 590 | EB | 29.1 |
| Alloy 4 | 591 | 632 | EB | 28.9 |
| AA7150-T77 | 586 | — | EB | 28.6 |
| AA7150-T77 | 579 | — | EB | 29.2 |
| AA7150-T77 | 537 | — | EA | 33.2 |

F = no failure after 40 days.

[0086]

TABLE 2b

| Overview of corrosion performance of the alloys of Table 1 (30 mm plates) compared to three reference alloys (AA7150-T76, AA7150-T74, AA7150-T6); alloys 1-4 aged to T79-T76: | |
|--|---------------|
| | SCC threshold |
| Alloy 1 | NF at 172 MPa |
| Alloy 2 | NF at 240 MPa |
| Alloy 3 | NF at 240 MPa |
| Alloy 4 | NF at 240 MPa |
| AA7150-T76 | 117-172 MPa |
| AA7150-T74 | 240 MPa |
| AA7150-T6 | <48 MPa |

NF = no failure after 40 days.

[0087] As can be seen from Tables 2a, 2b alloys 1, 2 and 4 show better strength/toughness combinations. Alloys 2, 3 and 4 all have an acceptable EXCO performance wherein alloys 2, 3 and 4 have a significant higher compression yield strength than alloy No. 1 (M7050-alloy). Alloys 2 and 4 exhibit a property balance that makes them very suitable for upper-wing applications in aerospace thereby showing a balance of properties which is better than those of conventional 7150-T77 alloys. However, it is still possible to use a T77-temper for the inventive alloys as shown in Table 3.

TABLE 3

| Alloys 2 and 4 tempered according to T77 temper conditions, overview of strength, toughness and corrosion performance. | | | | | |
|---|---------------|-----------------|------|--------------------------------|---------------|
| | Rp-L (MPa) | CYS-LT (MPa) | EXCO | K _{IC} -LT (MPa√m) | SCC threshold |
| Alloy 2 | 585 | 613 | EA | 32.2 | NF at 240 MPa |
| Alloy 4 | 607 | 641 | EA | 26.4 | NF at 240 MPa |

[0088] Further SCC testing was performed on the promising alloy No. 4 wherein alloy 4-samples were prepared according to the procedure described in ASTM G-47-98 (standard test methods for determining susceptibility to stress corrosion cracking of AA7000-series aluminium alloy products) and exposed to the corrosive atmosphere according to ASTM G-44-94 (alternate immersion in accordance with the standard practice for evaluating stress corrosion cracking resistance of metals and alloys by alternate immersion in 3.5% NaCl solution).

[0089] Four different stress levels were chosen for samples of alloy 4 as shown in Table 4. For each stress level three samples were exposed to the test environment (ASTM G-44). One was taken out after 1 week while the other two were exposed for 40 days. When no cracking had occurred during the exposure the tensile properties were determined as shown in Table 4.

TABLE 4

| Overview of tensile strength properties of alloy 4 after exposure to four different stress levels, pre-stress was acting in LT direction. | | | |
|---|---------------------|---------------------------|---------|
| Alloy 4 | Pre-stress [MPa] | Tensile strength [MPa] | |
| | | 1 week | 40 days |
| | 300 | 524.3 | 428.0 |
| | 340 | 513.1 | 416.9 |
| | 380 | 503.1 | 424.5 |
| | 420 | 515.5 | 425.1 |

[0090] As can be seen from Table 4, no decrease in residual strength was measured with increasing load which means that no measurable stress corrosion appeared after 40 days as far as tensile strength properties are concerned.

EXAMPLE 2

[0091] When higher strength levels are required and toughness properties are less important conventional AA7055-T77 alloys are preferred instead of AA7150-T77 alloys as an alloy for upper wing applications. The present invention therefore disclosed optimised copper and magnesium windows which show properties equal or better than conventional AA7055-T77 alloys.

[0092] 11 different aluminum alloys were cast into ingots having the following chemical composition as set out in Table 5.

TABLE 5

| Chemical composition of 11 alloys, in wt. %, balance aluminium and inevitable impurities, Zr = 0.08, Si = 0.05, Fe = 0.08. | | | | |
|--|------|------|-----|------|
| Alloy | Cu | Mg | Zn | Mn |
| 1 | 2.40 | 2.20 | 8.2 | 0.00 |
| 2 | 1.94 | 2.33 | 8.2 | 0.00 |
| 3 | 1.26 | 2.32 | 8.1 | 0.00 |
| 4 | 2.36 | 1.94 | 8.1 | 0.00 |
| 5 | 1.94 | 1.92 | 8.1 | 0.00 |
| 6 | 1.30 | 2.09 | 8.2 | 0.00 |
| 7 | 1.92 | 1.54 | 8.1 | 0.00 |
| 8 | 1.27 | 1.57 | 8.1 | 0.00 |
| 9 | 2.34 | 2.25 | 8.1 | 0.07 |
| 10 | 2.38 | 2.09 | 8.1 | 0.00 |
| 11 | 2.35 | 1.53 | 8.2 | 0.00 |

[0093] Strength and toughness properties were measured after pre-heating the cast alloys for 6 hours at 410° C. and then hot rolling the alloys to a gauge of 28 mm. Thereafter, solution heat treating was applied at 475° C. and water quenching. Ageing was done for 8 hours at 120° C. and 8 to 10 hours at 155° C. (T79-T76-temper). The results are shown in Table 6.

TABLE 6

| Overview of strength and toughness of 11 alloys according to Table 5 in the identified directions. | | | | | |
|--|-----|-----|-----|-----|-------------|
| Alloy | Rp | | Rm | | Kq L - T |
| | L | LT | L | LT | |
| 1 | 628 | 596 | 651 | 633 | 28.9 |
| 2 | 614 | 561 | 642 | 604 | 29.3 |
| 3 | 566 | 544 | 596 | 582 | 39.0 |
| 4 | 614 | 568 | 638 | 604 | 33.0 |
| 5 | 595 | 556 | 620 | 590 | 37.1 |
| 6 | 562 | 513 | 590 | 552 | 38.6 |
| 7 | 549 | 509 | 573 | 542 | 41.7 |
| 8 | 530 | 484 | 556 | 522 | 41.9 |
| 9 | 628 | 584 | 644 | 618 | 26.6 |
| 10 | 614 | 575 | 631 | 606 | 28.1 |
| 11 | 568 | 529 | 594 | 568 | 36.6 |

[0094] While alloys 3 to 8 and 11 displayed good toughness properties alloys 1 to 5 and 9 and 10 displayed good strength properties. Hence, alloys 3, 4 and 5 show a good balance of strength and toughness so that it is clear to have a copper content of above 1.3 and a magnesium content of above 1.6 (in wt. %) when zinc is present in an amount of 8.1. Such amounts are lower limits for the copper and magnesium windows. As can be seen from Table 6 the toughness will drop to un-acceptable low-levels when copper and magnesium levels are too high (alloys 1, 2, 9 and 10).

EXAMPLE 3

[0095] The influence of manganese was investigated on the properties of the inventive alloy. An optimum manganese level was found between 0.05 and 0.12 in alloys with a high amount of zinc. The results are shown in Tables 7 and 8. All not mentioned chemistry properties and processing parameters are similar to those of Example 2.

TABLE 7

| Chemical composition of three alloys (Mn-0, Mn-1 and Mn-2), in wt. %, balance aluminium and inevitable impurities, Zr = 0.08, Si = 0.05, Fe = 0.08. | | | | |
|---|------|------|-----|------|
| Alloy | Cu | Mg | Zn | Mn |
| Mn-0 | 1.94 | 2.33 | 8.2 | 0.00 |
| Mn-1 | 1.94 | 2.27 | 8.1 | 0.06 |
| Mn-2 | 1.96 | 2.29 | 8.2 | 0.12 |

[0096]

TABLE 8

| Overview of strength and toughness of three alloys according to Table 7 in the identified directions. | | | | | |
|---|-----|-----|-----|-----|-------------|
| Alloy | Rp | | Rm | | Kq L - T |
| | L | LT | L | LT | |
| Mn-0 | 614 | 561 | 642 | 604 | 29.3 |
| Mn-1 | 612 | 562 | 635 | 602 | 31.9 |
| Mn-2 | 612 | 560 | 639 | 596 | 29.9 |

[0097] As shown in Table 8 the toughness properties decrease while strength properties increase. For alloys with high amounts of zinc an optimised manganese level is between 0.05 and 0.12.

EXAMPLE 4

[0098] When higher strength levels are required and toughness properties are less important conventional AA7055-T77 alloys are preferred instead of AA7150-T77 alloys as an alloy for upper wing applications. The present invention therefore discloses optimised copper and magnesium windows which show properties equal or better to conventional AA7055-T77 alloys.

[0099] Two different aluminium alloys were cast into ingots having the following cal composition as set out in Table 9.

TABLE 9

| Chemical composition of three alloys, in wt. %, balance aluminium and inevitable impurities, Zr = 0.08, Si = 0.05, Fe = 0.08; (Ref = AA7055 alloy). | | | | | | | | | |
|---|------|------|------|------|------|------|---------|------|------|
| Alloy | Si | Fe | Cu | Mn | Mg | Cr | Zn | Ti | Zr |
| 1 | 0.05 | 0.09 | 2.24 | 0.01 | 2.37 | 0.01 | 7.89 | 0.04 | 0.10 |
| 2 | 0.04 | 0.07 | 1.82 | 0.08 | 2.18 | 0.00 | 8.04 | 0.03 | 0.10 |
| Ref. | | | 2.1– | | 1.8– | | 7.6–8.4 | | |
| | | | 2.6 | | 2.2 | | | | |

[0100] Alloys 1 and 2 were tested with regard to their strength properties. These properties are shown in Table 10. Alloy 2 has been tempered in accordance with two temper conditions (T79-T76 and T77). Reference alloy AA7055 has been measured in T77 temper (M-Ref) while the technical data of an AA7055 reference alloy in a T77 temper are given as well (as identified by Ref).

TABLE 10

| Overview of strength of the two inventive alloys of Table 9, alloy No. 2 in two temper conditions, reference alloy (AA7055) measured (M-Ref) and tech sheet (Ref). | | | | | | | |
|--|---------|------|-------|-------|------|-------|-------|
| Alloy | Temper | Rp-L | Rp-LT | Rp-ST | Rm-L | Rm-LT | Rm-ST |
| 1 | T79-T76 | 604 | 593 | 559 | 634 | 631 | 613 |
| 2 | T79-T76 | 612 | 598 | 571 | 645 | 634 | 618 |
| 2 | T77 | 619 | 606 | 569 | 640 | 631 | 610 |
| Ref | T77 | 614 | 614 | — | 634 | 641 | — |
| M-Ref | T77 | 621 | 611 | 537 | 638 | 634 | 599 |

[0101] The toughness properties in LT and TL direction as well as the compression yield strength properties in L and LT direction as well as the corrosion performance characteristics are shown in Table 11.

TABLE 11

| Toughness and CYS properties of the two inventive alloys of Table 9 in different temper conditions and different test directions, NF = no failure after 40 days at designated stress levels, otherwise days are stated after which the specimen failed. | | | | | | | |
|--|---------|--------------------------|--------------------------|-------|--------|------|---------------|
| Alloy | Temper | K _{IC} (L-T) | K _{IC} (T-L) | CYS-L | CYS-LT | EXCO | SCC |
| 1 | T79-T76 | 21.0 | — | 596 | 621 | EC | 2, 3, 8 |
| 2 | T79-T76 | 28.9 | 27.1 | 630 | 660 | EB | NF at 172 MPa |
| 2 | T77 | 28.8 | 26.5 | 628 | 656 | EA | NF at 210 MPa |
| Ref | T77 | 28.6 | 26.4 | 621 | 648 | EB | NF at 103 MPa |
| M-Ref | T77 | — | — | — | — | EB | NF at 103 MPa |

[0102] The inventive alloy has similar tensile properties as a conventional AA7055-T77 alloy. However, the properties in the ST direction are better than those of the conventional AA7055-T77 alloy. Also the stress corrosion performance is better than of an AA055-T77 alloy. The inventive alloy can therefore be used as an inexpensive substitute for AA7055-T77 tempered alloys which is also useable for age-creep forming, thereby showing a superior compression yield strength and corrosion resistance.

[0103] 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. The present invention is defined by the claims appended hereto.

1. A wrought high strength Al—Zn alloy product with an improved combination of corrosion resistance and toughness, said alloy comprising essentially of (in weight percent):

Zn 6.0 to 9.5

Cu 1.3 to 2.4

Mg 1.5 to 2.6

Nm<0.12

Zr<0.20

Cr<0.10

Fe<0.25

Si<0.25

Ti<0.10

Hf and/or v<0.25, and

optionally ce and/or sc<0.20,

other elements each less than 0.05 and less than 0.25 in total, balance aluminium, and wherein (in weight percent):

0.1[Cu]+1.3<[Mg]<0.2[Cu]+2.15.

2. Alloy according to claim 1, wherein the amount (in weight %) of Mg is in a range of 0.2[Cu]+1.3<[Mg]<0.1[Cu]+2.15.

3. Alloy according to claim 1, wherein the amount (in weight %) of Mg is in a range of 0.2[Cu]+1.4<[Mg]<0.1[Cu]+1.9.

4. Alloy according to claim 1, wherein the alloy product has an exfoliation corrosion resistance (“EXCO”) of EB or better.

5. Alloy according to claim 1, wherein the alloy product has an exfoliation corrosion resistance (“EXCO”) of EA or better.

6. Alloy according to claim 1, wherein the amount (in weight %) of Cu is in a range of 1.5 to 2.1.

7. Alloy according to claim 1, wherein the amount (in weight %) of Cu is in a range of 1.5 to 2.0.

8. Alloy according to claim 1, wherein the amount (in weight %) of Zr is in a range of 0.05 to 0.15.

9. Alloy according to claim 1, wherein the amount (in weight %) of Mg and Cu is about 1.93 when the amount (in weight %) of Zn is about 8.1.

10. Alloy according to claim 1, wherein the amount (in weight %) of Zn is in a range of 6.1 to 8.3.

11. Alloy according to claim 1, wherein the amount (in weight %) of Zn is in a range of 6.1 to 8.3 and Mn is lower than 0.05.

12. Alloy according to claim 1, wherein the amount (in weight %) of Mn is in a range of 0.06 to 0.12 when the amount of Zn is above 7.6.

13. Alloy according to claim 1, wherein the amount (in weight %) of Fe is less than 0.12.

14. Alloy according to claim 1, wherein the amount (in weight %) of Si is less than 0.12.

15. Alloy according to claim 1, wherein the alloy has been artificially aged to a T79 or T76 temper in a two-step ageing procedure.

16. Alloy according to claim 15, wherein the two-step ageing procedure consists of a first heat treatment at a temperature in a range of 105° C. to 135° C. for 2 to 20 hours, and a second heat treatment at a higher temperature than 135° C. but below 210C for 4 to 12 hours.

17. Alloy according to claim 1, wherein the product is a plate product.

18. Alloy according to claim 1, wherein the product is a plate product having a thickness is a range of 15 to 45 mm.

19. Alloy according to claim 18, wherein the plate product is a thin aircraft member.

20. Alloy according to claim 18, wherein the plate product is an elongate structural shape member of an aircraft.

21. Alloy according to claim 18, wherein the plate product is an upper-wing member of an aircraft.

22. Alloy according to claim 18, wherein the plate product is a thin skin member of an upper-wing of an aircraft.

23. Alloy according to claim 18, wherein the plate product is stringer of an aircraft.

24. Alloy according to claim 18, wherein the plate product is stringer of an upper-wing of an aircraft.

25. Method for producing a wrought high-strength Al—Zn alloy product according to claim 1 with an improved combination of corrosion resistance and toughness, comprising the steps of:

a) casting an ingot with the following composition (in weight percent):

Zn 6.0 to 9.5

Cu 1.3 to 2.4

Mg 1.5 to 2.6

Mn<0.12

Zr<0.20

Cr<0.10

Fe<0.25

Si<0.25

Ti<0.10

Hf and/or V<0.25, optionally Ce and/or Sc<0.20,

other elements each less than 0.05 and less than 0.50 in total, balance aluminium, wherein (in weight percent):

$0.1[\text{Cu}] + 1.3 < [\text{Mg}] < 0.2[\text{Cu}] + 2.15$,

b) homogenising and/or pre-heating the ingot after casting,

c) hot working the ingot and optionally cold working into a worked product,

d) solution heat treating and

e) quenching the solution heat treated product.

25. Method according to claim 24, wherein the worked and solution heat-treated product is artificially aged, and wherein the ageing step comprises a first heat treatment at a temperature in a range of 105° C. to 135° C. for 2 to 20 hours, and a second heat treatment at a higher temperature than 135° C. but below 210° C. for 4 to 12 hours.

26. Method according to claim 25, wherein the worked and solution heat-treated product is artificially aged, and wherein the ageing step comprises a third heat treatment at a temperature in a range of 105° C. to 135° C. for more than 20 hours and less than 30 hours.

27. Method according to claim 25, wherein the worked and solution heat-treated product is artificially aged, and

wherein the ageing step consists of a first heat treatment at a temperature in a range of 105° C. to 135° C. for 2 to 20 hours, and a second heat treatment at a higher temperature than 135° C. but below 210° C. for 4 to 12 hours.

28. Method according to claim 24, characterized by artificially ageing the worked and solution heat-treated product with a two-step ageing procedure to a T79 or T76 temper.

29. Method according to claim 24, wherein after homogenising and/or pre-heating the ingot after casting, hot working the ingot and optionally cold working into a worked product having a thickness in the range of 15 mm to 45 mm.

30. Method according to claim 29, wherein the plate product is a thin aircraft member.

31. Method according to claim 29, wherein the plate product is an elongate structural shape member of an aircraft.

32. Method according to claim 29, wherein the plate product is an upper-wing member of an aircraft.

33. Method according to claim 29, wherein the plate product is a thin skin member of an upper-wing of an aircraft.

34. Method according to claim 29, wherein the plate product is stringer of an aircraft.

35. Method according to claim 29, wherein the plate product is stringer of an upper-wing of an aircraft.

36. Alloy according to claim 1, wherein the amount (in weight %) of Zn is in a range of 6.1 to 8.3 and Mn is lower than 0.02.

37. Alloy according to claim 1, wherein the amount (in weight %) of Zn is in a range of 6.1 to 7.0 and Mn is lower than 0.05.

38. Alloy according to claim 1, wherein the amount (in weight %) of Zn is in a range of 6.1 to 7.0 and Mn is lower than 0.02.

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