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(54) A LOW COST, LOW DENSITY, SUBSTANTIALLY AG-FREE AND ZN-FREE ALUMINUM-LITHIUM PLATE ALLOY FOR AEROSPACE APPLICATION

(57) The present invention is directed to aluminum-lithium alloys, specifically aluminum - copper - lithium - magnesium - manganese alloys. The aluminum-lithium alloy of the present invention comprises from 3.6 to 4.1 wt. % Cu, 0.8 to 1.05 wt. % Li, 0.6 to 1.0 wt. % Mg, 0.2 to 0.6 wt. % Mn, up to 0.12 wt. % Si, up to 0.15 wt. % Fe, from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements, up to 0.10 wt. % Ti, up to 0.15 wt. % incidental elements

with the total of incidental elements not exceeding 0.35 wt. %, and the balance being aluminum. Preferably, Ag is not intentionally added and should not be more than 0.05 wt. % as a non-intentionally added element. Preferably, Zn is not intentionally added and should not be more than 0.2 wt. % as a non-intentionally added element. The amount of Cu in weight percent is at least equal to or higher than four times the amount of Li in weight percent.

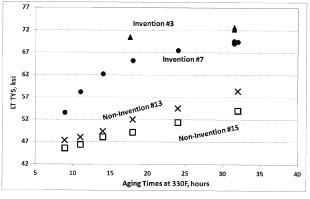


FIG. 1

Description

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BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention generally relates to Aluminum-Copper-Lithium-Magnesium based alloy products.

2. Description of Related Art

[0002] In order to reduce aircraft weight for better fuel efficiency, low density aluminum-lithium alloys are being aggressively pursued by airframe and aluminum material manufacturers. Beside density, the material strength, fracture toughness, fatigue resistance, and corrosion resistance are required simultaneously for aerospace applications. In addition, the cost of material has to be considered for the sustainable solution of aluminum lithium products.

[0003] Therefore, it is an extreme challenge to produce aluminum-lithium (Al-Li) plate products that meet all above requirements. As a consequence, there are only limited registered Al-Li alloys capable of producing higher than 0.5" thickness plate products. The examples of existing alloys are 2050 (up to 6.5" thickness), 2195 (up to 2.25" thickness), 2060 (up to 1.5" thickness) and 2196 (up to 1.0" thickness) based on "Registration Record Series - Tempers for Aluminum Alloys Production" published in 2011 and "Addendum to 2011 Tan Sheets of Registration Record Series - Tempers for Aluminum and Aluminum Alloys Production" published in 2017 by The Aluminum Association. It should be mentioned that all above Al-Li plate alloys are high cost Ag containing alloys. Silver (Ag) is added to many new generation Al-Li alloys in order to improve the final product properties.

[0004] In addition, the popularity of using high cost Ag in Al-Li alloys can be demonstrated by a significant amount of Al-Li alloy patents and patent applications. Thus, it is a significant challenge to provide a low cost Al-Li sheet via eliminating Ag addition while simultaneously maintaining the product performance that Ag provides as demonstrated by these prior art examples.

[0005] Obviously, the Li is the most critical element for Al-Li alloys. Too low of a level of Li cannot reduce the density and improve the properties enough. However, too high of a level of Li can cause undesirable performance such as low short transverse fracture toughness, and high anisotropy of tensile properties.

[0006] The Cu is another important element and has to be controlled within a certain range for desirable product performance.

[0007] The Mg is another element to be added in a certain range in order to primarily enhance the strength and secondarily reduce the density.

[0008] The Zn is also another element to be considered for Al-Li alloy. However, the addition of Zn can also negatively impact the density.

[0009] In general, prior Al-Li alloy compositions didn't succeed to simultaneously achieve low density, low cost, high strength, good damage tolerance, fatigue resistance, and corrosion properties for Al-Li alloys capable of producing plate products. To achieve all of these is an extreme metallurgical challenge, especially without the use of Ag addition which significantly increase the product cost.

BRIEF SUMMARY OF THE INVENTION

[0010] The present invention provides a low cost, high performance, high Mg, substantially Ag-free and Zn-free, low density Al-Li alloy suitable for making transportation components, such as aerospace structural components. Aluminum-lithium alloys of the present invention comprise from 3.6 to 4.1 wt. % Cu, 0.8 to 1.05 wt. % Li, 0.6 to 1.0 wt. % Mg, 0.2 to 0.6 wt. % Mn, up to 0.12 wt. % Si, up to 0.15 wt. % Fe, from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements, up to 0.10 wt. % Ti, up to 0.15 wt. % incidental elements with the total of incidental elements not exceeding 0.35 wt. %, and the balance being aluminum. Preferably, Ag is not intentionally added and should not be more than 0.05 wt. % as a non-intentionally added element. Preferably, Zn is not intentionally added and should not be more than 0.2 wt. % as a non-intentionally added element. The amount of Cu in weight percent is at least equal to or higher than 4 times the amount of Li in weight percent in the inventive alloy.

[0011] The inventive alloy has improved properties over the prior art. Preferably, the inventive alloy has a tensile yield strength (TYS) along rolling (L) direction as function of plate gage (ga) that is higher than 75.0-1.4*ga, preferably higher than 76.2-1.4*ga, and more preferably higher than 77.0-1.4*ga. Preferably, the inventive alloy has a tensile yield strength (TYS) along long transverse (LT) direction that is higher than 71.2-1.4*ga, preferably higher than 72.2-1.4*ga, and more preferably higher than 72.7-1.4*ga. Preferably, the inventive alloy has a fracture toughness (KIc) along the orientation of Long Transverse - Rolling (T-L) that is higher than 28-1.0*ga, preferably higher than 29-1.0*ga, and more preferably

higher than 29.5-1.0*ga. Preferably, the inventive alloy has a fracture toughness (Klc) along the orientation of Rolling Long Transverse (L-T) that is higher than 28.8-0.6*ga, preferably higher than 30.8-0.6*ga, and more preferably higher than 31.8-0.6*ga. The units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively. Methods for manufacturing wrought aluminum-lithium alloy products of the present invention are also provided.

[0012] The aluminum-lithium alloy of the present invention is a plate, extrusion or forged wrought product having a thickness of 0.5 to 8.0 inch. It has been surprisingly discovered that the aluminum-lithium alloy of the present invention having no Ag, or very low amounts of non- intentionally added Ag, no Zn, or very low amounts of non-intentionally added Zn, and high Mg content is capable of producing 0.5 to 8.0 inch thickness plate products with excellent strength and fracture toughness properties and desirable corrosion resistance performance. Another aspect of the present invention is a method to manufacture aluminum-lithium alloys of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

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[0013] The features and advantages of the present invention will become apparent from the following detailed description of a preferred embodiment thereof, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a graph showing the strength aging response between invention alloys and non-invention alloys.

FIG. 2 is a graph showing the comparison of strength and fracture toughness between a substantially Ag-free invention alloys and Non-invention alloys (substantially Ag-free) of 3 inch plates; The minimum LT TYS is 67 ksi; Preferred Minimum LT TYS is 68ksi; and more preferred Minimum LT TYS is 68.5ksi; Minimum Klc T-L is 25 ksi*in^{1/2}; Preferred Minimum Klc T-L is 26 ksi*in^{1/2}.

FIG. 3 is a graph showing the comparison of strength and fracture toughness between a substantially Ag-free invention alloys and Non-invention alloys (substantially Ag-free) of 3 inch plates. Minimum L TYS is 70.8 ksi; Preferred Minimum L TYS is 72 ksi; More preferred Minimum L TYS is 72.8 ksi; Minimum Klc L-T is 27 ksi*in^{1/2}; Preferred Minimum Klc L-T is 29 ksi*in^{1/2}; More preferred Minimum Klc L-T is 30 ksi*in^{1/2}.

FIG. 4 is a graph showing the comparison of LT TYS vs. Klc T-L between a substantially Ag-free invention alloys and high cost Ag-containing non-invention alloys of 3 inch plates.

FIG. 5 is a graph showing the comparison of L TYS vs. KIc L-T between low cost substantially Ag-free invention alloys and high cost Ag-containing non-invention alloys of 3 inch plates.

FIG. 6 is a graph showing the LT TYS as function of plate thickness of invention alloy plates. Minimum is 71.2-1.4*ga; Preferred Minimum is 72.2-1.4*ga; More preferred Minimum is 72.7-1.4*ga.

FIG. 7 is a graph showing the L TYS as function of plate thickness of invention alloy plates. Minimum is 75.0-1.4*ga; Preferred Minimum is 76.2-1.4*ga; More Preferred Minimum is 77.0-1.4*ga.

FIG. 8 is a graph showing the K1c T-L as function of plate thickness of invention alloy plates. Minimum is 28-1.0*ga; Preferred Minimum is 29-1.0*ga; More Preferred Minimum is 29.5-1.0*ga.

FIG. 9 is a graph showing the Klc L-T as function of plate thickness of invention alloy plates. Minimum is 28.8-0.6*ga; Preferred Minimum is 30.8-0.6*ga; More preferred Minimum is 31.8-0.6*ga.

FIG. 10 are photos showing the typical surface appearances after 672 hours MASTMASSIS testing exposure times (left Sample #6 with 3 inch plate thickness and right Sample #11 with 6 inch plate thickness).

FIG. 11 are photos showing the grain structures of Sample #1: 1" thickness invention alloy plate.

FIG. 12 are photos showing the grain structures of Sample #2: 2" thickness invention alloy plate.

FIG. 13 are photos showing the grain structures of Sample #3: 3" thickness invention alloy plate.

FIG. 14 are photos showing the grain structures of Sample #9: 4" thickness invention alloy plate.

FIG. 15 are hotos showing the grain structures of Sample #10: 6" thickness invention alloy plate.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention is directed to aluminum-lithium alloys, specifically aluminum - copper - lithium - magnesium - manganese alloys. The aluminum-lithium alloy of the present invention comprises from 3.6 to 4.1 wt. % Cu, 0.8 to 1.05 wt. % Li, 0.6 to 1.0 wt. % Mg, 0.2 to 0.6 wt. % Mn, up to 0.12 wt. % Si, up to 0.15 wt. % Fe, from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements, up to 0.10 wt. % Ti, up to 0.15 wt. % incidental elements with the total of incidental elements not exceeding 0.35 wt. %, and the balance being aluminum. Preferably, Ag is not intentionally added and should not be more than 0.05 wt. % as a non-intentionally added element. Preferably, Zn is not intentionally added and should not be more than 0.2 wt. % as a non-intentionally added element. The amount of Cu in weight percent is at least equal to or higher than 4 times the amount of Li in weight percent in the inventive alloy.

[0015] In an alternate preferred embodiment, the aluminum-lithium alloy comprises from 3.7 to 4.0 wt. % Cu, 0.9 to 1.0 wt. % Li, 0.7 to 0.9 wt. % Mg along with 0.2 to 0.6 wt. % Mn, up to 0.12 wt. % Si, up to 0.15 wt. % Fe, from 0.03 to

0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements, up to 0.10 wt. % Ti, up to 0.15 wt. % incidental elements with the total of incidental elements not exceeding 0.35 wt. %, and the balance being aluminum. Preferably, Ag is not intentionally added and should not be more than 0.05 wt. % as a non-intentionally added element. Preferably, Zn is not intentionally added and should not be more than 0.2 wt. % as a non-intentionally added element. The amount of Cu in weight percent is at least equal to or higher than 4 times the amount of Li in weight percent in the inventive alloy.

[0016] The aluminum-lithium alloy of the present invention can be used to produce wrought products, having a thickness range of 0.5 - 8.0 inch. In addition to low density and low cost, the aluminum-lithium alloys of the present invention are wrought products having high strength, stronger damage tolerance, and excellent fatigue and corrosion resistance properties.

[0017] Such products are suitable for use in many structural applications, especially for aerospace structural components such as spar, rib, and integrally machined structural parts. The aluminum-lithium alloy of the present invention can be used for the fabrication of components using several manufacturing processes such as high speed machining. [0018] Copper is added to the aluminum-lithium alloy in the present invention in the range of 3.6 to 4.1 wt. %, mainly to enhance the strength but also to improve the combination of strength and fracture toughness. An excessive amount of Cu can result in unfavorable intermetallic particles which can negatively affect material properties such as ductility and fracture toughness. In these cases the interaction of Cu with other elements such as Li and Mg must also be considered. Thus in the alternative embodiments, the upper or lower limit for the amount of Cu may be selected from 3.6, 3.7, 3.8, 3.9, 4.0, and 4.1 wt. %. In the preferred embodiment, the Cu is from 3.7 to 4.0 wt. % to provide compositions that enhance specific product performance while maintaining relatively high performance in the remaining attributes as compared to the prior art.

[0019] Lithium is added to the aluminum-lithium alloy in the present invention in the range of 0.8 to 1.05 wt. %. The primary benefit for adding Li is to reduce the density and increase the elastic modulus. Combined with other elements, such as Cu, Li is critical in improving the strength, damage tolerance and corrosion performance. Li contents that are too high, however, can negatively impact fracture toughness, and anisotropy of tensile properties. In addition to the upper and lower limits listed above for Cu, the present invention includes the alternative embodiments wherein the upper or lower limit for the amount of Li may be selected from 0.8, 0.9, 1.0, and 1.05 wt. %. In one preferred embodiment, Li is in the range of 0.9 to 1.0 wt. %.

[0020] The Cu/Li ratio significantly affects the desirable T1 strengthening phase, which is critical for strength, fracture toughness, and anisotropy of tensile properties. The present invention requires the Cu/Li ratio should be higher than 4.0 in terms of wt. % Cu / wt. % Li.

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[0021] Mg is added to the aluminum-lithium alloy in the present invention in the range of 0.6 to 1.0 wt. %. The primary purpose of adding Mg is to enhance the strength with the secondary purpose of reducing the density. However, Mg levels that are too high can reduce Li solubility in the matrix, thus negatively impacting the aging potential for higher strength. In addition to the upper and lower limits listed above for Cu and Li, the present invention includes alternative embodiments wherein the upper or lower limit for the amount of Mg may be selected from 0.6, 0.7, 0.8, 0.9, and 1.0 wt. %. In one preferred embodiment, Mg is in the range of 0.7 to 0.9 wt. %.

[0022] In one embodiment, Ag is not intentionally added in the aluminum-lithium alloy of the present invention. Ag may exist in the alloy as a result of a non-intentional addition. In this case, the Ag should not be more than 0.05 wt. %. In addition to the upper and lower limits listed above for Cu, Li, and Mg, the present invention includes alternate embodiments wherein the upper or limit for the amount of Ag may be selected from 0.05, 0.04, 0.03, 0.02, and 0.01 wt.% The prior art teaches that Ag is necessary to improve the final product properties and is therefore included in many aluminum-lithium alloys as well as many patents and patent applications. However, Ag significantly increases the cost of the alloys. In the embodiment of the aluminum-lithium alloy of the present invention, Ag is not intentionally included in order to reduce the cost. It is surprising to find that the aluminum-lithium alloy of the present invention, without the addition of Ag for providing low cost, can be used to produce high strength, high fracture toughness, and excellent corrosion resistance plate products suitable for structural applications particularly in aerospace.

[0023] The addition of Zn can negatively affect the density and therefore Zn is not added in the present invention. Zn may exist in the alloy as a result of a non-intentional addition. In this case, the Zn should not be more than 0.2 wt. %. In addition to the upper and lower limits listed above for Cu, Li, Mg, and Ag, the present invention includes alternate embodiments having less than 0.15 wt. % Zn, less than 0.10 wt.% Zn, less than 0.05 wt.% Zn.

[0024] Mn is intentionally added to improve the grain structure for better mechanical isotropy and formability. In addition to the upper and lower limits listed above for Cu, Li, Mg, Ag, and Zn, the present invention includes alternative embodiments wherein the upper or lower limits for the amounts of Mn may be selected from 0.2, 0.3, 0.4, 0.5, and 0.6 wt. %.

[0025] Ti can be added up to 0.10 wt. %. The purpose of adding Ti is mainly for grain refinement in casting. In addition to the upper and lower limits listed above for Cu, Li, Mg, Ag, Zn, and Mn, the present invention includes alternative embodiments wherein the upper limit for the amount of Ti may be selected from 0.01, 0.02, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.10 wt. % Ti.

[0026] Si and Fe may be present in the aluminum-lithium alloy of the present invention as impurities but are not intentionally added. In addition to the upper and lower limits listed above for Cu, Li, Mg, Ag, Zn, Mn, and Ti, the present invention includes alternate embodiments wherein the alloy includes ≤ 0.12 wt. % for Si, and ≤ 0.15 wt. % for Fe, preferably ≤ 0.05 wt. % for Si and ≤ 0.08 wt. % for Fe. In one embodiment, the aluminum-lithium alloy of the present invention includes a maximum content of 0.12 wt. % for Si, and 0.15 wt. % for Fe. In one preferred embodiment, the maximum contents are 0.05 wt. % for Si and 0.08 wt. % for Fe.

[0027] The aluminum-lithium alloy of the present invention may also include low levels of "incidental elements" that are not included intentionally. The "incidental elements" means any other elements except Al, Cu, Li, Mg, Zr, Zn, Mn, Ag, Fe, Si, and Ti.

[0028] The low cost, high performance, high Mg content Al-Li alloy of the present invention may be used to produce wrought products. In one embodiment, the aluminum-lithium alloy of the present invention is capable of producing rolled products, preferably, a plate product in the thickness range of 0.5 to 8.0 inch. In the alternative embodiments, the upper or lower limit for the thickness may be selected from 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 inch

[0029] The rolled products may be manufactured using known processes such as casting, homogenization, hot rolling, solution heat treating and quenching, stretching, and ageing treatments. The ingot may be cast by traditional direct chill (DC) casting method. The ingot may be homogenized at temperatures from 482 to 543°C (900 to 1010°F). The hot rolling temperature may be from 357 to 482°C (675 to 900°F). The products may be solution heat treated at temperature range of 482 to 538°C (900 to 1000°F). The wrought products are cold water quenched to room temperature and may be stretched up to 15%, preferably from 2 to 8%. The quenched and stretched product may be subjected to any aging practices known by those skilled in the art including, but not limited to, one-step aging practices that produce a final desirable temper, such as T8 temper, for better combination of strength, fracture toughness, and corrosion resistance which are highly desirable for aerospace members. The aging temperature can be in the range of 121 to 205°C (250 to 400°F) and preferably from 149 to 182°C (300 to 360°F) and the aging time can be in the range of 2 to 60 hours, preferably from 10 to 48 hours.

[0030] The unique chemistry along with proper processing of present patent application results in plate products with surprising novel and basic material characteristics. In one embodiment, the tensile yield strength (TYS) along rolling (L) direction as function of plate gage (ga) is higher than 75.0-1.4*ga, preferably higher than 76.2-1.4*ga, and more preferably higher than 77.0-1.4*ga. The tensile yield strength (TYS) along long transverse (LT) direction is higher than 71.2-1.4*ga, preferably higher than 72.2-1.4*ga, and more preferably higher than 72.7-1.4*ga. The fracture toughness (Klc) along the orientation of Long Transverse - Rolling (T-L) is higher than 28-1.0*ga, preferably higher than 29-1.0*ga, and more preferably higher than 29.5-1.0*ga. The fracture toughness (Klc) along the orientation of Rolling - Long Transverse (L-T) is higher than 28.8-0.6*ga, preferably higher than 31.8-0.6*ga. The units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

[0031] The following examples illustrate various aspects of the invention and are not intended to limit the scope of the invention.

Examples: Industrial Scale Ingots - 1 to 6 Inches Thick Plates

[0032] Twenty seven (27) industrial scale 16" (406mm) thick ingots of Al-Li alloys were cast by DC (Direct Chill) casting process and produced to 1" to 6" thickness plates. It is well known that the properties of final plate products are strongly affected by the processing. The properties of plates from industrial scale process can be dramatically different from that from lab scale processing due to different chemistry segregation, as-cast structure, hot rolling related crystallographic texture, and solution heat treatment quenching rate.

[0033] Table 1 gives the chemical compositions and final plate thickness. There are three groups: (1) "Invention", (2) "Non-Invention (Substantially Ag-free)" and (3) "Non-Invention (Ag)". The third group is obviously not the invention alloy due to the high cost Ag element and/or along with other conditions that do not meet invention alloy chemical composition limits. In the second group, samples are not invention alloys due to the combination of Cu/Li ratio, Cu, Li, and Zn limits. For example, the Cu/Li ratios for sample 12, 13 14, and 16 are lower than 4.0. The Cu contents in sample 13 and 15 are lower than 3.6 wt. %. The Li content in Sample 13 is higher than 1.05 wt. %. The Zn content in Sample 16 is higher than 0.2 wt. %

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Table 1: Chemical compositions of sample

	Sample		Gage,											
Invention?	ID	Lot	in	Si	Fe	Cn	Mn	Mg	<u>-</u>	\mathbf{Zr}	Li	Ag	Zn	Cu/Li
		130432B8	П	0.03	0.05	3.85	95.0	0.71	0.03	0.10	0.92	0.00	0.05	4.2
	2	130408B8	2	0.03	0.04	3.80	95.0	0.70	0.02	0.10	98.0	0.00	0.05	4.4
	3	130275B1	33	0.04	0.04	3.88	95.0	0.74	0.02	0.11	0.84	0.00	0.04	4.6
U	4	130285B0	3	0.03	0.04	3.74	0.35	0.70	0.03	0.10	06.0	0.00	90.0	4.1
ıoi	5	187413B0	ε	0.03	90.0	3.64	0.35	0.77	00.00	0.11	0.92	0.00	0.04	4.0
ıuə	9	187292B8	æ	0.02	90.0	3.74	0.33	89.0	0.03	0.11	0.92	0.00	0.03	4.1
ΛU	7	652929A1	3	0.03	0.05	3.80	0.34	0.61	0.03	0.10	92.0	0.00	0.00	5.0
I	&	187267B0	3.2	0.03	0.04	3.98	0.42	0.72	0.02	0.10	88.0	0.00	0.01	4.5
	6	130415B3	4	0.03	0.05	3.73	0.34	0.70	0.02	0.10	98.0	0.00	0.03	4.3
	10	130369B2	9	0.03	0.04	3.73	0.35	0.72	0.02	0.10	88.0	0.00	0.03	4.2
	Ξ	187382B7	9	0.03	0.56	3.80	0.32	0.70	0.04	0.10	0.87	00.0	0.05	4.4
	TOTAL STATE OF THE													
τ	12	187432B0	3	0.02	0.05	3.94	0.33	0.92	0.03	0.11	1.00	0.00	0.03	3.9
ıoi	13	652851A7	3	0.03	80.0	3.36	0.35	96.0	0.02	0.10	1.21	00.0	0.00	2.8
	14	652867A3	3	0.03	0.07	3.62	95'0	1.02	0.02	0.10	1.07	0.00	0.00	3.4
	15	652868A1	33	0.03	0.05	3.39	0.35	0.99	0.02	0.10	08.0	00.0	0.00	4.2
	16	652950A7	ε	0.03	0.05	3.70	95.0	1.05	0.03	0.10	1.01	0.00	0.51	3.7
				100										
	17	115697B5	1	0.03	0.05	3.84	0.35	0.40	0.02	0.10	1.15	0.28	0.03	3.3
	18	652795A6	П	0.03	0.05	3.79	00.0	0.42	0.02	60.0	1.19	0.44	0.53	3.2
(8 7	19	115621B5	2	0.03	0.05	3.82	0.35	0.41	0.02	0.10	1.00	0.28	90.0	3.8
√) u	20	187433B8	3	0.05	0.05	4.35	0.04	95.0	0.03	0.11	68.0	0.19	90.0	4.9
ıoi	21	652784A0	3	0.04	0.05	3.88	0.33	06.0	0.02	60.0	08.0	0.26	0.37	4.8
ıuə	22	652916A8	3	0.03	0.05	3.71	95.0	1.05	0.02	60.0	1.02	0.28	0.00	3.6
ΛU	23	534647A3	3	0.02	0.04	3.67	0.37	0.37	0.03	80.0	0.92	0.31	0.07	4.0
I-u	24	652850A9	4	0.03	0.05	3.84	0.35	0.40	0.02	0.10	66.0	0.27	0.00	3.9
oN	25	115664B5	5	0.03	0.05	3.78	0.34	0.45	0.02	0.10	1.05	0.28	0.02	3.6
	26	652790A7	9	0.03	0.05	3.72	0.34	0.42	0.02	60.0	66.0	0.28	0.04	3.8
	27	115615B7	9	0.03	0.05	3.77	0.34	0.38	0.02	0.10	96.0	0.28	0.03	3.9

[0034] The ingots were homogenized at temperatures from 496 to 538°C (925 to 1000°F). The hot rolling temperatures were from 371 to 466°C (700 to 870°F). The ingots were hot rolled at multiple passes into 1" to 6" thickness. The rolled plates were solution heat treated at a temperature range from 493 to 532°C (920 to 990°F). The plates were cold water quenched to room temperature. All example plates were stretched by 2 to 7% in terms of plastic strain. The stretched plates were further aged to T8 temper for strength, fracture, fatigue resistance, and corrosion resistance performance evaluation. The aging temperature was from 160°C (320°F) to 171°C (340°F) for 8 to 70 hours.

[0035] The strength and fracture toughness as a function of aging process is one critical characteristic for alloy performance. The selected substantially Ag-free addition 3" invention and non-invention alloy plates were evaluated under 166°C (330°F) aging temperature at different aging times. Table 2 gives the tensile and fracture toughness testing results. Tensile in LT direction at quarter thickness (T/4) was conducted under ASTM B557 specification. The plane strain fracture toughness (KIc) in T-L orientations at middle thickness (T/2) was measured under ASTM E399 using CT specimens.

[0036] For the same substantially Ag-free alloys, as demonstrated in FIG. 1, invention alloys have much faster / better strength response as aging time increases than non-invention alloys. Such significant difference is mainly due to the distinctive chemical composition difference between invention alloys and non-invention alloys.

Table 2: The strength and fracture toughness as function of aging time at 330°F

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20	Invention?	Sample ID	Lot	Aging Time at 330F, hours	T/4 LT UTS, Ksi	T/4 LT TYS, Ksi	T/4 LT EL, %	T/2 K1c T-L ksi-√in
0.5				18	77.0	70.5	8.0	30.3
25				18	76.8	70.3	7.5	29.3
				31	78.6	72.7	6.5	30.7
		,	120275D1	31	78.6	72.3	6.5	30.9
		3	130275B1	31	78.3	72.2	7.5	28.1
30				31	78.2	72.1	7.5	27.2
				50	78.5	72.9	8.0	26.2
				50	78.4	73.0	8.0	25.9
				18	76.2	69.7	9.0	31.2
35				18	76.0	69.5	8.5	31.4
				31	77.6	71.5	8.0	28.6
		4	130285B0	31	77.3	71.3	8.0	29.1
	a	4	130263B0	31	77.4	71.7	7.0	28.5
40	Invention			31	77.5	71.5	7.5	29.0
	i e			50	78.2	72.7	8.0	26.5
	_ I			50	77.9	72.3	6.5	26.7
				9	66.0	53.5	16.0	43.9
45				11	68.0	58.2	13.5	41.3
				14	71.3	62.2	11.5	36.2
				18	73.2	65.2	9.0	33.6
				24	74.9	67.5	7.5	31.3
50		7	652929A1	31	76.8	69.5	8.0	28.8
		/	032929A1	31	76.5	69.0	7.5	29.0
				32	75.7	69.4	7.3	29.6
				41	73.9	69.4	5.8	
55				44	76.2	70.3	4.0	27.4
				48	75.8	70.4	7.0	
				67	75.4	69.8	7.5	26.1

	Invention?	Sample ID	Lot	Aging Time at 330F, hours	T/4 LT UTS, Ksi	T/4 LT TYS, Ksi	T/4 LT EL, %	T/2 K1c T-L ksi-√in
5				9	63.9	47.3	19.0	43.6
				11	64.4	48.0	18.5	42.4
				14	64.8	49.4	17.5	41.7
				18	65.8	52.0	17.5	39.6
				24	65.8	54.5	14.0	36.8
10		13	652851A7	32	73.9	58.4	10.5	33.4
		13	632631A/	41	71.6	64.8	7.3	
				44	73.6	68.1	5.0	25.1
				44	72.8	64.9	6.0	26.6
				44	73.1	66.2	4.5	26.5
15				48	73.3	67.4	6.0	
				67	73.0	66.6	6.0	23.2
				9	65.7	47.6	19.5	45.9
				11	65.2	48.9	17.5	46.4
				14	66.2	49.8	17.5	43.5
20				18	67.4	52.5	16.5	41.0
	•			24	68.4	54.7	13.5	38.6
	Ag	14	652867A3	32	70.3	59.8	11.5	34.4
	{o }	14	03280/A3	41	72.9	65.9	6.3	
	()			44	73.2	67.5	5.0	27.2
25	ion			44	74.5	66.7	6.5	28.6
	ınt			44	74.0	66.1	5.5	
	1V6			48	73.9	67.9	6.0	
	Non-Invention (No Ag)			67	74.5	68.8	4.5	25.1
	Vor			9	62.6	45.6	20.0	51.7
30	2			11	62.8	46.4	23.0	51.6
				14	63.5	48.1	21.0	50.0
		15	652868A1	18	64.0	49.2	20.0	48.8
		13	032000A1	24	64.9	51.4	18.5	45.7
25				32	65.9	54.0	16.0	43.0
35				44	69.6	62.9	10.0	33.9
				44	69.5	62.8	9.0	33.9
				9	66.2	49.4	18.5	48.0
				11	67.5	50.9	19.0	48.1
40				14	67.8	51.9	18.0	47.5
40				18	68.6	54.9	16.0	44.5
		16	652950A7	24	69.8	56.0	13.5	
		10	032330A1	32	71.9	60.3	11.5	
				41	73.6	65.7	5.7	
45				44	73.2	67.9	4.8	26.1
-				48	75.4	69.8	5.5	
				67	72.8	69.7	4.5	24.5

[0037] Based on the lab aging results, the desired aging practice with balanced strength and fracture toughness was selected for production aging treatment. The production aged plates were comprehensively evaluated for tensile, fracture, corrosion and fatigue resistance.

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[0038] Table 3 and 4 give the tensile properties along L, LT, and L45 (45° off the rolling direction) directions at quarter thickness (T/4) and middle thickness (T/2) for all production aged plates. Table 5 gives the fracture toughness at the orientations of L-T, T-L and S-L at quarter thickness (T/4) and middle thickness (T/2) for all production aged plates.

Table 3: The tensile properties along L, LT, and L45 directions at quarter thickness (T/4) for production aged plates

	P	Plate Information	nation						T/4 Te	T/4 Tensile Properties	perties			
				Aging		17/1	1 7/1	T/4	1/4	1/4	1/4	T/4	T/4	$\mathbf{T}/4$
•	ŀ	Sample	Gage,	Temper	Aging	7 7 1	1/4 L	7	L45	L45	L45	L	<u>[</u>	
Invention?	Lot	1	ņ	ature,	hours	,		EL,	UTS,	TYS,	EL,	UTS,	TYS,	EL,
				oF.		KSI	KSI	%	Ksi	Ksi	%	Ksi	Ksi	%
	130408B8	2	2.0	330	32	77.3	74.3	11.0	75.1	8.89	7.5	77.2	71.7	9.5
						9.87	75.2	11.0	75.2	68.7	13.0	77.1	71.5	10.0
	120001	,	ć	000	ć	7.67	76.5	0.6	77.2	9.07	9.5	78.6	72.7	6.5
	1302/3B1	'n	3.0	330	76	0.08	9.9/	7.5	77.3	9.07	11.0	78.6	72.3	6.5
	00000		Ċ	000	ć	78.9	75.7	8.5	76.1	9.69	11.0	77.6	71.5	8.0
	15028280	4	3.0	330	76	78.0	74.7	9.5	76.3	69.4	11.0	77.3	71.3	8.0
	040	Ų	Ċ	000	ć	8.9/	74.3	11.0	75.2	69.5	12.0	76.8	71.2	9.5
	18/415B0	^	3.0	330	76	7.77	75.2	10.0	75.4	69.3	12.0	76.4	6.07	11.0
u	00000		,	020	ç	9.77	74.3	11.0	76.0	69.5	11.0	9.92	70.9	8.0
oiti	18/292B8	9	5.0	330	76	77.4	74.1	0.6	76.1	9.69	11.0	6.97	71.2	8.5
19A	1 4 00000	t	,	000	ć	77.8	74.1	7.5	75.5	6.89	0.6	8.97	69.5	8.0
uI	652929A1	_	3.0	056	75	79.0	75.2	7.0	76.0	69.4	7.5	76.5	0.69	7.5
						i C	i i	(,	(Ó	1	i	ţ
	187267B0	&	3.2	330	32	78.7	75.5	9.5	76.0	69.3	9.0	5.77	/1.0	c./
						8.9/	73.8	11.0	76.1	9.69	12.0	77.2	71.0	8.5
	12041502	•	0.4	020	Ç	75.9	72.7	8.5	75.2	9.89	7.5	75.9	8.69	7.0
	150415B5	٧	4. O.	330	7¢	75.8	72.6	0.6	75.3	68.9	10.0	76.2	70.5	5.5
	1202/001	01	0.7	220	23	74.1	9.07	8.0	73.0	66.1	6.0	73.4	66.4	4.5
	130309182	ΩI	0.0	056	76	74.0	70.4	6.5	72.6	0.99	3.5	73.1	66.5	4.5
	p. 100000	-	0.7	020	23	74.2	70.7	7.0	73.8	9.99	0.6	74.2	67.2	0.9
	18/382B/	I	0.0	056	76	74.2	70.7	8.5	73.7	66.2	8.0	74.1	67.0	5.0

50			Invention?						(g <i>l</i>		I-u	10/	I			.,,	invention?			<u> </u>							itnə								
45	Pla		Lot			187432B0	C 10 C 3 7	02.2831A/	27298659	022001A3		652868A1		PI		<u> </u>	F01		30167311	CG170C11	187433B8	00000	04787659	0.77607700	65701648	0771070	534647A3	0.4.020.23	65.283UA9	115664115	112004133	652790A	7	115615B	7
45	Plate Information		Sample	a		12	13	13	71	14		15		Plate Information		Sample	P		01	13	20	2	,	77	ιι	77	23	6	74	30	C7	90	707	77	<u> </u>
40	ation		Gage,			3.0	, 0	5.0	3.0	0.6		3.0		ation		Gage	'n		,	7	,,)	,,	J	"	C	3.0	-	4	2	0	v	ر	9	,
35		Aging	Temper	ature, OF	4	330	240	240	340	240		340			Aging	Temper	ature,	F	310	210	330	2	330	٥٥٥	340	0+0	310	000	220	000	270	220	076	320	010
			Aging	Sinon		32	ç	5 7	2,	+ 7		24				Aging	hours		00	70	~	0.	33	J.C.	2	†	27	2	7 7	ć	†	ç	†	24	1
30		1 17/L	UTS,	Ksi	81	80.3	72.1	73.3	74.2	75.9	70.0	68.3			E	1/4 L	C13,	Z.	81.6	0.08	84.3	84.1	79.5	82.0	76.5	78.0	77.8	79.1	79.5	80.3	80.1	78.3	78.5	6.77	78.0
25		T/4 I	TYS,	Ksi	78.0	77.0	68.7	8.69	9:69	70.2	65.2	64.0				1/4 L	175,	2	77.6	76.1	80.4	80.1	76.1	78.2	71.6	74.3	73.7	74.6	74.6	76.2	75.9	73.8	73.9	73.8	73.8
		1/4	7 5	, , , ,	9.5	10.0	8.5	10.0	7.5	9.5	11.0	13.0			T/4	_	EL,	%	11.0	11.0	8.5	9.0	5.0	6.0	7.0	6.0	8.6	7.5	8.0	6.0	5.5	6.5	7.5	8.5	6.0
20	T/4 Ter	T/4	L45	Kei,	79.2	78.7	71.6	72.1	73.2	73.2	68.7	68.5		T/4 Ter	T/4	L45	UTS,	Ksi	78.1	77.8	83.4	83.3	9.77	78.7	75.1	75.3	77.1	78.2	78.3	0.62	79.3	6.9/	77.2	78.4	78.5
15	I/4 Tensile Properties	T /4	L45	Kei,	72.0	71.3	64.0	64.8	65.0	64.9	61.6	61.3		I/4 Tensile Properties	T/4	L45	TYS,	Ksi	70.6	70.1	75.9	75.9	70.4	71.6	8.79	68.0	70.0	70.1	69.4	71.8	71.6	70.5	70.1	71.2	70.8
	perties	1/4	L45	, , , ,	11.0	11.0	9.0	8.0	10.0	8.0	13.0	10.0		perties	T/4	L45	EL,	%	14.0	14.0	9.5	9.0	4.5	8.0	5.5	5.5	6.3	7.5	7.5	3.5	6.5	3.0	3.5	4.7	5.0
10		T/4		C 13,	80 1	79.7	72.8	73.1	74.5	74.0	9.69	69.5			T/4	LI	UTS,	Ksi	79.9	662	84.4	84.3	79.3	79.2	75.5	75.0	78.0	78.8	78.7	79.2	80.1	9.9/	77.0	77.8	75.9
5		T/4	LT	Kei Kei	73.5	73.0	64.9	66.2	2.99	66.1	62.9	62.8			T/4	LJ	TYS,	Ksi	73.2	73.2	77.6	77.8	72.7	72.7	69.0	69.2	71.2	71.4	71.1	72.2	73.1	69.5	8.69	71.2	71.2
		T/4		%,	08	8.5	6.0	4.5	6.5	5.5	10.0	9.0			T/4	L	EL,	%	12.0	10.0	5.5	5.5	8.5	3.0	3.5	4.0	6.3	4.2	5.0	4.0	5.5	3.5	3.5	3.5	2.0

Table 4: The tensile properties along L, LT, and L45 directions at middle thickness (T/2) for production aged plates

		Plate Inf	Plate Information	ı						T/2]	Tensile Properties	Propert	ies				
+uomu_		Sam	Cogo	Aging Tomp	, is	T/2 L	T/2	T/2	T/2	T/2	T/2	T/2	T/2	1/2	T/2	T/2	T/2
ion?	Lot	ple	je gr.	eratur	hours	UTS,	TXS.			TVS		Z E	IXS.			TVS	2 E
		9		e, °F		Ksi	Ksi.	%	Ksi,	Ksi	%	Ksi,	Ksi	%	Ksi,	Ksi	%
	130432	1-	-	330	10	81.4	LLL	11.0	72.6	0.79	15.0	79.3	74.4	11.0	74.2	9.99	4.5
	B8	-T	1	056	10	81.3	8.77	11.0	72.5	6.99	14.0	79.2	74.2	12.0	75.3	64.0	5.0
	130408	·	Ĺ	330	33	79.2	75.4	8.5	71.2	0.99	13.0	77.3	72.2	11.0	9.57	65.1	8.5
	B8	1	1	220	37	79.4	75.5	9.5	71.0	65.7	14.0	77.0	71.8	10.0	74.9	64.3	8.0
	130275	r	,	220	Ç	80.7	77.2	7.5	73.5	68.1	9.5	79.1	73.5	6.5	76.4	0.89	3.0
	B1	ი	n	220	76	8.08	77.1	8.5	73.6	68.4	9.0	6.87	73.4	7.5	76.5	6.79	3.0
	130285	-	,	330	23	79.3	75.6	8.0	72.8	67.1	12.0	6.77	72.4	8.0	75.5	66.4	4.0
	B0	4	n	220	25	79.1	75.2	8.0	72.5	67.2	12.0	78.1	72.4	8.5	75.6	6.99	4.0
	187413	ų	,	0,00	ç	79.2	76.4	10.0	71.9	8.79	12.0	77.5	73.1	9.5	75.4	9.79	4.0
u	B0	n	n	250	76	79.2	76.3	8.5	71.9	9.79	13.0	9.77	73.2	9.5	75.2	67.3	3.0
oita	187292	7	,	220	00	6.87	75.2	11.0	72.3	67.2	12.0	7.77	72.3	8.0	75.5	9:99	4.0
ΙĐΛ	B8	0	n	230	25	78.8	75.2	11.0	72.2	67.2	11.0	8.77	72.6	8.5	75.6	2.99	5.0
uI	652929	ľ	ć	330	66	7.67	74.4	8.0	73.2	0.99	9.5	76.2	6.69	0.9	74.3	65.0	3.0
	A1	`	n	220	37	0.08	75.7	7.0	72.2	65.5	11.0	9.77	71.3	6.5	73.8	64.9	4.0
	187267	0	2.01	330	30	8.62	75.9	9.5	73.0	9.79	10.0	7.7.7	72.1	7.5	75.9	2.99	4.0
	B0	0	3.21	250	32	8.62	75.8	8.0	72.7	67.3	9.0	9.77	71.7	8.0	75.4	67.2	4.0
	130415	0	V	330	33	77.3	73.4	8.5	74.9	68.2	9.0	75.6	69.4	7.5	73.0	64.7	4.3
	B3	^	t	OCC	75	77.2	73.3	7.5	71.8	66.4	9.5	75.2	70.2	3.0	72.7	64.6	4.3
	130369	10	7	330	33	74.6	9.07	6.5	69.3	63.3	7.0	70.5	64.1	4.0	9.07	62.3	3.5
	B2	10	0	220	25	75.1	71.0	6.5	0.69	63.0	7.0	70.4	64.3	5.0	70.4	62.1	2.5
	187382	-	9	330	33	75.4	71.2	8.5	70.7	64.5	7.5	71.9	65.2	6.5	70.8	63.1	4.0
	B7	11	o	ncc	25	75.3	71.1	8.5	71.4	65.2	10.0	72.8	66.7	4.4	70.3	63.4	3.4

0.9

61.2

8.69

65.6

71.4

9.5

60.5

8.59

8.0

669

74.2

A1

r													_
		T/2	ST	EL,	%	3.0	5.0	1.0	2.0	1.0	1.0	5.0	0.9
5		T/2	ST	TYS,	Ksi	68.3	68.4	67.9	67.9	64.9	64.2	60.2	61.2
		T/2	S	UTS,	Ksi	77.8	78.1	70.7	9.07	73.2	72.3	6.69	8 69
10		T/2	<u></u>	E,	%	8.0	10.0	4.5	7.0	5.5	5.0	0.6	7.5
15	ies	T/2		TYS,	Ksi	74.9	74.8	9.79	8.79	68.7	9.69	64.3	9 59
	T/2 Tensile Properties	T/2		UTS,	Ksi	80.2	80.2	73.2	74.0	75.4	75.2	70.4	71.4
20	[ensile]	T/2	145	EL,	%	0.6	11.0	9.5	8.0	8.0	9.5	14.0	9.5
	T/2 1	T/2	L45	rys,	Ksi	69.7	69.4	62.2	62.5	8.49	64.9	60.1	5 09
25		T/2	L45	UTS,	Ksi	75.1	75.0	69.4	69.3	9.07	70.5	66.4	8 2 9
		T/2	_	EL,	%	10.0	7.5	7.0	0.9	4.5	5.5	0.6	0.8
30		T/2	_	YS,	Ksi	78.3	78.3	71.6	71.6	74.6	74.2	69.2	6 69
25		T/2				81.7	81.6	75.7	75.6	9.87	78.4	73.4	74.2
35				onrs			75		, +,7		t, 	,	
40			₹				•						_
40		Aging	Temp	eratur	e, ºF	022	230	240	340	04.0	340	340	, 1,
45	Plate Information	i	Gage,	.II		ć	C	ζ	n	,	n	3	n
	Plate In	S. m	nla	<u> </u>		1,	71	1.2	CI	7	‡	15	
50			101	3		187432	B0	652851	A7	652867	A3	898759	A1
55			Invent	ion?			u		nəv BA			N	
L.						_							_

		T/2	ST	EĽ,	11.0	7.5	8.0	6.5	8.5	8.0	2.0	1.0	2.0	1.5	1.0	1.0	4.1	3.0	2.0	2.5	2.0	3.0	2.5	2.5	2.5
5		T/2	\mathbf{ST}	TYS,	2.79	8.69	74.1	75.4	66.4	66.1	72.8	72.8	6.99	67.2	64.7	65.5	9:59	9.99	6.3	0.79	6.99	0.79	8.79	64.5	64.2
		T/2	\mathbf{ST}	CTS,	813	81.7	6.88	87.7	6.87	78.2	82.4	82.7	75.7	76.2	73.1	73.8	74.1	77.7	77.7	75.7	75.6	77.5	78.5	72.7	72.6
10		T/2	<u>[</u>	EL,	10.0	11.0	4.5	5.5	11.0	10.0	4.5	0.9	5.5	5.0	6.5	5.0	8.9	5.0	2.5	3.5	3.5	4.5	4.2	3.0	3.5
15	ties.	L/2	LI	TYS,	78.0	77.6	83.7	83.8	75.7	75.6	81.0	81.2	73.4	73.6	6.69	6.69	70.1	72.7	73.0	73.3	73.0	71.3	71.5	68.5	9.89
	Tensile Properties	Z/L		UTS, Kei	83.9	83.7	88.7	88.7	81.7	81.7	9.58	<i>L</i> '98	79.5	7.67	0.97	77.3	9.9/	6.67	0.67	5.67	79.1	78.8	9.87	74.5	74.7
20		L/2	L45	EL,	15.0	13.0	11.0	9.0	13.0	15.0	7.0	7.5	5.5	8.5	7.0	9.0	9.3	7.5		5.5	5.5	5.0	4.5	4.7	4.5
	T/2	T/2	L45	TYS,	70.4	70.2	73.6	73.2	8.89	68.1	74.2	74.3	9.89	68.2	9.99	65.9	65.1	68.3		69.4	69.3	2.99	6.99	8.99	6.99
25		$\mathbf{L}/2$	L45	UTS,	6.9/	76.5	81.4	81.0	75.1	74.9	80.2	80.4	74.6	75.6	72.5	71.8	71.5	75.5		76.1	75.9	74.0	73.7	73.0	73.0
30		T/2	_	EL,	11.0	10.0	5.5	6.5	10.0	10.0	7.5	8.0	7.5	6.5	5.5	0.9	9.3	6.5	7.0	4.7	4.0	7.5	5.5	5.5	0.9
30		T/2	_	TYS,	81.2	81.3	85.6	6'98	79.0	79.3	93.6	83.4	77.0	77.4	74.7	75.5	73.4	77.8	77.0	77.1	77.5	68.2	79.3	74.2	74.5
35		T/2	_	UTS,	85.6	85.7	9.98	90.1	83.7	84.0	87.8	9.78	80.9	81.4	6.87	79.5	78.2	83.1	82.4	81.2	81.5	75.5	84.2	78.5	78.9
			Aging	hours		15	5	7	00	07	10	01	33	76	ć	74	27	, C	+	VC	+	2,4	+7	ć	47
40	_	Aging	Temper	ature, °F	4	310	000	370	310	210	000	230	220	000	07.0	240	310	330	340	330	320	330	320	000	320
45	Plate Information		Gage,	Ë			-	1	C	1	·	n	,	ņ	,	Ç	3.0	_	t	3	,	v	,	7	o
	Plate In	Com	Sam	18		1.7	1.0	10	10	19	00	07		77	ć	77	23	У.	† 7	36	6.7	36	20	7.0	17
50			+0		115697	B5	652795	9Y	115621	B5	187433	B8	652784	Α0	652916	A8	534647 A3	652850	A9	115664	B5	652790	A7	115615	B7
55			Invent	ion?								(6	₹V)	uo	iju	әлі	ıI-uo	N							

Table 5: Fracture toughness at the orientations of L-T, T-L and S-L at quarter thickness (T/4) and middle thickness (T/2) for all final 10 15 20 25 30 35 40 45 50

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T/4 T-L ksi-√in 27.5 24.9 25.5 26.9 26.4 28.2 27.0 27.3 27.1 28.3 26.8 27.6 27.4 26.0 25.0 26.1 25.1 ksi-√in T/4 L-T 27.8 27.8 28.6 28.6 28.3 28.4 32.3 29.3 29.8 29.7 29.6 31.3 30.4 28.9 29.7 Fracture Toughness T/2 S-L ksi-√in 26.1 25.2 25.7 25.9 23.9 24.0 24.9 24.7 25.5 27.0 25.8 26.0 25.9 25.0 25.4 26.1 25.1 26.1 23.1 T/2 T-L ksi-√in 30.2 27.4 26.8 28.1 28.0 28.8 27.9 28.6 28.0 29.0 28.2 28.5 29.0 25.3 29.1 26.2 25.7 30.1 T/2 L-T ksi-√in 32.6 32.1 32.2 31.4 33.9 33.8 33.0 33.6 30.9 32.6 31.5 31.2 33.0 32.8 30.0 34.3 30.7 32.2 31.1 Aging hours 2 32 32 32 32 32 32 32 32 32 32 Aging Temperature, 330 330 330 330 330 330 330 330 330 330 330 Plate Information Gage, in 3.21 0 3 3 ŝ 3 m 4 9 9 Sample ID 10 \equiv $^{\circ}$ 3 4 S 9 ∞ 6 production aged plates 30432B8 130408B8 130369B2 187382B7 130285B0 187413B0 187292B8 652929A1 130415B3 187267B0 130275B1 Lot Invention? Invention

50		Invention Lot	187437B0	OG 201/01	7 V 130037		o N		657868 A 1	147000700
	Plate I	Sample ID	12	7	5	CI	1.4	<u>+</u>	7.	C1
40	Plate Information	Gage, in	۲	Ò	C	n	2	n	"	,
35	u	Aging Temperature, °F	330	ACC	076	340	01/2	0+6	340	OF C
30		Aging hours	37	26	70	4 7	7.0	†	7.7	t-7
20 25		T/2 L-T ksi-√in	25.3	24.8	31.6	30.6	33.0	32.1	42.9	42.5
	Fract	T/2 T-L ksi-√in	24.3	24.5	26.6	26.5	28.6		33.9	33.9
15	Fracture Toughness	T/2 S-L ksi-√in	23.6	23.3	20.8	22.4	23.0	23.0	31.6	29.7
10	SS	T/4 L-T ksi-√in	23.6	23.0			30.7		40.7	
5		T/4 T-L ksi-√in	23.4	22.7	25.3		27.5		34.0	

		Plate I	Plate Information				Fract	Fracture Toughness	SS	
Invention ?	Lot	Sample ID	Gage, in	Aging Temperature, °F	Aging hours	T/2 L-T ksi-√in	T/2 T-L ksi-√in	T/2 S-L ksi-√in	T/4 L-T ksi-√in	T/4 T-L ksi-√in
	11560705	1.	-	210	7	34.0	32.6	28.8		
	11309/D3	1 /	-	310	CI	33.3	32.3	27.9		
	9 4 502.059	1.0	+-	220	77	18.7	18.4			
	02/12/20	10	1	320	†	18.5	18.7	17.0		
	11560105	10	c	210	00	32.8	31.5	27.9		
	1130211	13	1	310	07	33.4	30.9	28.7		
	107433100	00	ç	230	01	21.6	21.1	20.3	20.0	20.7
(8	10/433D0	07	n	220	10	22.2	20.9	19.5	19.9	21.0
(A)	0412764		,	220	33	27.5	25.8	25.6	26.7	23.7
uo	077,0470	77	n	330	37	27.1	25.4	24.2		
iìn	65201648	77	3	340	7.0	31.8	29.6	26.6	31.1	29.1
ЭЛU	02710720	77	r .	0+0	†	31.6	30.3	27.3		
ıĮ-u(534647A3	23	3.0	310	27	35.9	30.9	28.2		
N	04058659	70	-	330	7,0	31.3	25.8	23.1	29.4	26.0
	02700000	†	i	026	†	31.6	25.7	23.9		
	11566AD5	30	v	220	20	26.8	25.2	23.0	25.0	24.2
	CG+00C11	C7	J.	320	† 7	26.7	24.9	22.6	25.1	24.3
	7.007.039	36	V	330	7.0	30.0	27.3	26.0	31.8	27.8
	12/06/7700	707	J.	020	†	29.9	27.0	26.2		
	11561587	7.0	9	320	7,0	29.0	24.3	23.9	28.0	24.4
	/GCIOCII	1		020	+ 7	28.5	24.6	22.7	27.3	23.5

[0039] Table 3 to 5 shows that the low cost invention alloy with unique chemical composition has surprisingly better material properties in terms of the combination of strength and fracture toughness. As an example, FIG. 2 gives the comparison of LT TYS strength and K1c T-L fracture toughness between substantially Ag-free invention alloys and Non-

invention alloys (No Ag) of 3 inch plates. The invention alloys have a better combination of strength and fracture toughness. The minimum LT TYS can be 67 ksi and minimum K1c T-L can be 25 ksi*in $^{1/2}$ for 3" plate. Preferably, the minimum LT TYS can be 68 ksi and minimum K1c T-L can be 26 ksi*in $^{1/2}$ for 3" plate. More preferably, the minimum LT TYS can be 68.5 ksi and minimum K1c T-L can be 26.5 ksi*in $^{1/2}$ for 3" plate.

[0040] The similar distinctiveness can be demonstrated in FIG. 3 for 3" L TYS and K1c L-T properties. The minimum L TYS can be 70.8 ksi and minimum K1c L-T can be 27 ksi * in $^{1/2}$ for 3" plate. Preferably, the minimum L TYS can be 72.0 ksi and minimum K1c L-T can be 29 ksi * in $^{1/2}$ for 3" plate. More preferably, the minimum L TYS can be 72.8 ksi and minimum K1c L-T can be 30 ksi * in $^{1/2}$ for 3" plate.

[0041] FIG. 4 and 5 gives the comparison of LT TYS vs. K1c T-L and L TYS vs. K1c L-T between low cost substantially Ag-free invention alloys and high cost Ag containing non-invention alloys of 3 inch plates. It surprisingly shows that there is no significant difference between Ag containing non invention alloys and substantially Ag-free invention alloys in terms of the combination of strength and fracture toughness.

[0042] FIG. 6 to 9 gives the strength and fracture toughness as a function of plate thickness for invention alloy plates. The tensile yield strength (TYS) along long transverse (LT) direction is higher than 71.2-1.4*ga, preferably higher than 72.2-1.4*ga, and more preferably higher than 72.7-1.4*ga. The tensile yield strength (TYS) along rolling (L) direction as function of plate gage (ga) is higher than 75.0-1.4*ga, preferably higher than 76.2-1.4*ga, and more preferably higher than 77.0-1.4*ga. The fracture toughness (K1c) along the orientation of Long Transverse - Rolling (T-L) is higher than 28-1.0*ga, preferably higher than 29.5-1.0*ga. The fracture toughness (K1c) along the orientation of Rolling - Long Transverse (L-T) is higher than 28.8-0.6*ga, preferably higher than 30.8-0.6*ga, and more preferably higher than 31.8-0.6*ga. The units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

[0043] Corrosion resistance is a key design consideration for airframe manufacturers. The MASTMASSIS test is generally considered to be a good representative accelerated corrosion test method for Al-Li based alloys.

[0044] The MASTMASSIS test was based on ASTM G85-11 Annex-2 under dry-bottom conditions. The sample size was 4.5" L x 4.5" LT at middle of sheet thickness. The temperature of the exposure chamber through the duration of the test was 49 ± 2 °C. The testing through thickness location is T/2 (center of thickness). The testing plane is L-LT plane. The testing duration times were 24, 48, 96, 168, 336, 504, and 672hrs.

[0045] FIG. 10 gives the typical surface appearances after 672 hours MASTMASSIS testing exposure times. The left photo is from invention alloy Sample #6 with 3 inch plate thickness and right photo is from invention alloy Sample #11 with 6 inch plate thickness. The tested surfaces are very clean and shiny. No exfoliation is evident for all the exposure times. The excellent corrosion resistance of pitting/EA can be concluded for all exposure times for all invention alloy plates.

[0046] Stress corrosion cracking (SCC) resistance is also critical for aerospace application. The standard stress corrosion cracking resistance testing was performed in accordance with the requirements of ASTM G47 which is alternate immersion in a 3.5% NaCl solution under constant deflection. Three specimens were tested per sample. The stress

levels are 45 ksi and 50 ksi.

[0047] Table 6 gives the SCC testing results for Sample 6, 7, 8, 10 with final production ageing treatment. All specimens survived 30 days testing without failures under 45 ksi or 50 ksi stress levels in ST direction.

Table 6: The SCC testing results for Sample 6, 7, 8, 10 with final production ageing treatment

			•	•		
Sample ID	Lot	Gage, in	Stress	Repeat 1	Repeat 2	Repeat 3
6	187292B8	3.0	45	>30days	>30days	>30days
7	652929A1	3.0	45	>30days	>30days	>30days
7	652929A1	3.0	45	>30days	>30days	>30days
8	187267B0	3.2	50	>30days	>30days	>30days
10	130369B2	60	45	>30days	>30days	>30days

[0048] The fatigue property was tested in accordance with the requirements of ASTM E466. Four LT smooth specimens were tested from each plate at plate thickness center along long transverse (LT) direction. Specimen was tested at 240MPa (35 ksi). Table 7 gives the fatigue testing results of invention alloy plates. The majority of fatigue test specimens had no failures after 300,000 cycles and all plates met the common industrially accepted criterion, i.e. 120,000 cycles of logarithm average of four specimens.

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Table 7: The smooth fatigue testing results of invention alloy plates

Sample ID	Lot#	Gage, in	Specimen-1	Specimen-2	Specimen-3	Specimen-4	Log Average
1	130432B8	1	>300,000	>300,000	>300,000	>300,000	>300,000
2	130408B8	2	>300,000	>300,000	>300,000	>300,000	>300,000
3	130275B1	3	>300,000	>300,000	>300,000	>300,000	>300,000
4	130285B0	3	>300,000	>300,000	>300,000	>300,000	>300,000
5	187413B0	3	>300,000	>300,000	>300,000	>300,000	>300,000
6	187292B8	3	>300,000	>300,000	>300,000	>300,000	>300,000
7	652929A1	3	289,683	196,242	244,917	>300,000	>254,222
8	187267B0	3.2	>300,000	>300,000	>300,000	>300,000	>300,000
9	130415B3	4	>300,000	>300,000	>300,000	>300,000	>300,000
10	130369B2	6	126,731	157,529	117,225	121,511	129,858
11	187382B7	6	243,681	>300,000	285,136	>300,000	>281,209

[0049] The material performance is strongly related to material grain structure, which is greatly affected by alloy chemical composition along with thermal mechanical processing procedure. Specifically for Al-Li plate products, an unrecrystallized grain structure is desirable for better strength, fracture toughness and corrosion resistance performance. FIG. 11 to 15 gives the grain structures of different thickness invention alloy plates. All the invention alloy plates have unrecrystallized grain structures at both quarter thickness (T/4) and middle thickness (T/2).

[0050] While specific embodiments of the invention have been disclosed, it will be appreciated by those skilled in the art that various modifications and alterations to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth if the appended claims and any and all equivalents thereof. **[0051]** What is disclosed is:

1. A low cost, low density, and high performance Al-Li alloy comprising:

from 3.6 to 4.1 wt. % Cu, from 0.8 to 1.05 wt. % Li,

from 0.6 to 1.0 wt.% Mg, from 0.2 to 0.6 wt.% Mn,

less than 0.05 wt.% Ag, less than 0.2 wt.% Zn,

from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements

up to 0.10 wt.% Ti, up to 0.12 wt.% Si,

up to 0.15 wt.% Fe,

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up to 0.15 wt. % each incidental elements, with the total incidental elements not exceeding 0.35 wt. %,

with the balance being aluminum, and

wherein the amount of Cu in weight percent is at least equal to or higher than four times the amount of Li in weight percent.

- 2. The aluminum-lithium alloy of statement 1, comprising 3.7 to 4.0 wt. % Cu.
- 3. The aluminum-lithium alloy of statement 1, comprising 0.9 to 1.0 wt. % Li.
- 4. The aluminum-lithium alloy of statement 1, comprising 0.7 to 0.9 wt. % Mg.
- 5. The aluminum-lithium alloy of statement 1, wherein no Ag is intentionally added to the aluminum alloy.
- 6. The aluminum-lithium alloy of statement 1, wherein no Zn is intentionally added to the aluminum alloy.
- 7. The aluminum-lithium alloy of statement 1, comprising less than 0.10 wt % Zn.
- 8. The aluminum-lithium alloy of statement 1, comprising less than 0.05 wt % Zn.
- 9. The aluminum-lithium alloy of statement 1, comprising a maximum of 0.05 wt. % Si.
- 10. The aluminum-lithium alloy of statement 1, comprising a maximum of 0.08 wt.% Fe.
- 11. A low cost, low density, and high performance Al-Li alloy comprising:

from 3.7 to 4.0 wt. % Cu, from 0.9 to 1.0 wt. % Li, from 0.7 to 0.9 wt.% Mg, from 0.2 to 0.6 wt.% Mn,

less than 0.05 wt.% Ag, less than 0.2 wt.% Zn,

from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements

up to 0.10 wt.% Ti, up to 0.12 wt.% Si,

up to 0.15 wt.% Fe,

up to 0.15 wt. % each incidental elements, with the total of these incidental elements not exceeding 0.35 wt. %, with the balance being aluminum, and

wherein the amount of Cu in weight percent is at least equal to or higher than four times the amount of Li in weight percent.

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- 12. The aluminum-lithium alloy of any of statements 1 to 11, wherein said aluminum-lithium alloy is in the form of a rolled, extruded, or forged product, and has a thickness from about 0.5 to about 8.0 inch.
- 13. The aluminum-lithium alloy of statement 12, wherein said aluminum-lithium alloy has a thickness from about 0.5 to about 6.0 inch.
- 14. A rolled product comprising an aluminum-lithium alloy according to any of statements 1 to 11, having a thickness from about 0.5 to about 8.0 inch., exhibiting in a solution heat-treated, quenched, stretched and artificially aged condition:

a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 75.0-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 71.2-1.4*ga., a minimum Fracture Toughness (K1c) along the orientation of Long Transverse - Rolling (T-L) of 28-1.0*ga., and a minimum Fracture Toughness (K1c) along the orientation of Rolling - Long Transverse (L-T) of 28.8-0.6*ga., wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

²⁵ 15. A rolled product comprising an aluminum-lithium alloy according to any of statements 1 to 11, having a thickness from about 0.5 to about 8.0 inch., exhibiting in a solution heat-treated, quenched, stretched and artificially aged condition:

a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 76.2-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 72.2-1.4*ga., a minimum Fracture Toughness (K1c) along the orientation of Long Transverse - Rolling (T-L) of 29-1.0*ga., and a minimum Fracture Toughness (K1c) along the orientation of Rolling - Long Transverse (L-T) of 30.8-0.6*ga, wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

16. A rolled product comprising an aluminum-lithium alloy according to any of statements 1 to 11, having a thickness from about 0.5 to about 8.0 inch., exhibiting in a solution heat-treated, quenched, stretched and artificially aged condition:

a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 77.0-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 72.7-1.4*ga., a minimum Fracture Toughness (K1c) along the orientation of Long Transverse - Rolling (T-L) of 29.5-1.0*ga., and a minimum Fracture Toughness (K1c) along the orientation of Rolling - Long Transverse (L-T) of 31.8-0.6*ga, wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

- 45 17. The rolled product of any of statements 14 to 16, wherein said product alloy has a thickness from about 0.5 to about 6.0 inch.
 - 18. A method of manufacturing a low cost, low density, and high performance Al-Li alloy, the method comprising:
 - a. casting stock of an ingot of aluminum alloy comprising the aluminum-lithium alloy product according to any one of statements 1-17 producing a cast stock
 - b. homogenizing the cast stock producing a homogenized cast stock;
 - c. hot working the homogenized cast stock by one or more methods selected from the group consisting of rolling, extrusion, and forging forming a worked stock;
 - d. solution heat treating (SHT) the worked stock, producing a SHT stock;
 - e. cold water quenching said SHT stock to produce a cold water quenched SHT stock;
 - f. stretching the cold water quenched SHT stock to produce stretched stock; and
 - g. artificially ageing of the stretched stock.

19. The method of statement 18, wherein said step of homogenizing includes homogenizing at temperatures from 482 to 543°C (900 to 1010°F); wherein said step of hot working includes hot rolling at a temperature of 357 to 482°C (675 to 900°F); wherein said step of solution heat treating includes solution heat treated at temperature range from 482 to 538°C (900 to 1000°F); wherein said step of stretching includes stretching from 2% to up to 15%; and wherein said step of artificially ageing includes aging at a temperature of from 121 to 205°C (250 to 400°F) and the aging time can be in the range of 2 to 60 hours.

20. The method of statement 19, wherein said step of artificially ageing includes aging at a temperature of from 149 to 182°C (300 to 360°F) and the aging time can be in the range of 10 to 48 hours.

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Claims

1. A low cost, low density, and high performance Al-Li alloy comprising:

from 3.6 to 4.1 wt. % Cu, from 0.8 to 1.05 wt. % Li, from 0.6 to 1.0 wt.% Mg, from 0.2 to 0.6 wt.% Mn,

less than 0.05 wt.% Ag, less than 0.2 wt.% Zn,

from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements,

up to 0.10 wt.% Ti,

up to 0.12 wt.% Si,

up to 0.15 wt.% Fe,

up to 0.15 wt. % each incidental elements, with the total incidental elements not exceeding 0.35 wt. %, with the balance being aluminum, and

wherein the amount of Cu in weight percent is at least equal to or higher than four times the amount of Li in weight percent.

- 2. The aluminum-lithium alloy of claim 1, comprising 3.7 to 4.0 wt. % Cu.
- 30 3. The aluminum-lithium alloy of claim 1 or 2, comprising 0.9 to 1.0 wt. % Li.
 - The aluminum-lithium alloy of any one of claims 1 to 3, comprising 0.7 to 0.9 wt. % Mg.
 - 5. The aluminum-lithium alloy of any one of claims 1 to 4, wherein no Ag is intentionally added to the aluminum alloy.

6. The aluminum-lithium alloy of any one of claims 1 to 5, wherein no Zn is intentionally added to the aluminum alloy.

7. The aluminum-lithium alloy of any one of claims 1 to 5, comprising less than 0.10 wt % Zn optionally comprising less than 0.05 wt % Zn.

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8. The aluminum-lithium alloy of any one of claims 1 to 7, comprising a maximum of 0.05 wt. % Si;

and / or

comprising a maximum of 0.08 wt.% Fe.

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9. The aluminum-lithium alloy of any one of claims 1 to 8, comprising:

from 3.7 to 4.0 wt. % Cu, from 0.9 to 1.0 wt. % Li,

from 0.7 to 0.9 wt.% Mg, from 0.2 to 0.6 wt.% Mn,

less than 0.05 wt.% Ag, less than 0.2 wt.% Zn,

from 0.03 to 0.16 wt. % of at least one grain structure control element selected from the group consisting of Zr, Sc, Cr, V, Hf, and other rare earth elements

up to 0.10 wt.% Ti,

up to 0.12 wt.% Si,

up to 0.15 wt.% Fe,

up to 0.15 wt. % each incidental elements, with the total of these incidental elements not exceeding 0.35 wt. %, with the balance being aluminum, and

wherein the amount of Cu in weight percent is at least equal to or higher than four times the amount of Li in

weight percent.

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- **10.** The aluminum-lithium alloy of any of claims 1 to 9, wherein said aluminum-lithium alloy is in the form of a rolled, extruded, or forged product, and has a thickness from about 0.5 to about 8.0 inch; wherein, optionally, said aluminum-lithium alloy has a thickness from about 0.5 to about 6.0 inch.
- **11.** A rolled product comprising an aluminum-lithium alloy according to any of claims 1 to 9, having a thickness from about 0.5 to about 8.0 inch., exhibiting in a solution heat-treated, quenched, stretched and artificially aged condition:
- a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 75.0-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 71.2-1.4*ga., a minimum Fracture Toughness (Klc) along the orientation of Long Transverse Rolling (T-L) of 28-1.0*ga., and a minimum Fracture Toughness (Klc) along the orientation of Rolling Long Transverse (L-T) of 28.8-0.6*ga, wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.
 - **12.** The rolled product of claim 11 comprising an aluminum-lithium alloy according to any of claims 1 to 9, having a thickness from about 0.5 to about 8.0 inch., either exhibiting in a solution heat-treated, guenched, stretched and artificially aged condition:
- a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 76.2-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 72.2-1.4*ga., a minimum Fracture Toughness (KIc) along the orientation of Long Transverse Rolling (T-L) of 29-1.0*ga., and a minimum Fracture Toughness (KIc) along the orientation of Rolling Long Transverse (L-T) of 30.8-0.6*ga, wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively;

exhibiting in a solution heat-treated, quenched, stretched and artificially aged condition:

a minimum Tensile Yield Strength (TYS) along rolling (L) direction as function of plate gage (ga) of 77.0-1.4*ga., a minimum Tensile Yield Strength (TYS) along long transverse (LT) direction of 72.7-1.4*ga., a minimum Fracture Toughness (KIc) along the orientation of Long Transverse - Rolling (T-L) of 29.5-1.0*ga., and a minimum Fracture Toughness (KIc) along the orientation of Rolling - Long Transverse (L-T) of 31.8-0.6*ga, wherein the units for gage (ga), strength, and fracture toughness are inch, ksi, and ksi*in^{1/2} respectively.

- 13. The rolled product of claim 11 or 12, wherein said product alloy has a thickness from about 0.5 to about 6.0 inch.
 - 14. A method of manufacturing a low cost, low density, and high performance Al-Li alloy, the method comprising:
 - a. casting stock of an ingot of aluminum alloy comprising the aluminum-lithium alloy product according to any one of claims 1-13 producing a cast stock;
 - b. homogenizing the cast stock producing a homogenized cast stock;
 - c. hot working the homogenized cast stock by one or more methods selected from the group consisting of rolling, extrusion, and forging forming a worked stock;
 - d. solution heat treating (SHT) the worked stock, producing a SHT stock;
 - e. cold water quenching said SHT stock to produce a cold water quenched SHT stock;
 - f. stretching the cold water quenched SHT stock to produce stretched stock; and
 - g. artificially ageing of the stretched stock.
 - **15.** The method of claim 14, wherein said step of homogenizing includes homogenizing at temperatures from 482 to 543°C (900 to 1010°F); wherein said step of hot working includes hot rolling at a temperature of 357 to 482°C (675 to 900°F); wherein said step of solution heat treating includes solution heat treated at temperature range from 482 to 538°C (900 to 1000°F); wherein said step of stretching includes stretching from 2% to up to 15%; and wherein said step of artificially ageing includes aging at a temperature of from 121 to 205°C (250 to 400°F) and the aging time can be in the range of 2 to 60 hours
- wherein, optionally, said step of artificially ageing includes aging at a temperature of from 149 to 182°C (300 to 360°F) and the aging time can be in the range of 10 to 48 hours.

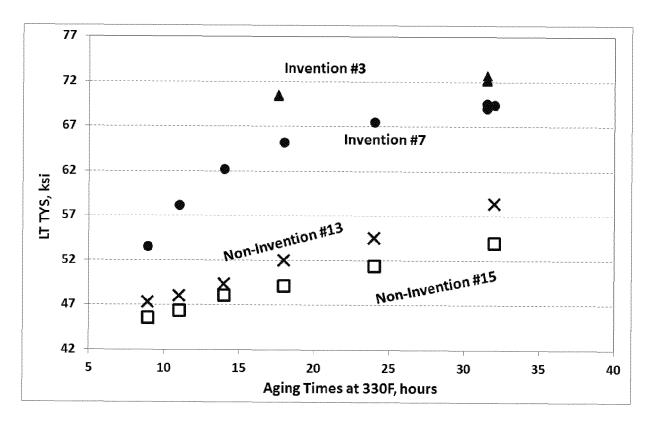


FIG. 1

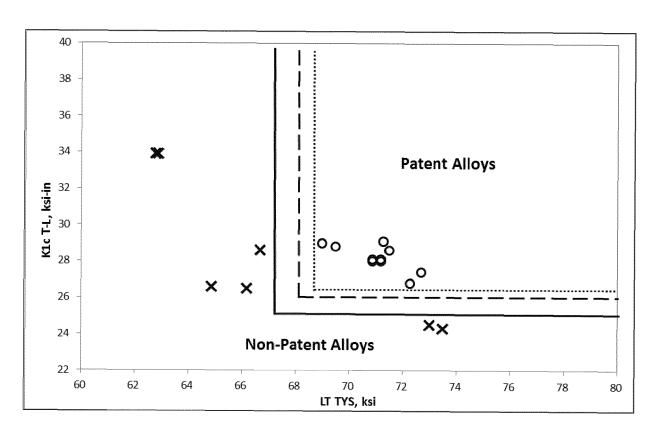


FIG. 2

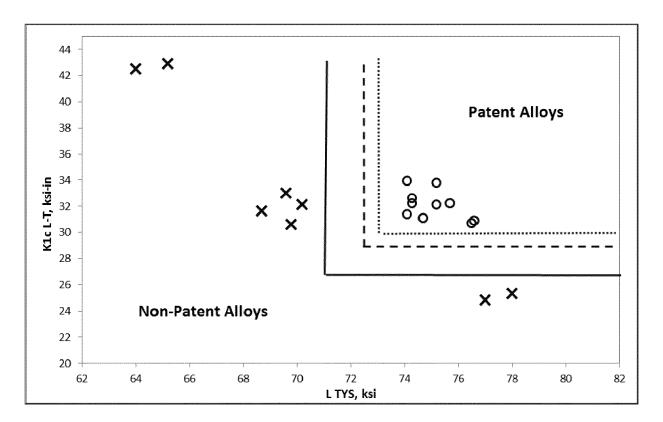


FIG. 3

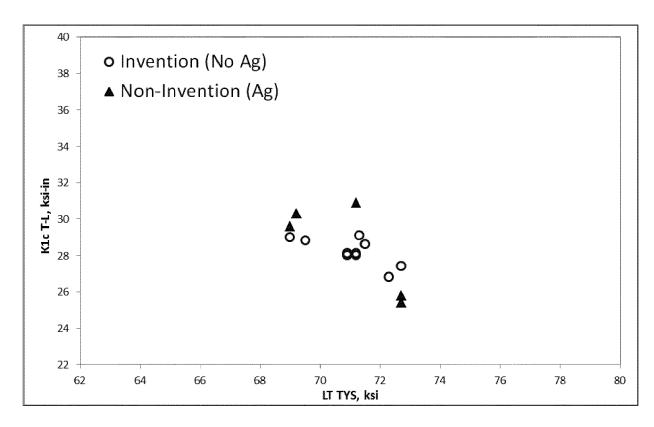


FIG. 4

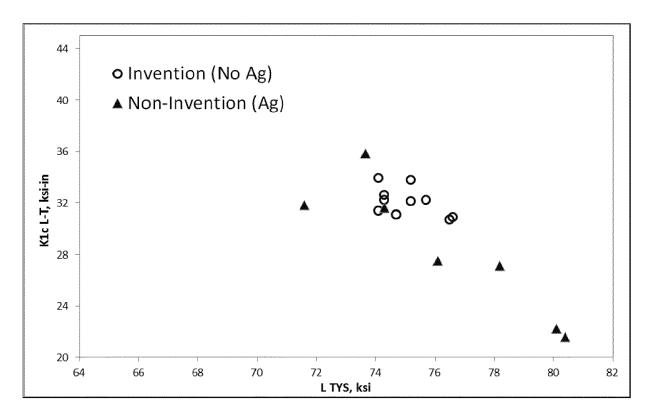


FIG. 5

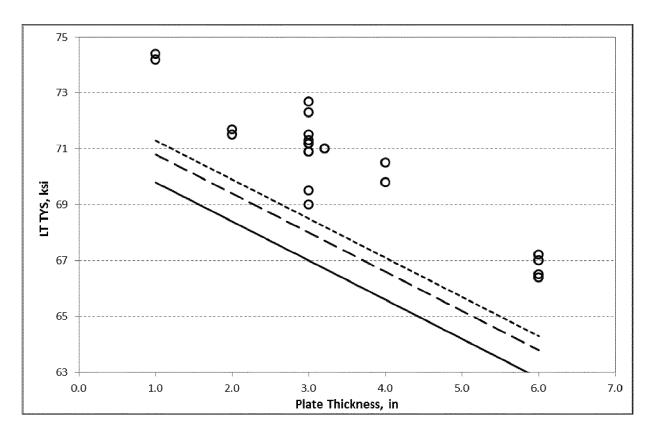


FIG. 6

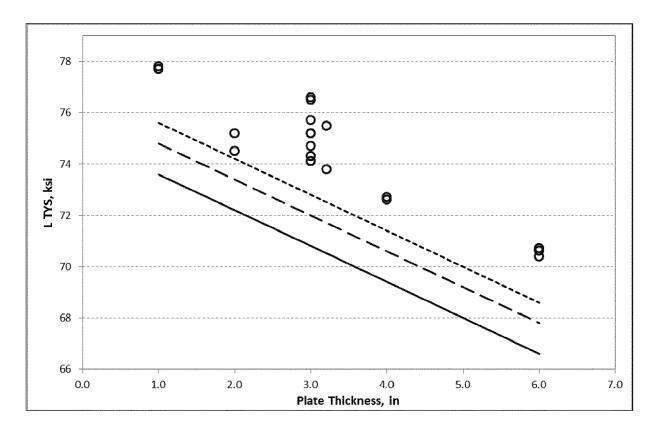


FIG. 7

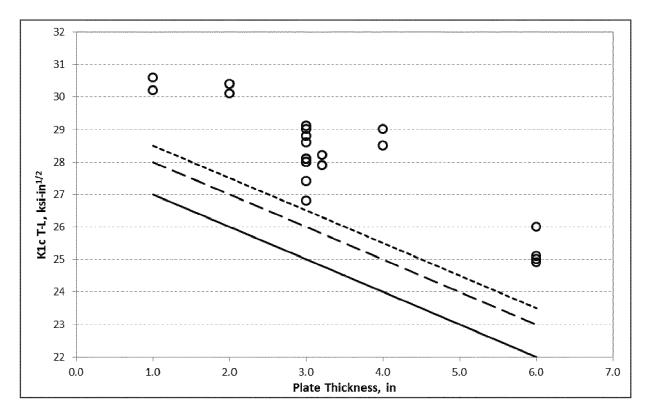


FIG. 8

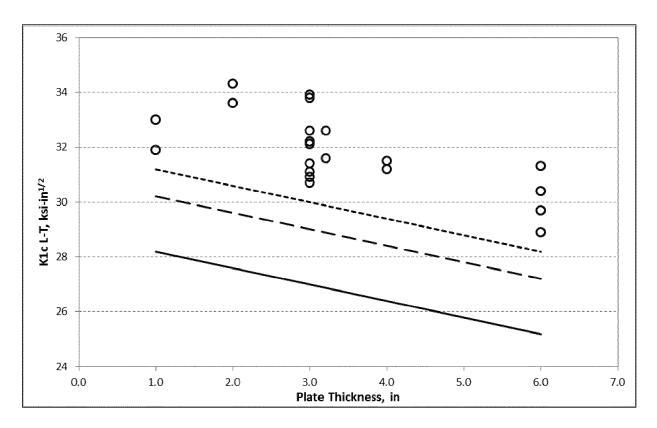


FIG. 9

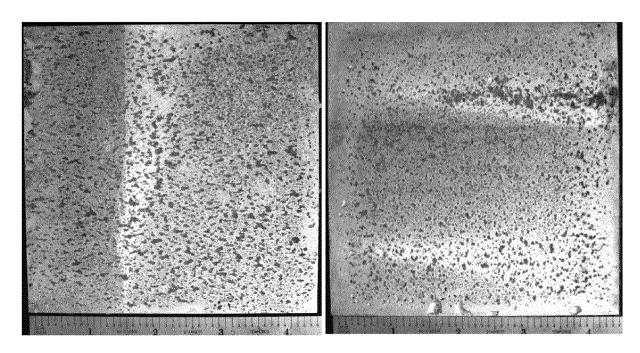


FIG. 10

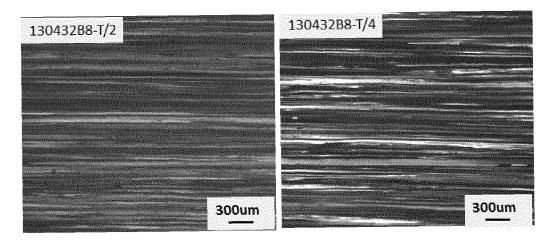


FIG. 11

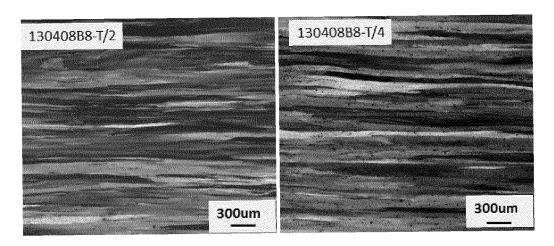


FIG. 12

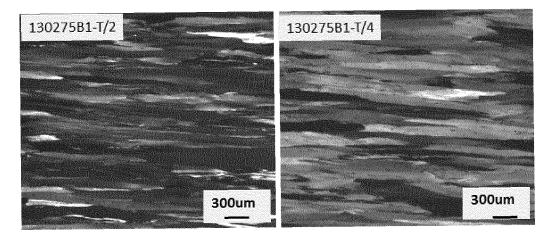


FIG. 13

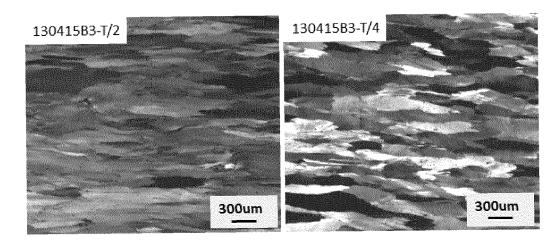


FIG. 14

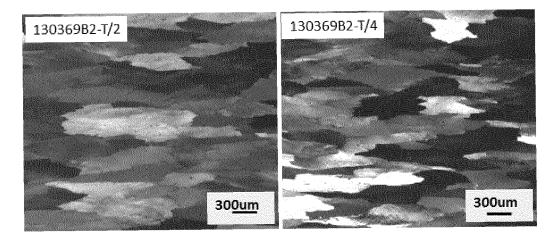


FIG. 15



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İ	The present search report has b	een drawn up for all claims				
Place of search		·	te of completion of the search		Examiner	
Munich		15 May 20	19	Brown, Andrew		
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			& : member of the same patent family, corresponding document			

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