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(54) **HIGH STRENGTH 7XXX SERIES ALUMINUM ALLOY PRODUCTS AND METHODS OF MAKING SUCH PRODUCTS**

(57) The present invention is directed to a thick plate high strength 7xxx aluminum alloy product comprising 8.0 to 8.4 wt.% Zn, 1.5 to 2.0 wt.% Mg, 1.1 to 1.5 wt.% Cu, and 0.05 to 0.15 wt.% Zr, 4.0 to 5.3 of Zn/Mg weight percentage ratio, 0.14 to 0.19 of Cu/Zn weight percentage ratio, and 10.7 to 11.6 wt.% of Cu+Mg+Zn. This alloy can be fabricated to produce 3-10 inch thick plate, extrusion or forging products, and is especially suitable for aerospace structural components, especially large commercial airplane wing structure applications. The product provides high strength, high damage tolerance performance as well as better corrosion resistance performance suitable for aerospace application.

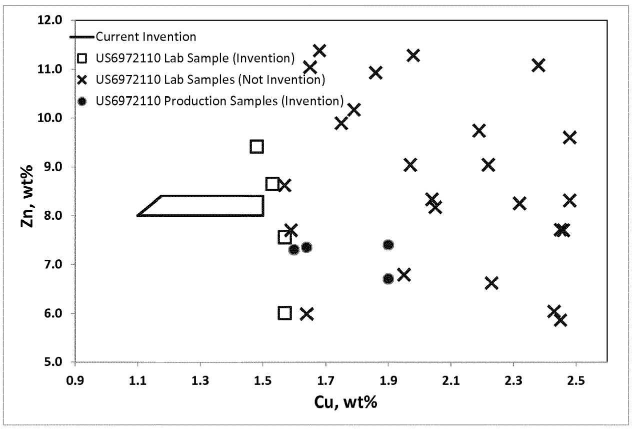

FIG. 1

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This present invention generally relates to high strength 7xxx aluminum alloy products and methods for making such products.

2. Background

[0002] High strength 7xxx (Al-Zn) aluminum alloy products are extensively used in aerospace structure application, in which the material strength, fracture toughness, fatigue resistance, and corrosion resistance are required simultaneously. In order to aggressively reduce aircraft weight for fuel efficiency, thick plate, high strength 7xxx aluminum alloys are being pursued assertively by airframe manufacturers and aluminum material manufacturers. This is especially critical for large size commercial aircraft in which a significant amount of large parts are fabricated through monolithic fabrication processing for cost reduction. A thick plate is required for such large monolithic components. However, the combination of high strength and high thickness imposes an extreme metallurgical challenge to produce such thick plate, high strength, aluminum products for the aluminum manufacturing industry. Due to such extreme metallurgical challenges, only very limited commercial products are currently available for this key aerospace application based on the most recent "Aluminum Association: 2011 Yellow/Tan Sheets" and "Addendum to 2011 Edition of Yellow/Tan Sheets" for aluminum and aluminum alloy products registered in Aluminum Association.

[0003] The chemical composition of an aluminum alloy product has a phenomenal influence on the final production properties. In 7xxx series aluminum alloys, the high levels of Zn, Mg and Cu are usually added in order to achieve high strength and corrosion resistance. However, compositions with too high Zn and Mg content generally negatively affect stress corrosion cracking (SCC) resistance and fracture toughness performance. Additionally, concentrations of Cu that are too high also significantly increase the risk of high level of undesirable coarse Al_2MgCu particles and macro-segregation from plate surface to center. During casting, large Al_2CuMg particles can form during solidification. Such large particles normally can be dissolved during subsequent homogenization and solution heat treatment. If the Cu content is too high, however, this could promote extreme high levels of Al_2CuMg particles, which cannot be dissolved during subsequent thermal treatments. Those undissolved Al_2CuMg particles significantly reduce the strength and damage tolerance performance.

[0004] In order to achieve aging precipitation hardening, Cu, Mg and Zn alloying element have to be in solid solution before aging. This is generally achieved through the processing steps of Solution Heat Treatment, followed by cold water quench. With the higher Mg, Zn and Cu levels, it is extremely difficult to dissolve all constituent particles, which consume a significant amount of added alloying elements, into solid solution. More importantly, the higher levels of alloying element increase the potential coarse particles precipitation during quenching. This is especially critical for thick plate with slow cooling rate during quench. It is easier to achieve better strength and other properties for a thin cross section product than for a thick cross section product of high strength 7xxx aluminum alloy. As cross section increases the quench related cooling rate in the plate significantly decreases, resulting in not only lowering overall strength but also the fracture toughness. This phenomenon is also referred to as high strength 7xxx thick plate quench sensitivity, which is of great concern in high strength 7xxx aluminum alloy.

[0005] In summary, the combination of the complicated age hardening behavior, specific quenching condition for thick plate, strict damage tolerance and corrosion requirements necessitates a very fine, optimized, and probably very narrow chemistry range that needs to be discovered. There is a strong need of such new alloys in aerospace application, especially for large size commercial aircraft.

BRIEF SUMMARY OF THE INVENTION

[0006] Thick plate high strength 7xxx aluminum alloy products comprise Zn from 8.0 to 8.4 wt.%, Mg from 1.5 to 2.0 wt.% and Cu from 1.1 to 1.5 wt.%, 4.0 to 5.3 of Zn/Mg weight percentage ratio, 0.14 to 0.19 of Cu/Zn weight percentage ratio, and 10.7 to 11.6 wt.% of Cu+Mg+Zn, one or more elements selected from the group consisting of up to 0.2% Zr, up to 0.2% Sc, up to 0.2% Hf, and the balance A1, and impurities.

[0007] In one embodiment of the present invention, the thick plate high strength 7xxx aluminum alloy product is produced using precisely controlled thermal mechanical processes.

[0008] Preferably, the alloy can be fabricated to a thickness of 3-10 inch, more preferably 4-10 inch, even more preferably 4-8 inches thickness plates, extrusions, and forging products. In one embodiment, the aluminum alloy product also provides necessary short-transverse ductility, damage tolerance performance as well as corrosion resistance performance required for aerospace applications. Such plates, forgings and extrusions are suitable for use in making aerospace structural components like large commercial airplane wing components,

[0009] It has been surprisingly discovered that an aluminum alloy having a high Zn chemistry, associated with precise Mg and Cu content, Zn/Mg and Cu/Zn weight percentage ratios along with deliberately controlled thermal mechanical processing, is capable of producing 3 to 10" gauge thick products with high strength, better damage tolerance, and corrosion properties never achieved before.

[0010] In one embodiment, the high strength 7xxx thick plate aluminum product offers a promising opportunity for significant fuel efficiency and cost reduction advantage for commercial airplanes, especially large size commercial aircraft. An example of such application of the present invention is the integral design wing box, which requires thick cross section 7xxx aluminum alloy products. Material strength is a key design factor for weight reduction. Also, important are Short Transverse (ST) tensile ductility, damage tolerance, corrosion resistance performance, such as exfoliation and stress corrosion resistance, and fatigue crack growth resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] 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 a comparison of the Cu and Zn levels between 32 chemistries in US patent 6,972,110 and present invention range;
FIG. 2 is a graph showing the strength and fracture toughness of 4" invention and non-invention alloy plates;
FIG. 3 is a graph showing the strength and fracture toughness of 6" invention and non-invention alloy plates;
FIG. 4 is a graph showing the strength and fracture toughness of 7.5" invention and non-invention alloy plates;
FIG. 5 is a graph showing the effect of Cu+Mg+Zn on fracture toughness of 7.5" thick plate showing that too low or too high Cu+Mg+Zn gives worse fracture toughness;
FIG. 6 is a graph showing the effect of Cu/Zn ratio on fracture toughness of 7.5" thick plate; and
FIG. 7 is a graph showing the effect of Zn/Mg ratio on fracture toughness of 6" thick plate.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The thick plate high strength 7xxx aluminum alloy product comprises 8.0 to 8.4 wt.% Zn, 1.5 to 2.0 wt.% Mg, 1.1 to 1.5 wt.% Cu, 4.0 to 5.3 of Zn/Mg weight percentage ratio, 0.14 to 0.19 of Cu/Zn weight percentage ratio, and 10.7 to 11.6 wt.% of Cu+Mg+Zn, one or more elements selected from the group consisting of up to 0.2 wt.% Zr, up to 0.2 wt.% Sc, and up to 0.2 wt.% Hf, and the balance A1, and impurities.

[0013] The upper or lower limits for the ranges provided above are understood to include all of the numbers provided within the range. It is understood that within the range of 8.0 to 8.4 wt.% Zn, the upper or lower limit for the amount ofZn may be selected from 8.0, 8.1, 8.2, 8.3 and 8.4 wt.% Zn. It is understood that within the range of 1.5 to 2.0 wt.% Mg, the upper or lower limit for the amount of Mg may be selected from 1.5, 1.6, 1.7, 1.8, 1.9 and 2.0 wt.% Mg. It is understood that within the range of 1.1 to 1.5 wt.% Cu, the upper or lower limit for the amount of Cu may be selected from 1.1, 1.2, 1.3, 1.4 and 1.5 wt.% Cu. It is understood that within the range of 4.0 to 5.3 Zn/Mg weight percentage ratio, the upper or lower limit for the Zn/Mg weight percentage ratio may be selected from 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5.0, 5.1, 5.2 and 5.3 Zn/Mg weight percentage ratio. It is understood that within the range of 0.14 and 0.19 Cu/Zn weight percentage ratio, the upper or lower limit for the Cu/Zn weight percentage ratio may be selected from 0.14, 0.15, 0.16, 0.17, 0.18 and 0.19 Cu/Zn weight percentage ratio. It is understood that within the range of 10.7 to 11.6 wt.% Cu+Mg+Zn, the upper or lower limit for the amount of Cu+Mg+Zn may be selected from 10.7, 10.8, 10.9, 11.0, 11.1, 11.2, 11.3, 11.4, 11.5 and 11.6 wt.% Cu+Mg+Zn.

[0014] The unique chemistry range along with the ratios of Zn/Mg and Cu/Zn in accordance with the present invention gives the distinctive thermodynamic and kinetic behaviors of precipitations during quenching and aging heat treatment.

[0015] Zn and Mg are generally added to produce metastable and/or stable $MgZn_2$ (η' and/or η Phase) and its variant phases, which are the predominant precipitation hardening phases. However, the actual chemical compositions of age hardening phases are far more complicated than 1:2 atomic ratio of Mg/Zn. The Zn/Mg weight percentage ratio in the range of 4.0 to 5.3 surprisingly gives the optimized physical metallurgy suitable for thick plate high strength and fracture toughness properties.

[0016] Copper is generally added in order to improve SCC resistance performance. Cu can significantly increase the breakdown potentials, resulting in better corrosion resistance performance. During quenching and aging process, Cu can substitute with Zn in $MgZn_2$ type phase to form $Mg(ZnCuAl)_2$ phases in grain boundary and/or matrix. Therefore, the level of Cu should be carefully considered for different Zn and Mg levels as well as the plate thickness which affects the precipitation during quenching. The Cu/Zn ratio in the range of 0.14 to 0.19 surprisingly gives the optimized physical metallurgy suitable for thick plate high strength and fracture toughness properties.

[0017] In one embodiment, the thick plate high strength 7xxx aluminum alloy product includes ≤0.12 wt.% Si, preferably ≤0.05 wt.% Si. In one embodiment, the thick plate high strength 7xxx aluminum alloy product includes ≤0.15 wt.% Fe, preferably ≤0.08 wt.% Fe. In one embodiment, the thick plate high strength 7xxx aluminum alloy product includes ≤ 0.2 wt.% Mn. In one embodiment, the thick plate high strength 7xxx aluminum alloy product includes ≤0.04 wt.% Cr, preferably no Cr is added to the alloy other than that provided as an impurity. In one embodiment, the thick plate high strength 7xxx aluminum alloy product includes ≤0.06 wt.% Ti.

[0018] The thick plate high strength 7xxx aluminum alloy product of the present invention may also include low level of "impurities" that are not included intentionally. The "impurities" means any other elements except above described Al, Zn, Mg, Cu, Zr, Sc, Hf, Si, Fe, Mn, Cr and Ti.

[0019] Preferably, the thick plate high strength 7xxx aluminum alloy products, such as plates, forgings and extrusions, are suitable for use in making aerospace structural components like large commercial airplane wing components. Preferably, the alloy has a thickness of 3 - 10 inch, preferably 4 - 10 inch, more preferably 4 - 8 inch for producing plates, extrusion, and forging products. In one embodiment, the aluminum alloy product also provides necessary damage tolerance performance as well as corrosion resistance performance required for aerospace application.

[0020] The present invention has various advantageous mechanical and physical properties. In one embodiment of the present invention the term "high strength" means the minimum Long-Transverse (LT) yield strength at quarter-thickness (th/4) is (74 - 0.56 * plate thickness in inch) ksi, and the minimum LT ultimate strength at th/4 is (78 - 0.36 * plate thickness in inch) ksi. In one embodiment of the present invention, the thick plate high strength 7xxx aluminum alloy product has fracture toughness values of a minimum 27 ksi-in$^{1/2}$ at th/4. In one embodiment of the present invention, the ST tensile ductility is at least (7 - 0.5 * plate thickness in inch)%. In one embodiment of the present invention improved exfoliation, such as better than or equal to EA EXCO rating per ASTM G34 at th/10 and th/2, may be observed. In one embodiment of the present invention, improved stress corrosion resistance, such as at least 20 days at 25 ksi and preferably at least 20 days at 30 ksi per ASTM G47 in a T7651 temper, may be observed.

[0021] In one embodiment of the present invention, the thick plate high strength 7xxx aluminum alloy product is produced using a precise chemistry range along with precisely controlled thermal mechanical processes. In one embodiment, this thick plate high strength 7xxx aluminum alloy product is used in aerospace applications.

[0022] As indicated, the thick plate high strength 7xxx aluminum alloy product may be used to produce plates, extrusions, and forging products. In one embodiment, the thick plate high strength 7xxx aluminum alloy product is used to produce a wrought product that is a rolled thick plate including any of the chemistries provided in the above-mentioned embodiments. The rolled thick plate may be manufactured using known process conditions such as homogenization, hot-rolling, solution heat treatments and ageing treatments.

[0023] In one embodiment, ingots of the thick plate high strength 7xxx aluminum alloy product may be cast, homogenized, hot rolled, solution heat treated, cold water quenched, optionally stretched, and aged to desired temper. In one embodiment, the thick plate high strength 7xxx aluminum alloy is a plate subjected to a final T7651 and T7451 tempers in the thickness range from 3 inch to 10 inch. The ingots may be homogenized at temperatures from 454 to 491 °C (849 to 916°F). The hot rolling start temperature may be from 385 to 450 °C (725 to 842°F). The exit temperature may be in a similar range as the start temperature. The plates may be solution heat treated at temperature range from 454 to 491 °C (849 to 916°F). The plates are cold water quenched to room temperature and may be stretched at about 1.5 to 3%. The quenched plate may be subjecting to any known aging practices known by those of skill in the art including, but not limited to, two-step aging practices that produce a final T7651 or T7451 temper. When using a T7651 temper, the first stage temperature may be in the range of 100 to 140 °C (212 to 284 °F) for 4 to 24 hours and the second stage temperature may be in the range of 135 to 200 °C (275 to 392 °F) for 5 to 20 hours.

[0024] Table 1 compares the present invention alloy chemistry with other aluminum alloy products currently available based on the most recent "Aluminum Association: 2014 Yellow/Tan Sheets" and "Aluminum Standard and Data 2013" for more than 4" thick plates with T7651 temper. It should be mentioned that although there are more commercial alloys available for lower than 4" thickness plates and T7451 temper, only very few alloys are available for thicker than 4" plates with high strength T7651 temper.

[0025] As shown in Table 1, the invention alloy has distinguished chemistry with other alloys. AA7140 and AA7081 have much lower Zn than present invention alloy, and AA7085 has lower Zn than invention alloy. The Zn is very critical for high strength property. In addition, the Cu/Zn weight percentage ratios of AA7065 and AA7140 alloy are much higher than that of current invention alloy. The high Cu/Zn weight percentage ratio can significantly reduce the strength potential since the Cu may consume more Mg during solidification to form undesirable Al_2CuMg particles.

Table 1

Alloy	Gage Range	Cu, Min.	Cu, Max.	Mg, Min.	Mg, Max.	Zn, Min.	Zn, Max.	Zn/Mg, min.	Zn/Mg, max.	Cu/Zn, min.	Cu/Zn, max.	Mg+Cu+Zn, min.	Mg+Cu+Zn, max.
7140	4" to 10"	1.30	2.30	1.50	2.40	6.20	7.00	2.58	4.67	0.19	0.37	9.0	11.7
7081	1" to 6"	1.20	1.80	1.80	2.20	6.90	7.50	3.14	4.17	0.16	0.26	9.9	11.5
7085	4" to 7	1.30	2.00	1.20	1.80	7.00	8.00	3.89	6.67	0.16	0.29	9.5	11.8
7065	1" to 6"	1.90	2.30	1.50	1.80	7.10	8.30	3.94	5.53	0.23	0.32	10.5	12.4
Invention	**3" to 10"**	**1.1**	**1.5**	**1.5**	**2.0**	**8.0**	**8.4**	**4.00**	**5.30**	**0.14**	**0.19**	**10.7**	**11.6**

[0026] As shown in the Table 1, the closest product is AA7085-T7651, in which Zn is lower than the present invention. AA7085 was registered by Alcoa and described in United States Patent US 6,972,110. In this patent, 28 different chemistries were studied in lab scale samples and 4 commercial scale products. FIG. 1 shows a graph comparing the Cu and Zn levels between those 32 chemistries and present invention range. It clearly demonstrates the uniqueness of the current invention alloy. Although a very broad chemistry range was explored in US Patent 6,972,110, the chemistry range of the present invention alloy was not studied in US Patent 6,972,110.

[0027] 7xxx high strength aluminum alloys with high Zn were also explored in US Patent 6,790,407. It should be noticed that the alloys described in US Patent 6,790,407 intentionally require the addition of Cr, Ni, and hydrogen in certain levels for better grain structures, precipitations, and uniform non-metallic inclusions. In contrast, the present invention alloy requires none of these elements due to the potential negative impacts on fracture toughness. In US Patent 6,790,407, seven (7) alloys were specifically disclosed. All alloys except Alloy 2 in US Patent 6,790,407 have higher than 1.5 wt.% Cu. For Alloy 2 in US Patent 6,790,407, the Mg and Zn are much higher than those presently provided in the invention alloy which includes ranges of Cu and Mg are 1.1 to 1.5 wt.% and 1.5 to 2.0 wt.% respectively.

[0028] Although the following examples demonstrate various embodiments of the present invention, one of skill in the art should understand how additional thick plate high strength 7xxx aluminum alloy products can be fabricated in accordance with the present invention. The examples should not be construed to limit the scope of protection provided for the present invention.

Examples (Plant Trial)

[0029] Sixteen (16) industrial scale ingots were cast by commercial DC (Direct Chill) casting process and processed to different thickness plates. Table 2 gives the typical chemical compositions of selected plates with different gauges.

Table 2: Chemical compositions of industrial scale ingots

Sample ID	Patent Alloy	Si	Fe	Cu	Mg	Zn	Mn	Zr	Zn/Mg	Cu/Zn	Cu+Mg+Zn	Plate Thickness in
Alloy A	Yes	0.022	0.038	1.3	1.8	8.0	0.001	0.11	4.5	0.16	11.1	4
Alloy B	Yes	0.039	0.078	1.2	1.7	8.1	0.004	0.09	4.7	0.15	11.0	4
Alloy C	*No*	*0.04*	*0.063*	*1.2*	*2.1*	*8.1*	*0.005*	*0.10*	*3.9*	*0.15*	*11.4*	*4*
Alloy D	Yes	0.04	0.065	1.4	1.6	8.2	0.003	0.10	5.2	0.17	11.2	6
Alloy E	yes	0.039	0.054	1.5	1.6	8.2	0.133	0.04	5.0	0.18	11.3	6
Alloy F	Yes	0.032	0.055	1.2	1.7	8.2	0.001	0.10	4.9	0.15	11.1	6
Alloy G	*No*	*0.04*	*0.059*	*1.6*	*1.9*	*6.8*	*0.003*	*0.10*	*3.6*	*0.24*	*10.3*	*6*
Alloy H	*No*	*0.04*	*0.06*	*1.3*	*2.1*	*8.1*	*0.005*	*0.10*	*3.9*	*0.16*	*11.5*	*6*
Alloy I	Yes	0.035	0.06	1.4	1.6	8.2	0.003	0.11	5.1	0.18	11.2	7.5
Alloy J	Yes	0.039	0.062	1.5	1.6	8.2	0.003	0.11	5.1	0.18	11.2	7.5
Alloy K	Yes	0.033	0.054	1.3	1.9	8.0	0.002	0.11	4.1	0.16	11.2	7.5
Alloy L	Yes	0.039	0.056	1.4	1.7	8.1	0.129	0.04	4.8	0.17	11.2	7.5
Alloy M	*No*	*0.04*	*0.059*	*1.6*	*2.0*	*6.8*	*0.002*	*0.10*	*3.5*	*0.23*	*10.4*	*7.5*
Alloy N	*No*	*0.03*	*0.051*	*1.3*	*1.6*	*8.6*	*0.002*	*0.11*	*5.3*	*0.14*	*11.5*	*7.5*
Alloy O	*No*	*0.04*	*0.059*	*1.8*	*1.7*	*8.5*	*0.002*	*0.11*	*4.9*	*0.22*	*12.0*	*7.5*
Alloy P	*No*	*0.04*	*0.059*	*1.5*	*1.6*	*9.0*	*0.002*	*0.11*	*5.5*	*0.17*	*12.1*	*7.5*

[0030] Alloy A, B, D to F, and I to L are invention alloys. Alloy C is not an invention alloy since the Mg is too high and Zn/Mg weight percentage ratio is too low compared with the invention alloy. Alloy G is not an invention alloy since the Cu is too high, Zn is too low, Zn/Mg weight percentage ratio is too low, Cu/Zn weight percentage ratio is too high, and Cu+Mg+Zn is too low. Alloy H is not an invention alloy since the Mg is too high and Zn/Mg weight percentage ratio is too low. Alloy M is not an invention alloy since the Cu is too high, Zn is too low, Zn/Mg weight percentage ratio is too low, Cu/Zn weight percentage ratio is too high, and Cu+Mg+Zn is too low. Alloy N is not an invention alloy since the Zn is too high. Alloy O is not an invention alloy since the Cu is too high, Zn is too high, and Cu+Zn+Mg is too high. Alloy P is not an invention alloy since the Zn is too high, Zn/Mg weight percentage ratio is too high, and Cu+Mg+Zn is too high.

[0031] Ingots were homogenized, hot rolled, solution heat treated, quenched, stretched and aged to final T7651 temper plates in the thickness range from 4 inch to 7.5 inch. The ingots were homogenized at a temperature from 465 to 485 °C (869 to 905°F). The hot rolling start temperature is from 400 to 440 °C (752 to 824°F). The exit rolling temperature is in the similar range as start temperature. The rolling reduction of each pass was deliberately controlled to achieve target temperature during hot rolling process.

[0032] The plates were solution heat treated at temperature range from 470 to 485 °C (878 to 905°F), cold water quenched to room temperature and stretched at about 1.5 to 3%. A two-step aging practice was used to produce final T7651 temper. The first stage temperature is in the range of 110 to 130 °C (230 to 266 °F) for 4 to 12 hours and the second stage temperature is in the range of 145 to 160 °C (293 to 320 °F) for 8 to 20 hours.

[0033] Tables 3 give tensile and fracture toughness properties. The 0.2% offset yield strength (TYS) along transverse direction (LT) was measured at quarter thickness (T/4) under ASTM B557 specification. The plane strain fracture toughness (K_{1c}) in T-L orientations at quarter thickness (T/4) was measured under ASTM E399 using CT specimens.

Table 3: Tensile and fracture toughness properties of final T7651 temper plates

Sample ID	Patent Alloy	Plate Thickness in	LT TYS@T/4 ksi	LT UTS @T/4 ksi	LT Elongation @T/4 %	K1c T-L @T/4 ksi-in$^{1/2}$
Alloy A	Yes	4	72.2	77.8	10.4	28.65
Alloy B	Yes	4	73.2	77.6	11.0	27.2
Alloy C	*No*	*4*	*70.7*	*78.0*	*11.0*	*27.1*
Alloy D	Yes	6	73.0	78.0	6.9	27.9
Alloy E	yes	6	71.5	77.1	7.1	30.4
Alloy F	Yes	6	71.0	76.3	7.5	28.7
Alloy G	*No*	*6*	*69.1*	76.2	*8.3*	*26.1*
Alloy H	*No*	*6*	*69.9*	*77.7*	*7.9*	*24.8*
Alloy I	Yes	7.5	69.8	75.4	5.8	31.8
Alloy J	Yes	7.5	70.5	76.1	5.8	30.5
Alloy K	Yes	7.5	72.2	78.0	4.1	28.9
Alloy L	Yes	7.5	70.6	76.4	5.0	28.9
Alloy M	*No*	*7.5*	*70.1*	*77.1*	*5.0*	*26.7*
Alloy N	*No*	*7.5*	*68.2*	*74.3*	*5.2*	*30.1*
Alloy O	*No*	*7.5*	*72.3*	*77.9*	*4.6*	*24.9*
Alloy P	*No*	*7.5*	*68.3*	*75.2*	*6.4*	*27.9*

[0034] FIG. 2 is a graph showing a comparison of the strength and fracture toughness of invention alloys (Alloy A and B) and non-invention alloy (Alloy C) 4" thickness plates. With same industrial processing route and final plate thickness, the invention Alloy A and Alloy B have much better performance of strength and fracture toughness than Alloy C, which has too high Mg and too low Zn/Mg ratio than invention alloys. The results demonstrate that the invention alloys has surprisingly much better performance than non-invention alloy. It also demonstrates that the small chemistry deviation from invention alloy can severely decreases final production properties.

[0035] FIG. 3 is a graph showing the strength and fracture toughness of invention alloys (D, E, and F) and non-invention alloys (G and H) 6" thickness plates. Both Alloy G and H have lower fracture toughness with similar or lower strength than Alloy D to F invention alloys. Alloy G is not an invention alloy since the Cu is too high, Zn is too low, and Zn/Mg weight percentage ratio is too low, Cu/Zn weight percentage ratio is too high, and Cu+Mg+Zn is too low. Alloy H is not an invention alloy since the Mg is too high and Zn/Mg weight percentage ratio is too low. The results demonstrate that the invention alloys surprisingly have much better performance than non-invention alloy. It also confirms that even small chemistry deviation from invention alloy can severely decreases final production properties.

[0036] FIG. 4 is a graph showing the strength and fracture toughness of invention alloys (I to L) and non-invention alloys (M to P) 7.5" thickness plates. All non-invention alloys have lower combination of strength and fracture toughness compared with invention alloys. As shown in Table 2, Alloy M is not an invention alloy since the Cu is too high, Zn is too low, Zn/Mg weight percentage ratio is too low, Cu/Zn weight percentage ratio is too high, and Cu+Mg+Zn is too low. Alloy N is not an invention alloy since the Zn is too high. Alloy O is not an invention alloy since the Cu is too high, Zn is too high, and Cu+Zn+Mg is too high. Alloy P is not an invention alloy since the Zn is too high, Zn/Mg weight percentage ratio is too high, and Cu+Mg+Zn is too high. The results confirm that the invention alloys surprisingly has much better performance than non-invention alloys. It once again demonstrates that even small chemistry deviation from invention alloy can severely decreases final production properties.

[0037] FIG. 5 is a graph showing the fracture toughness as function of total Cu+Mg+Zn amount. It can been seen that the invention alloy range of 10.7 to 11.6% of total Cu+Mg+Zn gives the best performance. It is very critical to control total Cu+Mg+Zn in an optimized range in order to achieve both higher strength and better fracture toughness especially for thick plate product.

[0038] FIG. 6 is a graph showing the fracture toughness as function of total Cu/Zn weight percentage ratio. It can be seen that the range provided by the invention alloy Cu/Zn weight percentage ratio range of 0.14 to 0.19 gives better performance than other range. The beneficial impact of Cu on corrosion resistance performance is also strongly affected by Zn level. In addition, Cu contents that are too high also significantly increase the risk of undesirable coarse Al_2MgCu particles and macro-segregation from plate surface to center. Therefore, the ratio of Cu/Zn is very critical for high strength, high damage tolerance, and corrosion resistance performance required by aerospace application.

[0039] Figure 7 gives the fracture toughness as function of Zn/Mg weight percentage ratio. It can be seen that the invention alloy Zn/Mg weight percentage ratio range of 4.0 to 5.3 gives the better performance than other range. The Zn/Mg ratio strongly affects the metastable and/or stable $MgZn_2$ (η' and/or η Phase) and its variant phases at different aging stages.

[0040] The more comprehensive strength and fracture toughness at different through layers and orientations were evaluated for invention alloys A, E, and K with 4", 6" and 7.5" plate thickness respectively. Table 4 gives the comprehensive strength and fracture toughness testing results. T/2 represents half thickness of plate, L, LT and ST indicates rolling direction, long transverse direction, and short transverse direction respectively.

Table 4: The comprehensive strength and fracture toughness testing results

	Alloy A Invention Alloy	Alloy E Invention Alloy	Alloy K Invention Alloy
Plate Thickness (in.)	4.0	6.0	7.5
LT TYS @T/4 (ksi)	72.2	71.5	72.2
LT UTS @T/4 (ksi)	77.8	77.1	78.0
LT El. @ T/4 (%)	10.4	7.1	4.1
LT TYS @T/2 (ksi)		69.4	68.9
LT UTS @T/2 (ksi)		75.0	75.4
LT El. @T/2 (%)		6.0	5.9
L TYS @ T/4 (ksi)	73.4	72.5	73.3
L UTS @ T/4 (ksi)	77.1	75.7	76.7
L E1.@ T/4 (%)	15.3	9.5	10.6
L TYS @ T/2 (ksi)		73.7	74.6
L UTS @ T/2 (ksi)		78.1	79.6
LE1. @ T/2 (%)		9.2	8.8

(continued)

	Alloy A Invention Alloy	Alloy E Invention Alloy	Alloy K Invention Alloy
ST TYS @ T/2 (ksi)	65.5	68.4	68.5
ST UTS @ T/2 (ksi)	75.4	75.4	75.7
ST El. @ T/2 (%)	8.3	5.2	3.7
K1c L-T @ T/4 (ksi-in$^{1/2}$)	36.6	34.0	34.1
K1c T-L @ T/4 (ksi-in$^{1/2}$)	28.7	30.4	28.9
Klc S-L @ T/2 (ksi-in$^{1/2}$)	32.1	27.4	26.1

[0041] Stress corrosion resistance is 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. All specimens survived 30 days testing without failing under 30 ksi stress level in ST direction. Meanwhile, the exfoliation corrosion resistance was tested according to ASTM G34. The specimen size was 51 mm (2") in the LT direction and 102 mm (4") in the L direction. Testing was performed at thickness positions of surface (T/10) and plate center (T/2). All samples were rated as pitting based on ASTM G34.

[0042] Although the present invention has been disclosed in terms of a preferred embodiment, it will be understood that numerous additional modifications and variations could be made thereto without departing from the scope of the invention as defined by the following claims:

Claims

1. A thick plate high strength 7xxx aluminum alloy product comprising

   8.0 to 8.4 wt. % Zn,
   1.5 to 2.0 wt. % Mg,
   1.1 to 1.5 wt. % Cu, and

   one or more elements selected from the group consisting of up to 0.2 wt.% Zr, up to 0.2% wt. Sc, and up to 0.2 wt.% Hf, with the balance A1, and impurities
   wherein said alloy product has a Zn/Mg weight percentage ratio between 4.0 to 5.3, a Cu/Zn weight percentage ratio between 0.14 to 0.19, and an amount of Cu+Mg+Zn between 10.7 to 11.6 wt.%.

2. The aluminum alloy product of claim 1 comprising ≤0.12 wt.% Si; optionally comprising ≤0.05 wt.% Si.

3. The aluminum alloy product of claim 1 or 2 comprising ≤0.15 wt.% Fe; optionally comprising ≤0.08 wt.% Fe.

4. The aluminum alloy product of any one of claims 1 to 3 comprising ≤0.20 wt.% Mn.

5. The aluminum alloy product of any one of claims 1 to 4 comprising ≤0.04 wt.% Cr; and / or
   comprising ≤ 0.06 wt.% Ti.

6. The aluminum alloy product of any one of claims 1 to 5 consisting essentially of

   8.0 to 8.4 wt. % Zn,
   1.5 to 2.0 wt. % Mg,
   1.1 to 1.5 wt. % Cu,
   one or more elements selected from the group consisting of up to 0.2 wt.% Zr, up to 0.2 wt.% Sc, and up to 0.2 wt.% Hf,
   ≤0.12 wt.% Si,
   ≤0.15 wt.% Fe,
   ≤0.20 wt.% Mn,

≤0.04 wt.% Cr,

and ≤0.06 wt.% Ti
with the balance Al, and impurities
wherein said alloy product has a Zn/Mg weight percentage ratio between 4.0 to 5.3, a Cu/Zn weight percentage ratio between 0.14 to 0.19, and an amount ofCu+Mg+Zn between 10.7 to 11.6 wt.%..

7. The aluminum alloy product of any one of claims 1 to 6 wherein said aluminum alloy product is a 7.92 - 25.4 cm (3-10 inches) thick plate, extrusion, or forging product; or
wherein said aluminum alloy product is a 10.16 - 25.4 cm (4-10 inches) thick plate, extrusion, or forging product; or
wherein said aluminum alloy product is a 10.16 - 20.32 cm (4-8 inches) thick plate, extrusion, or forging product.

8. The aluminum alloy product of any one of claims 1 to 7 wherein the aluminum alloy product has a minimum Long-Transverse (LT) yield strength at quarter-thickness (th/4) of (510,2 - 0,152*th in mm) MPa ((74 - 0.56 * plate thickness in inch) ksi) and a minimum LT ultimate strength at th/4 of (537,8 - 0,098*th in mm) Mpa ((78 - 0.36 * plate thickness in inch) ksi).

9. A method of manufacturing a thick plate high strength 7xxx aluminum alloy product comprising the steps of:

a. casting stock of an ingot of a 7xxx aluminum alloy comprising the aluminum alloy product of any one of claims 1 to 8;
b. homogenizing the cast stock;
c. hot working the stock by one or more methods selected from the group consisting of rolling, extrusion, and forging;
d. solution heat treating (SHT) of the hot worked stock;
e. cold water quenching said SHT stock;
f. optionally stretching the SHT stock; and
h. ageing of the SHT, cold water quenched and optionally stretched stock to a desired temper.

10. The method of claim 9, wherein said step of homogenizing includes homogenizing at temperatures from 454 to 491 °C (849 to 916°F).

11. The method of claim 9 or 10, wherein said step of hot working includes hot rolling at a temperature of 385 to 450 °C (725 to 842°F).

12. The method of any one of claims 9 to 11, wherein said step of solution heat treating includes solution heat treating at temperature range from 454 to 491 °C (849 to 916°F).

13. The method of any one of claims 9 to 12, wherein said step of optionally stretching includes stretching at about 1.5 to 3%.

14. The method of any one of claims 9 to 13, wherein said step of ageing includes a two-step T7651 ageing process wherein a first stage temperature ranges from 100 to 140 °C (212 to 284 °F) for 4 to 24 hours and a second stage temperature ranges from 135 to 200 °C (275 to 392 °F) for 5 to 20 hours.

15. The method of any one of claims 9 to 14, wherein

b. said step of homogenizing includes homogenizing at temperatures from 454 to 491 °C (849 to 916°F);
c. said step of hot working includes hot rolling at a temperature of 385 to 450 °C (725 to 842°F);
d. said step of solution heat treating includes solution heat treating at temperature range from 454 to 491 °C (849 to 916°F);
e. said step of cold water quenching includes cold water quenching to room temperature;
f. said step of optionally stretching includes stretching at about 1.5 to 3%;
g. said step of ageing includes a two-step T7651 ageing process wherein a first stage temperature ranges from 100 to 140 °C (212 to 284 °F) for 4 to 24 hours and a second stage temperature ranges from 135 to 200 °C (275 to 392 °F) for 5 to 20 hours.

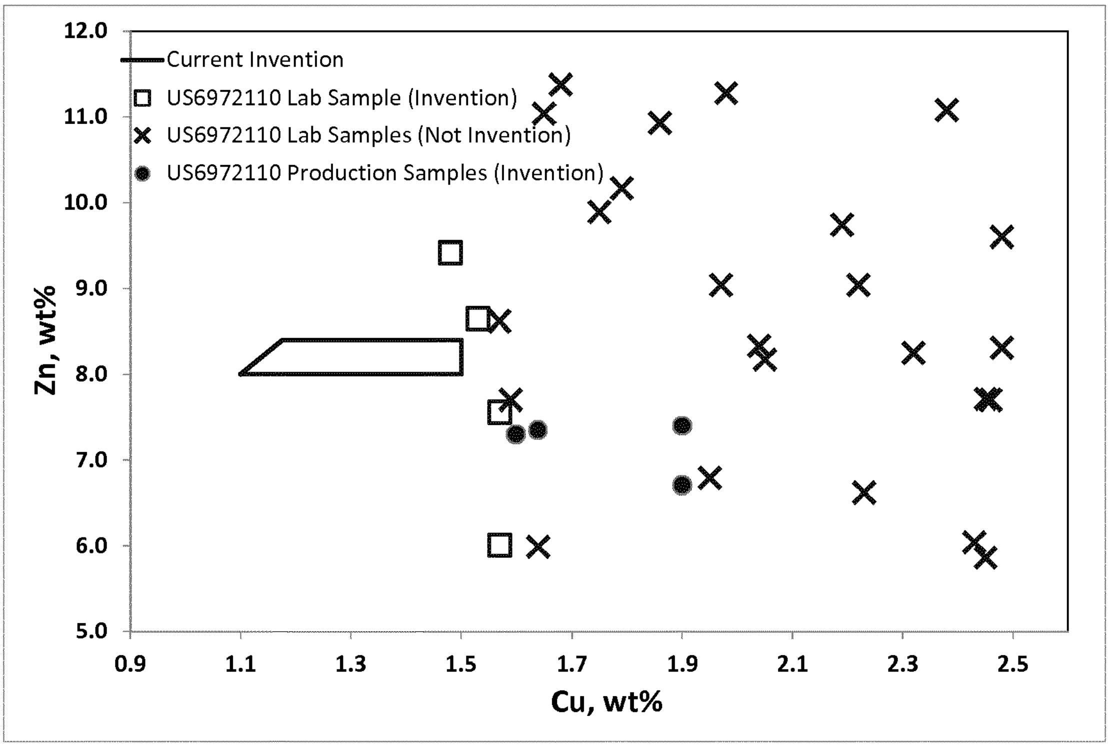

Current Invention
US6972110 Lab Sample (Invention)
US6972110 Lab Samples (Not Invention)
US6972110 Production Samples (Invention)
Zn, wt%
Cu, wt%
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
0.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5

FIG. 1

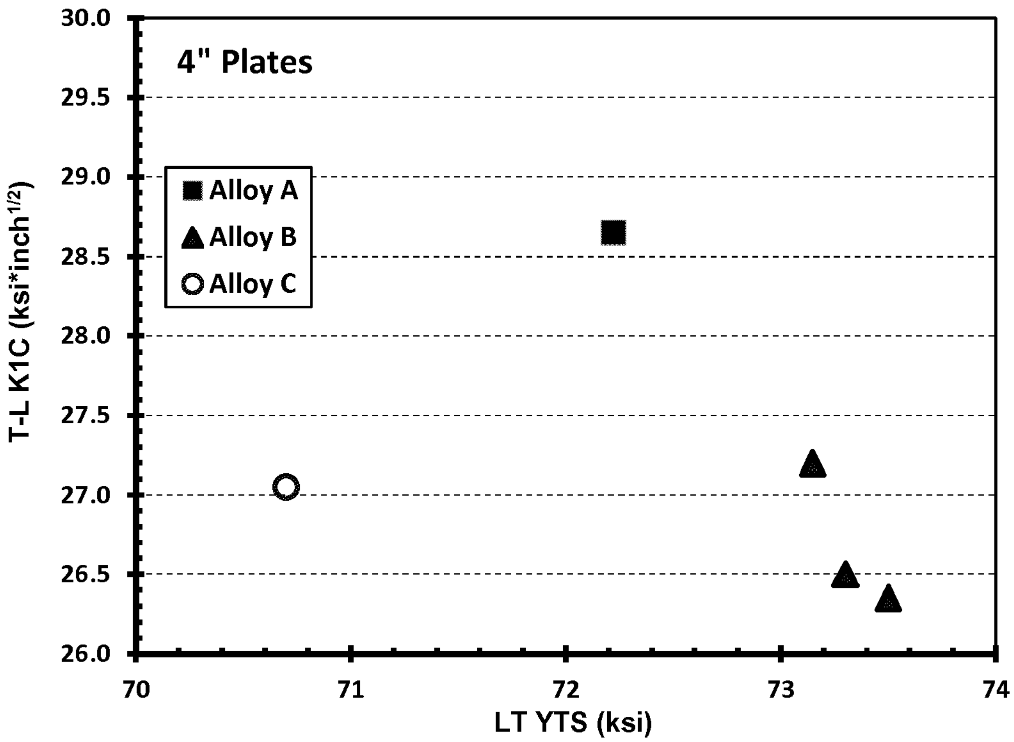

4" Plates
Alloy A
Alloy B
Alloy C
T-L K1C (ksi*inch1/2)
30.0
29.5
29.0
28.5
28.0
27.5
27.0
26.5
26.0
70
71
72
73
74
LT YTS (ksi)

FIG. 2

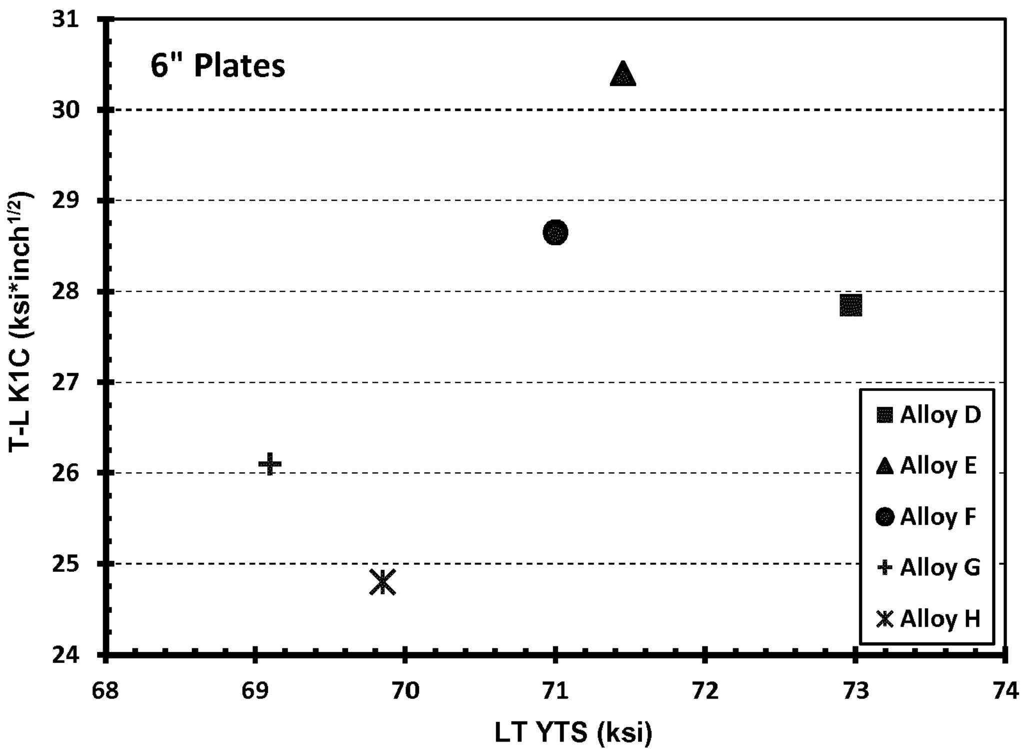

6" Plates
T-L K1C (ksi*inch^1/2)
LT YTS (ksi)
31
30
29
28
27
26
25
24
68
69
70
71
72
73
74
Alloy D
Alloy E
Alloy F
Alloy G
Alloy H

FIG. 3

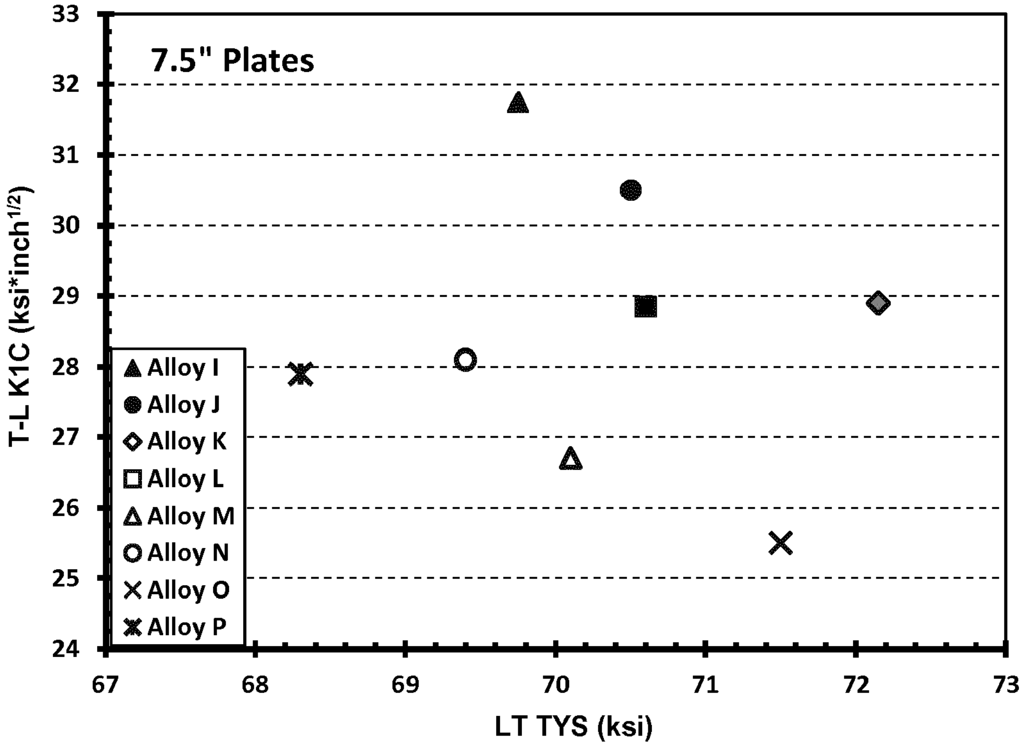

7.5" Plates
T-L K1C (ksi*inch^1/2)
LT TYS (ksi)
Alloy I
Alloy J
Alloy K
Alloy L
Alloy M
Alloy N
Alloy O
Alloy P
33
32
31
30
29
28
27
26
25
24
67
68
69
70
71
72
73

FIG. 4

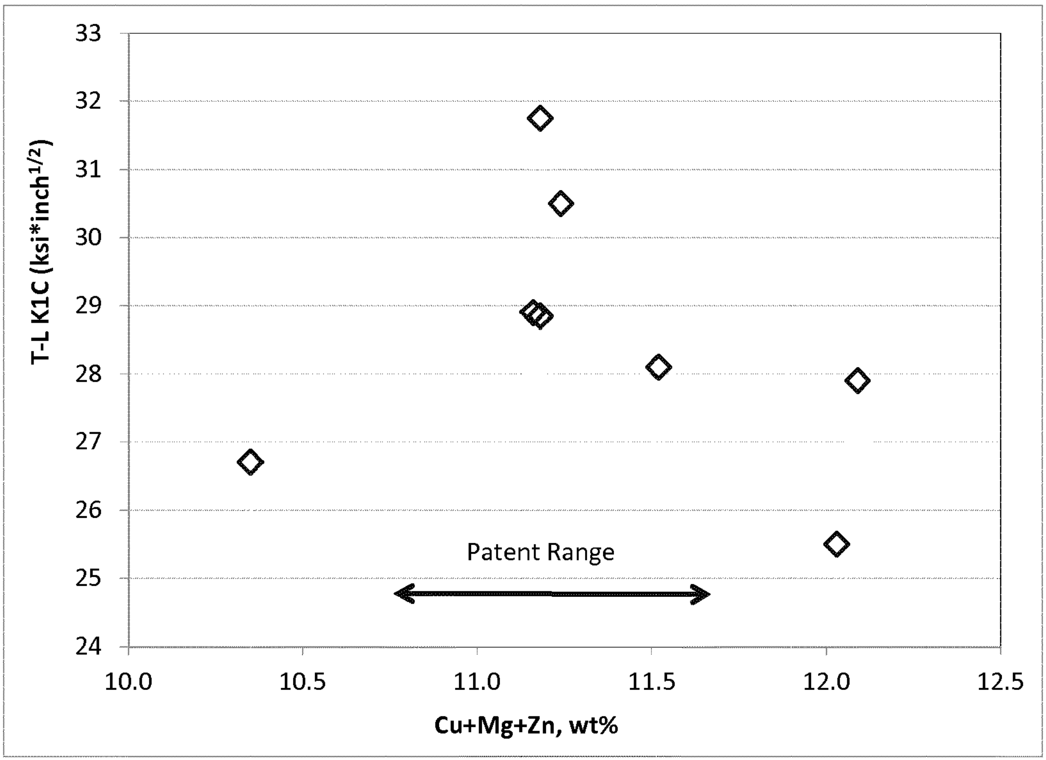

T-L K1C (ksi*inch^1/2)
33
32
31
30
29
28
27
26
25
24
Patent Range
10.0
10.5
11.0
11.5
12.0
12.5
Cu+Mg+Zn, wt%

FIG. 5

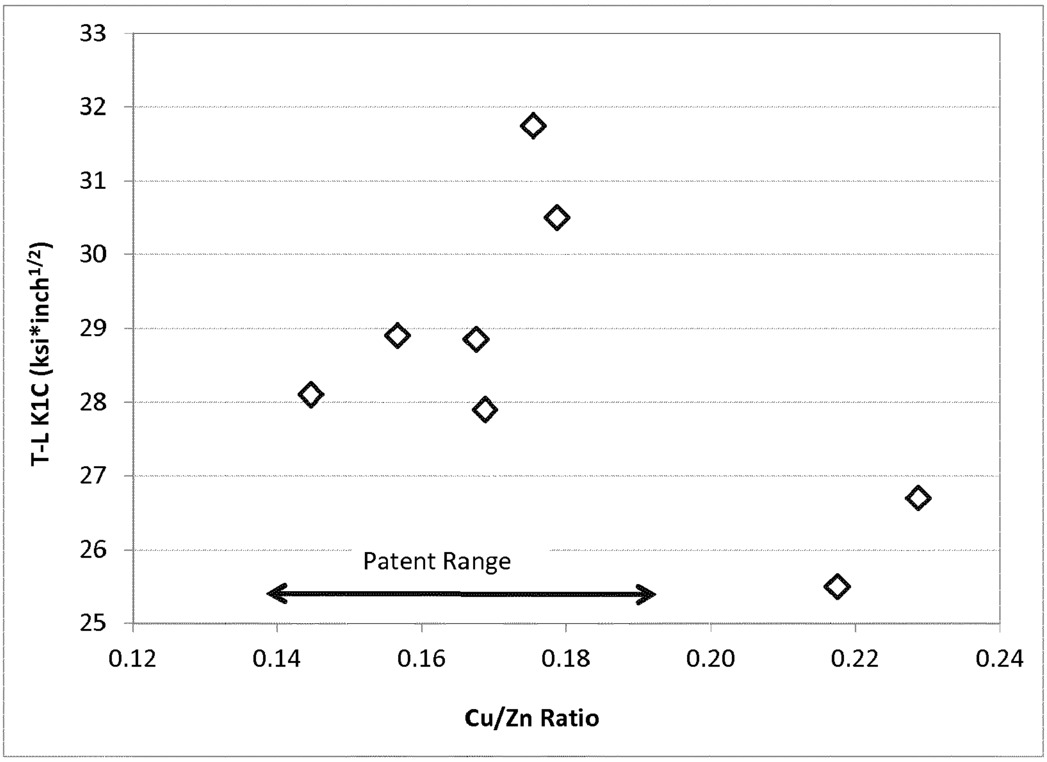
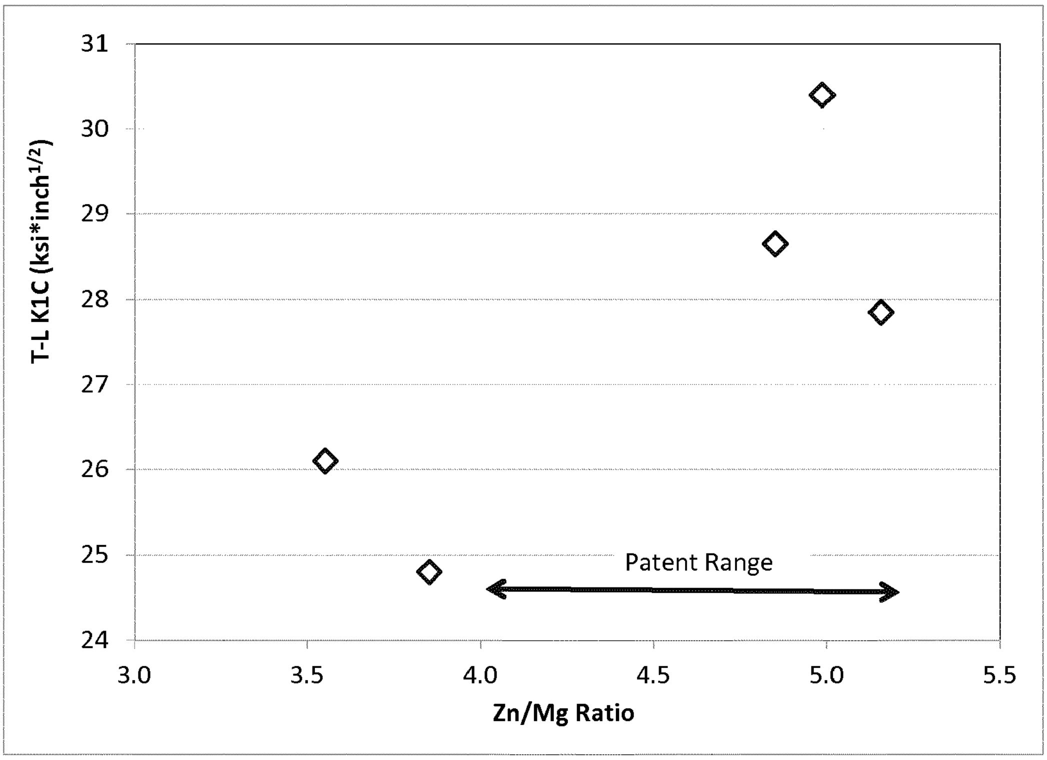

33
32
31
30
29
28
27
26
25
T-L K1C (ksi*inch$^{1/2}$)
Patent Range
0.12
0.14
0.16
0.18
0.20
0.22
0.24
Cu/Zn Ratio

FIG. 6



31
30
29
28
27
26
25
24
T-L K1C (ksi*inch^1/2)
Patent Range
3.0
3.5
4.0
4.5
5.0
5.5
Zn/Mg Ratio

FIG. 7

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EUROPEAN SEARCH REPORT

Application Number
EP 16 17 2536

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The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
Munich	26 September 2016	Abrasonis, Gintautas

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EUROPEAN SEARCH REPORT

Application Number
EP 16 17 2536

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
Munich	26 September 2016	Abrasonis, Gintautas

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P : intermediate document

T : theory or principle underlying the invention
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D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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26-09-2016

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