(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 001 446 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.05.2022 Bulletin 2022/21

(21) Application number: **21207643.4**

(22) Date of filing: **10.11.2021**

(51) International Patent Classification (IPC):
C22C 21/10 *(2006.01)* ***C22F 1/00*** *(2006.01)*
C22F 1/053 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C22C 21/10; C22F 1/002; C22F 1/053

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **11.11.2020 US 202063112294 P**
20.09.2021 US 202117479211

(71) Applicant: **Kaiser Aluminum Fabricated Products, LLC**
Foothill Ranch, CA 92610-2831 (US)

(72) Inventors:
- **LONG, Zhengdong**
  Spokane WA, 99223 (US)
- **GOMIERO, Philippe Paul**
  Spolane Valley WA, 99037 (US)
- **RASTOGI, Ravi**
  Liberty Lake WA, 99019 (US)
- **DIAO, Haoyan**
  Spokane Valley WA, 99016 (US)
- **SCHEURING, Jason Nicholas**
  Spokane WA, 99217 (US)

(74) Representative: **FRKelly**
27 Clyde Road
Dublin D04 F838 (IE)

(54) **HIGH STRENGTH AND HIGH FRACTURE TOUGHNESS 7XXX AEROSPACE ALLOY PRODUCTS**

(57) High strength and high fracture toughness 7xxx aluminum alloy products comprise 6.5 to 7.2 wt. % Zn, 1.55 to 1.95 wt. % Cu, 1.75 to 2.15 wt. % Mg, 0.095 to 0.15 wt. % Zr, incidental elements, and the balance Al. In one embodiment, the aluminum alloy product includes Mg/Cu and Zn/Mg ratios in the range of 1.05 to 1.35, and 3.2 to 4.0, respectively. This aluminum alloy product can be fabricated to produce plate, extrusion or forging products, and is especially suitable for aerospace structural components. The products have an excellent combination of strength, fracture toughness, K_{max} at the fatigue crack deviation point, ductility in different orientations, and corrosion resistance suitable for aerospace application.

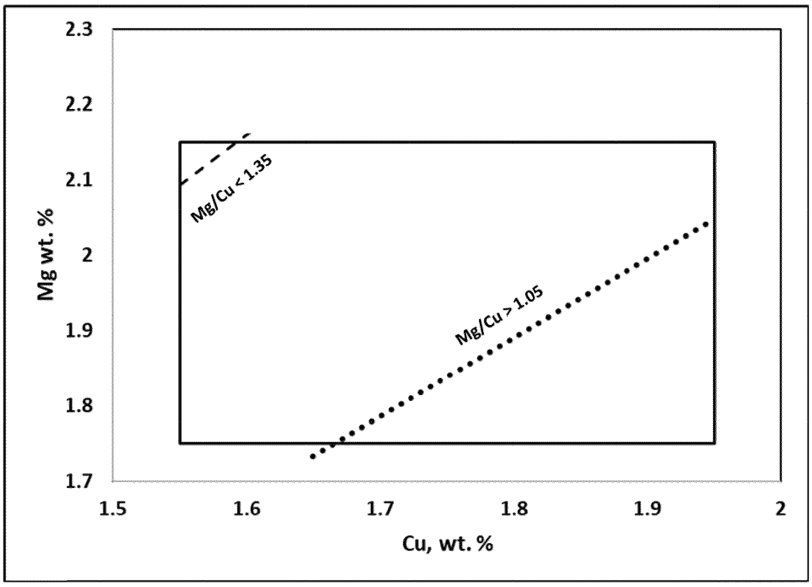

FIG. 1

Description

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit, under 35 U.S.C. 119(e), of U.S. Provisional Patent Application No. 63/112,294 filed November 11, 2020, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates to high strength 7xxx aluminum alloy products. The high strength 7xxx aluminum alloy can be fabricated to produce plate, extrusion or forging products suitable for aerospace structural components, especially large commercial airplane wing structure applications requiring better strength, fracture toughness, fatigue crack deviation resistance, anisotropic ductility, damage tolerance performance, and corrosion resistance performance.

2. Description of Related Art

[0003] The higher strength 7xxx aluminum alloys are being pursued assertively by airframe manufacturers and aluminum material manufacturers in order to aggressively reduce aircraft weight for fuel efficiency due to their extensive combination of material strength, ductility, fracture toughness, fatigue resistance, and corrosion resistance.

[0004] The combination of such complicated, comprehensive, and strict material performance demands from the aerospace applications necessitates a very finely optimized, and a very narrow chemistry range, to meet such requirements for commercial aircraft.

[0005] Obviously the strength, fracture toughness, and corrosion resistance performances are the most critical material properties, which are significantly affected by chemical composition. In 7xxx aluminum alloys, zinc is the major alloying element for achieving high strength through age strengthening. Zinc in the most commonly used 7050 and 7075 aerospace aluminum alloys is in the range of 5.1 to 6.7 wt.%. Magnesium is normally added along with zinc to produce MgZn2 and its variant phases, which are the predominant precipitation hardening phases. Aluminum alloys having higher Zn and Mg content usually have higher strength. However, higher Zn and Mg content also negatively affect stress corrosion cracking (SCC) resistance and fracture toughness performance. In 7xxx aluminum alloys, copper is added in order to improve SCC resistance performance. Meanwhile, the addition of Cu also improves material strength. Most of the Cu is believed to substitute Zn in the metastable MgZn2 phases. In general, Cu has approximately an equivalent effect on strength as the same weight percent of Zn addition.

[0006] In order to achieve aging precipitation strengthening, all added elements have to be in solid solution before aging. This is generally achieved through the processing steps of solution heat treatment (SHT), followed by rapid quenching. With the higher Mg, Zn and Cu levels, it is extremely difficult to dissolve all constituent particles, which consume a significant amount of added elements, into solid solution. Therefore, it is an extreme challenge to simultaneously achieve high strength, high fracture toughness, and desirable corrosion resistance for 7xxx aluminum alloys.

[0007] The additional new challenge for increased aircraft component utilization is the fatigue crack branching or deviation property. This is a phenomenon in which a crack suddenly changes its propagation direction away from the expected fracture plane under Mode I fatigue loading condition. Such crack deviation is an increasing concern for aircraft manufacturers since it is difficult to take into account during structural design.

[0008] In addition to the fatigue crack deviation performance, the anisotropic ductility of aluminum alloy thick plate is another increasingly critical characteristic for aerospace application, especially for monolithic part machining technology recently used in airframe manufacturing. The anisotropic ductility refers to significant ductility changes when the tensile testing orientation is in-between the commonly tested orientations, that are usually either parallel to or perpendicular to the material metal flow or microstructural direction, commonly notated as rolling direction (L). The ductility is usually significantly lower when tensile direction differs from the standard orientations that are determined by metal flow direction.

[0009] Another increasingly challenging aspect for aerospace applications is the Environmentally Assisted Cracking (EAC) property. This material property is believed to evaluate the alloy's resistance to hydrogen embrittlement, which can result in loss of strength and ductility due to a corrosion-like phenomenon. The testing is conducted under abnormally high humidity and temperature, in combination with high applied stresses. EAC property is also believed to be very sensitive to chemical composition.

[0010] In summary, the combination of the complicated age hardening behavior, as well as strict and comprehensive material performance necessitates a very narrow chemistry range. Aerospace applications have a strong need for such high performance alloys to attain ever increasing fuel efficiency targets.

BRIEF SUMMARY OF THE INVENTION

[0011] The high strength, fracture toughness, fatigue crack deviation resistance, and anisotropic ductility 7xxx aluminum alloy products such as plates, forgings and extrusions, suitable for use in making aerospace structural components like large commercial airplane wing components, comprises 6.5 to 7.2 wt. % Zn, 1.55 to 1.95 wt. % Cu, 1.75 to 2.15 wt. % Mg, 0.095 to 0.15 wt. % Zr, up to 0.15 wt. % incidental elements, with the total of these incidental elements not exceeding 0.35 wt. %, and the balance Al. In one embodiment, the aluminum alloy further comprises Mg/Cu and Zn/Mg ratios are in the range of 1.05 to 1.35, and 3.2 to 4.0 respectively.

[0012] It has been discovered that an aluminum alloy having an optimized chemistry range, associated with precise Zn, Mg and Cu content as well as Mg/Cu and Zn/Mg ratios is capable of producing plate products with high strength, desirable fracture toughness, fatigue crack deviation resistance, higher anisotropic ductility, damage tolerance, and corrosion resistance properties, in a combination that has never been achieved before.

[0013] A high strength 7xxx thick plate aluminum alloy product offers a promising opportunity for significant fuel efficiency and cost reduction advantage for commercial airplanes. An example of such an application for 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 ductility, damage tolerance, stress corrosion resistance, and fatigue crack growth resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0014] 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 Cu and Mg chemical compositions of the invention alloy used to make the present 7xxx aluminum alloy products;

FIG. 2 is a graph showing the Mg and Zn chemical compositions of the invention alloy used to make the present 7xxx aluminum alloy products;

FIG. 3 is a graph showing the Cu and Mg chemical composition of invention alloy used to make the present 7xxx aluminum alloy products compared to non-invention alloys;

FIG. 4 is a graph showing the Mg and Zn chemical composition of invention alloys used to make the present 7xxx aluminum alloy products compared to non-invention alloys;

FIG. 5 is a graph showing the strength of the present 7xxx aluminum alloy products using the invention alloy compared to non-invention alloy plates;

FIG. 6 is a graph showing a combination of strength and fracture toughness of the present 7xxx aluminum alloy products using the invention alloy compared to non-invention alloys for 3 inch thick plates;

FIG. 7 shows the fracture toughness sample orientations relative to the plate geometry;

FIG. 8 shows the overall coupon configuration; B=6.35mm; W=76.2mm; H=46mm; W1=95mm;

FIG. 9 is a graph showing the K_{max}-$_{dev}$ vs. strength of the present 7xxx aluminum alloy products using the invention alloy compared to non-invention alloy for 4 inch thick plates; and

FIG. 10 is a graph showing a combination of orthotropic strength and ductility of the present 7xxx aluminum alloy products using the invention alloy compared to non-invention alloys.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A high strength 7xxx aluminum alloy product is produced using a precise chemistry range. The high strength, fracture toughness, better fatigue crack deviation and anisotropic ductility 7xxx aluminum alloy product comprises, consists of, or consists essentially of, 6.5 to 7.2 wt. % Zn, 1.55 to 1.95 wt. % Cu, 1.75 to 2.15 wt. % Mg, 0.095 to 0.15 wt. % Zr, up to 0.15 wt. % incidental elements, with the total of these incidental elements not exceeding 0.35 wt. %, and the balance Al. In one embodiment, the aluminum alloy further comprises Mg/Cu and Zn/Mg ratios in the range of 1.05 to 1.35, and 3.2 to 4.0 respectively. The 7xxx aluminum alloy product provides high strength, high damage tolerance performance, better corrosion resistance as well as desirable fatigue crack deviation resistance, and better anisotropic ductility suitable for aerospace applications. FIG.1 and FIG. 2 show graphs of the chemical composition range for the key Cu, Mg and Zn elements used to make the 7xxx aluminum alloy product according to the present invention.

[0016] The present invention includes alternate embodiments wherein the upper or lower limit for the amount of Zn in the aluminum alloy product may be selected from 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, and 7.2 wt.%. In addition to the alternate upper and lower limits listed above for Zn, the present invention includes alternate embodiments wherein the upper or lower limit for the amount of Cu may be selected from 1.55, 1.60, 1.65, 1.70, 1.75, 1.80, 1.85, 1.90, and 1.95 wt.%. In addition to the alternate upper and lower limits listed above for Zn and Cu, the present invention includes alternate embodiments wherein the upper or lower limit for the amount of Mg may be selected from 1.75, 1.80, 1.85, 1.90, 1.95, 2.00, 2.05, 2.10, and 2.15 wt.%. In addition to the alternate upper and lower limits listed above for Zn, Cu, and Mg the present invention includes alternate embodiments wherein the upper or lower limit for the amount of Zr may be selected from 0.095, 0.10, 0.11, 0.12, 0.13, 0.14, and 0.15 wt.%. In addition to the alternate upper and lower limits listed above for Zn, Cu, Mg, and Zr, the present invention includes alternate embodiments wherein the upper or lower limit for the ratio of Mg/Cu may be selected from 1.05, 1.10, 1.15, 1.20, 1.25, 1.30, and 1.35. In addition to the alternate upper and lower limits listed above for Zn, Cu, Mg, Zr and Mg/Cu ratio, the present invention includes alternate embodiments wherein the upper or lower limit for the ratio of Zn/Mg may be selected from 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, and 4.0. In addition to the alternate upper and lower limits listed above, the present invention includes alternate embodiments wherein the upper limit for the incidental elements is 0.15, 0.12, 0.10, 0.08, 0.05, 0.02, and 0.10 wt.%. In addition to the alternate upper and lower limits listed above, the present invention includes alternate embodiments wherein the upper limit for the total incidental elements is 0.35, 0.30, 0.25, 0.20, 0.15, 0.12, 0.10, 0.08, 0.05, 0.02, and 0.10 wt.%.

[0017] In one embodiment, the aluminum alloy product is a thick plate including ≤0.12 wt.% Si, preferably ≤0.05 wt.% Si. In one embodiment, the aluminum alloy product is a thick plate including ≤0.15 wt.% Fe, preferably ≤0.10 wt.% Fe. In one embodiment, the aluminum alloy product is a thick plate including Zr in the range from 0.095 to 0.15 wt%. In one embodiment, the aluminum alloy product is a thick plate including ≤0.04 wt.% Cr, preferably no Cr is added to the alloy other than that provided as an impurity. In one embodiment, the aluminum alloy product is a thick plate including 0.005 - 0.10 wt.% Ti.

[0018] The aluminum alloy product 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 those described above (Al, Zn, Cu, Mg, Zr, Si, Fe, Cr, and Ti).

[0019] In a preferred embodiment, the aluminum alloy product of the present invention is a thick plate have a thickness of 1-10 inches. Alternatively, such thick plate products may have thicknesses of 1-3 inches, or 1-5 inches, or 3-5 inches, or 5-10 inches, or 5-8 inches, or 8-10 inches.

[0020] The ingots of the high strength aluminum alloy product may be cast, homogenized, hot rolled, solution heat treated, cold water quenched, optionally stretched, and aged to desired temper. A thick plate high strength aluminum alloy is a plate product provided in a T7651 or T7451 temper and in the thickness range of 1 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 a temperature range of 454 to 491 °C (849 to 916°F). The plates are cold water quenched to room temperature and may be stretched by about 1.5 to 3%. The quenched plate may be subjecting to any 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 or T7451 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.

[0021] High strength 7xxx aluminum alloy plate products preferably have a yield tensile strength (YTS) in the LT direction ≥ 67 ksi, or ≥ 68 ksi, or ≥ 70 ksi, or ≥ 71 ksi. These 7xxx aluminum alloy products may also have T-L K1c values ≥ 28 ksi-in$^{1/2}$, or ≥ 29 ksi-in$^{1/2}$, or ≥ 30 ksi-in$^{1/2}$. These 7xxx aluminum alloy products may also have K_{max}-$_{dev}$ values ≥ 33 NPa-m$^{1/2}$, or ≥ 34 MPa-m$^{1/2}$, or ≥ 35 MPa-m$^{1/2}$, or ≥ 36 MPa-m$^{1/2}$, or ≥ 37 MPa-m$^{1/2}$, or ≥ 38 MPa-m$^{1/2}$. These 7xxx aluminum alloy products may also have EAC values ≥ 100 days, or ≥ 110 days, or ≥ 120 days, or ≥ 130 days, or ≥ 140 days, or ≥ 150 days. These 7xxx aluminum alloy plate products may also have any combination of or all the aforementioned YTS in the LT direction, T-L K1c, K_{max}-$_{dev}$, and EAC values. In one embodiment of the present invention, these YTS and K1c values are found in thick plates having a thickness ≥ 3 inches, or ≥ 4 inches, and have the above-mentioned $K_{max-dev}$, and EAC values. The tensile testing was conducted based on ASTM B557 specification, the contents of which are expressly incorporated herein by reference. The plane strain fracture toughness (K_{1c}) was measured under ASTM E399, the contents of which are expressly incorporated herein by reference, using CT specimens. As described below, and incorporated herein, Environmentally Assisted Cracking (EAC) resistance is evaluated under the test conditions of Temperature=70°C, relative humidity=85% with a loading stress at 85% of Rp0.2 at ST direction centered at T/2 (middle of the thickness). The determination of external crack deviation ($K_{max-dev}$) are based on "anything that would normally invalidate the E647 FCG test". The contents of the E647 FCG test is expressly incorporated herein by reference.

[0022] Although the following examples demonstrate various embodiments of the present invention, one skilled in the art should understand how additional high strength 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.

<u>Examples (Plant Trial)</u>

[0023] Fifty (50) industrial scale plates were produced by commercial DC (Direct Chill) casting followed by homogenization, hot rolling, solution heat treatment, quenching, stretching and aging processes to different thickness plates.

Table 1 gives the chemical compositions of 50 commercial size plates.

[0024] Alloys 1 to 18 are invention alloys. Alloy 19 to 39 are 7050 type non-invention alloys since they have too high Cu, too low Zn, too low Mg/Cu ratio, and too low Zn/Mg ratio. Alloy 40 to 50 are 7075 type non-invention alloys since they have too high Mg, too low Zn, too high Mg/Cu ratio, and too low Zn/Mg ratio.

[0025] FIG. 3 and FIG. 4 are graphs showing the chemical composition difference between the present 7xxx aluminum alloy products made from the invention alloys compared to non-invention alloys.

Invension Alloy?	Plate ID	Gauge, in	Cu, wt. %	Mg, wt. %	Zn, wt. %	*Mg/Cu*	*Zn/Mg*	Cr, wt. %	Zr, wt. %	Ti, wt. %	Si, wt. %	Fe, wt. %
Invention Alloy	1	1	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	2	1	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	3	2	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
	4	2	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
	5	2	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	6	2	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	7	3	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	8	3	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	9	4	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
	10	4	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	11	4	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	12	4	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	13	4	1.72	1.98	6.85	1.15	3.46	0.00	0.12	0.015	0.03	0.07
	14	4	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
	15	6	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
	16	6	1.74	1.92	6.84	1.11	3.56	0.00	0.12	0.028	0.04	0.09
	17	8	1.74	1.92	6.84	1.11	3.56	0.00	0.12	0.028	0.04	0.09
	18	8	1.74	1.96	6.87	1.13	3.50	0.00	0.12	0.025	0.04	0.08
Non Invention Alloy (7050 Type Alloy)	19	1	2.15	2.26	6.22	1.05	2.75	0.01	0.09	0.034	0.05	0.09
	20	1	2.17	2.16	6.14	1.00	2.84	0.01	0.09	0.032	0.04	0.08
	21	2	2.19	2.19	6.15	1.00	2.81	0.01	0.09	0.027	0.04	0.09
	22	2	2.15	2.19	6.17	1.02	2.82	0.00	0.09	0.030	0.04	0.08
	23	3	2.16	2.17	6.14	1.01	2.83	0.01	0.09	0.031	0.05	0.09
	24	3	2.15	2.16	6.06	1.00	2.81	0.00	0.09	0.033	0.04	0.09
	25	4	2.16	2.05	6.20	0.95	3.02	0.00	0.11	0.024	0.04	0.08
	26	4	2.10	1.93	6.23	0.92	3.23	0.00	0.09	0.025	0.04	0.07
	27	4	2.19	2.07	6.27	0.95	3.03	0.00	0.12	0.033	0.04	0.08
	28	4	2.19	2.22	6.29	1.02	2.83	0.01	0.09	0.031	0.04	0.09
	29	4.0	2.17	2.06	6.13	0.95	2.97	0.00	0.11	0.033	0.05	0.09
	30	4	2.20	2.07	6.32	0.94	3.05	0.01	0.12	0.023	0.05	0.10
	31	5	2.20	2.04	6.14	0.93	3.01	0.00	0.12	0.025	0.05	0.09
	32	5	2.29	2.09	6.15	0.91	2.94	0.00	0.11	0.022	0.04	0.09
	33	6	2.19	2.02	6.27	0.92	3.11	0.01	0.11	0.018	0.04	0.07
	34	6	2.05	1.94	6.11	0.94	3.16	0.00	0.11	0.017	0.04	0.06
	35	6	2.16	1.97	6.14	0.92	3.11	0.00	0.11	0.021	0.03	0.06
	36	7	2.10	1.99	6.16	0.95	3.10	0.00	0.11	0.019	0.04	0.06
	37	7	2.14	1.96	6.10	0.92	3.11	0.00	0.11	0.016	0.03	0.07
	38	8	2.09	1.95	6.20	0.93	3.17	0.00	0.11	0.021	0.04	0.07
	39	8	2.05	1.94	6.11	0.94	3.16	0.00	0.11	0.017	0.04	0.06
Non Invention Alloy (7075 Type Alloy)	40	1	1.50	2.37	5.63	1.58	2.38	0.20	0.02	0.032	0.08	0.17
	41	2	1.50	2.53	5.71	1.69	2.26	0.20	0.01	0.023	0.09	0.18
	42	2	1.56	2.72	5.83	1.75	2.14	0.20	0.01	0.022	0.07	0.13
	43	3	1.50	2.49	5.68	1.66	2.28	0.20	0.02	0.030	0.11	0.22
	44	3	1.44	2.51	5.84	1.74	2.33	0.21	0.02	0.026	0.10	0.20
	45	4	1.65	2.49	5.66	1.51	2.27	0.21	0.01	0.027	0.06	0.13
	46	4	1.41	2.47	5.74	1.76	2.32	0.20	0.02	0.024	0.06	0.14
	47	5	1.47	2.58	5.83	1.75	2.26	0.20	0.00	0.031	0.05	0.11
	48	6	1.54	2.46	5.94	1.60	2.42	0.19	0.01	0.014	0.05	0.19
	49	7	1.60	2.67	5.95	1.67	2.23	0.20	0.01	0.030	0.08	0.15
	50	8	1.57	2.45	5.84	1.56	2.38	0.20	0.03	0.032	0.07	0.16

Table 1: Chemical compositions of industrial scale ingots

[0026] Ingots were homogenized, hot rolled, solution heat treated, quenched, stretched and aged to final temper plates in the thickness range from 1 inch to 8 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).

[0027] 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 and T7451 tempers. 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.

[0028] The final production plates were characterized for strength, fracture toughness, corrosion resistance, fatigue crack deviation resistance, and anisotropic ductility that are critical for aerospace applications.

[0029] The tensile testing was conducted based on ASTM B557 specification, the contents of which are expressly incorporated herein by reference. The plane strain fracture toughness (K_{1c}) was measured under ASTM E399, the contents of which are expressly incorporated herein by reference, using CT specimens. Table 2 gives the tensile properties and fracture toughness for aluminum alloy products using invention and non-invention alloy samples. The common terminologies familiar to those skilled in the art were used in this table for strength and fracture toughness.

[0030] Table 2 shows significantly better strength for aluminum alloy products using invention alloys (Sample 1-18) than non-invention alloys. The fracture toughness for aluminum alloy products is also better for invention alloy compared with 7050 type non-invention alloys.

[0031] Fig. 5 demonstrates the higher strength of aluminum alloy products using the invention alloys compared with non-invention alloys.

[0032] The strength and fracture properties have to be considered together for aerospace applications. The combination of strength and fracture toughness for aluminum alloy products made from invention alloys is much better than non-invention alloys based on Table 2. For instance, FIG. 6 demonstrates that 3" thick aluminum alloy plates made from the invention alloy have a better combination of strength and fracture toughness compared with non-invention alloys.

Invension Alloy?	Plate ID	Gauge, in	Temper	LT UTS (ksi)	LT YTS (ksi)	LT ELG (%)	L UTS (ksi)	L YTS (ksi)	L ELG (%)	ST UTS (ksi)	ST YTS (ksi)	ST ELG (%)	L-T KIC, ksi*in$^{1/2}$	T-L KIC, ksi*in$^{1/2}$	S-L KIC, ksi*in$^{1/2}$
Invention Alloy	1	1	T7451	78.9	72.1	14.6	80.7	73.9	15.0	*na*	*na*	*na*	38.5	31.3	*na*
	2	1	T7651	79.9	73.3	14.3	81.4	74.9	15.2	*na*	*na*	*na*	35.1	29.3	*na*
	3	2	T7451	77.9	70.3	12.5	76.9	70.7	16.2	*na*	*na*	*na*	38.4	28.5	*na*
	4	2	T7651	78.2	70.8	12.8	77.7	71.4	15.6	*na*	*na*	*na*	38.4	29.5	*na*
	5	2	T7451	77.9	70.8	12.7	76.6	70.2	15.7	76.4	66.7	7.7	38.9	30.2	31.7
	6	2	T7651	79.2	72.7	12.9	77.6	71.9	15.7	75.8	68.4	6.0	37.3	29.1	31.2
	7	3	T7451	77.3	70.4	11.7	76.5	70.1	14.6	75.4	65.0	7.6	40.1	30.7	30.1
	8	3	T7651	78.1	71.4	11.4	77.3	71.6	14.3	76.5	66.4	7.7	37.4	30.1	28.6
	9	4	T7451	77.1	69.6	10.2	74.4	69.6	15.3	74.8	64.9	7.5	39.6	29.8	27.6
	10	4	T7451	76.8	69.4	10.9	75.2	69.6	15.6	74.8	64.6	7.4	39.5	30.5	30.1
	11	4	T7451	77.4	69.9	10.6	75.3	69.9	15.2	75.0	65.0	7.6	39.1	30.6	28.7
	12	4	T7651	78.5	71.0	10.6	76.9	71.6	14.6	76.3	66.7	6.9	36.6	29.1	28.0
	13	4	T7651	78.5	72.0	10.5	76.0	71.4	15.3	76.5	66.5	6.8	38.2	30.1	29.2
	14	4	T7651	78.3	71.4	10.6	75.6	70.9	14.3	75.9	66.0	8.3	35.2	29.4	27.1
	15	6	T7651	76.8	69.1	6.0	76.8	71.7	10.2	74.3	65.5	5.0	32.5	26.0	24.4
	16	6	T7651	77.3	70.3	6.6	75.9	71.1	11.0	74.2	65.8	5.8	32.4	25.5	24.4
	17	8	T7651	75.0	67.7	4.3	75.4	69.9	8.7	71.6	63.1	3.9	32.2	25.1	24.6
	18	8	T7651	76.0	69.0	4.4	75.9	71.1	7.1	73.1	65.0	4.3	30.4	23.7	25.0
Non Invention Alloy (7050 Type Alloy)	19	1	T7451	74.3	65.6	13.4	74.3	65.7	14.7	*na*	*na*	*na*	32.5	27.3	*na*
	20	1	T7451	75.0	66.6	13.0	75.2	66.8	14.4	*na*	*na*	*na*	32.8	27.7	*na*
	21	2	T7451	75.5	65.9	12.0	74.9	66.5	13.8	*na*	*na*	*na*	34.2	28.2	*na*
	22	2	T7451	76.7	68.0	12.9	74.3	66.6	15.5	*na*	*na*	*na*	34.7	29.5	*na*
	23	3	T7451	74.0	65.2	10.7	74.0	65.3	12.7	71.0	59.7	6.6	33.0	26.5	24.2
	24	3	T7451	73.8	64.6	11.2	74.7	66.0	12.9	72.0	61.6	6.3	34.3	27.5	24.9
	25	4	T7451	75.8	64.3	10.1	73.9	67.0	14.9	73.2	62.8	6.1	36.7	27.6	26.6
	26	4	T7651	69.5	61.7	7.7	71.4	64.2	12.0	73.5	63.3	6.2	31.7	26.1	25.8
	27	4	T7651	72.7	63.9	9.8	75.9	67.6	12.7	71.1	63.1	3.3	28.9	22.3	20.4
	28	4	T7651	73.5	65.4	10.2	75.3	68.0	11.3	65.2	59.9	1.7	26.4	20.5	20.0
	29	4.0	T7651	75.7	66.7	10.3	73.6	66.5	14.8	73	62.2	6	36.1	26.1	23.3
	30	4	T7451	74.4	65.1	10.3	73.0	64.9	14.1	72.4	61.9	6.6	35.9	27.3	24.7
	31	5	T7451	73.1	63.7	7.2	73.5	65.5	12.5	71.2	60.7	5.2	30.4	22.1	23.8
	32	5	T7451	73.1	63.5	8.3	72.9	64.8	13.0	71.0	60.8	4.9	30.2	24.8	23.6
	33	6	T7451	74.3	62.2	8.8	74.1	66.1	12.2	72.1	60.3	6.4	31.8	24.8	25.7
	34	6	T7451	74.7	65.0	7.6	74.4	66.7	11.5	72.3	61.0	6.0	32.0	26.3	24.5
	35	6	T7451	73.8	64.3	6.9	74.3	66.2	11.2	71.5	60.9	6.0	34.1	28.2	25.8
	36	7	T7451	72.2	61.3	7.1	72.4	63.9	10.6	70.0	59.0	6.5	33.0	25.6	27.9
	37	7	T7451	72.2	60.3	7.2	72.5	63.6	11.2	70.6	60.2	5.7	32.0	26.4	27.5
	38	8	T7451	70.2	59.6	5.9	71.1	62.5	10.1	68.9	57.8	5.3	32.9	24.9	26.1
	39	8	T7451	70.6	60.6	5.3	72.3	63.5	9.7	68.9	58.7	5.0	32.2	24.9	26.9
Non Invention Alloy (7075 Type Alloy)	40	1	T7351	70.6	60.0	12.6	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	41	2	T7351	68.1	55.9	12.4	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	42	2	T7351	71.1	59.1	10.7	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	43	3	T7351	64.5	52.0	11.1	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	44	3	T7351	68.1	55.9	10.7	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	45	4	T7351	62.1	47.3	11.4	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	46	4	T7351	63.3	50.0	11.2	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	47	5	T7351	58.3	42.8	12.5	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	48	6	T7351	54.2	38.7	11.5	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	49	7	T651	59.2	39.6	12.0	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*
	50	8	T651	56.3	37.3	11.5	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*

Table 2: Tensile and fracture toughness of aluminum alloy plate products made from the invention alloy and non-invention alloy

[0033] The fatigue crack growth deviation was evaluated based on ASTM E647, the contents of which are expressly incorporated herein by reference. The coupon orientation is L-S, which has the highest chance to have crack deviation during crack propagation. FIG. 7 shows the orientation of this sample relative to the plate geometry. FIG. 8 illustrates the coupon configuration used herein. The standard Compact Tension, i.e. C(T), coupon was used for this test. The dimension B is 6.35mm and W is 76.2mm for all testing coupons. The FCGR testing procedure was according to ASTM E647 in general with the following specific requirements: (1) R = 0.1 and f=25 Hz; (2) Pre-cracking was conducted under constant load amplitude, and the starting ΔK reaches the ΔKi = 10 MPa*m$^{1/2}$ values at the end of pre-cracking. After pre-cracking, the testing is conducted under constant load amplitude at the same load as pre-cracking. The test was conducted at room temperature. The relative humidity (RH) is under normal lab environment.

[0034] The determination of external crack deviation was based on "anything that would normally invalidate the E647 FCG test" (e.g. crack growth out of plane by more than 20° or crack deviation after the remaining ligament criterion is exceeded). After the deviation branching point was determined, the crack length was calculated by three point weighted average method based on measurements taken on fracture sample. The equation for weighted average length is a = (front + back + 2* center) /4.

[0035] The fatigue cycles, crack length and K_{max}-$_{dev}$ at the crack deviation point are given in Table 4 for invention and non-invention alloy lots. FIG. 9 is a graph showing the comparison of the combination of strength and K_{max}-$_{dev}$ for aluminum alloy products made from the invention alloy compared to the non-invention alloys plates in the thickness range of 4 to 5 inches.

Table 4: The fatigue cycles, crack length and K_{max}-$_{dev}$ at the crack deviation points of 4 inch thick plates

Alloy	Plate ID	Temper	Plate Ga, in	Orientation	Loc	External Branching Cycles	Kmax at External Branching, MPa*m$^{1/2}$	LT-YTS ksi
Invention Alloy	9	T7451	4	L-S	T/2	91496	37.8	69.6
	9	T7451	4	L-S	T/2	87922	38.2	69.6
	14	T7651	4	L-S	T/2	91997	38.5	71.4
	14	T7651	4	L-S	T/2	88088	33.8	71.4
Non Invention Alloy (7050-type)	26	T7451	4	L-S	T/2	66630	40.8	63.7
	26	T7451	4	L-S	T/2	116766	29.6	63.7
	27	T7451	4	L-S	T/2	97437	32.9	66.8
	27	T7451	4	L-S	T/2	96752	31.0	66.8
	28	T7451	4	L-S	T/2	132635	33.2	66.8
	28	T7451	4	L-S	T/2	137664	27.3	66.8

[0036] The tensile properties, especially tensile ductility, can be significantly different for different testing directions. Such anisotropic material behavior is very important for high strength thick plate aerospace applications.

[0037] The orthotropic tensile coupons were extracted such that the gauge length was centered at T/2 location. The tensile direction is 45 degrees off thickness (ST) direction (ST-45). The testing results are given in Table 5. As demonstrated in FIG. 10, the aluminum alloy products made from the invention alloy has unexpectedly better combination of orthotropic strength and ductility.

Table 5: Anisotropic tensile properties for alloy lots for 4-4.25 inch thick plates.

Alloy	Plate ID	Gage, in	Location	Orientation ST to L	YTS (ksi)	UTS (ksi)	Elongation (%)
Invention Alloy	9	4	T/2	45	64.5	69.5	2.91
	9	4	T/2	45	64.7	70.1	3.2
	9	4	T/2	45	64.8	69.8	2.963
	14	4	T/2	45	66.2	70.8	2.75
	14	4	T/2	45	66.1	70.8	2.8
	14	4	T/2	45	66	70.2	2.26
Non Invention Alloy (7050-type)	29	4.1	T/2	45	62.9	66.8	1.90
	29	4.1	T/2	45	62.8	66.2	1.71

[0038] Stress corrosion resistance is critical for aerospace application. The standard stress corrosion cracking testing was performed in accordance with the requirements of ASTM G47, the contents of which are expressly incorporated herein by reference, which is alternate immersion in a 3.5% NaCl solution under constant deflection. Three specimens were tested per sample.

[0039] Table 6 gives the SCC testing results for both T7451 and T7651 tempers. It shows that the lots designated as T7451 temper pass the 35ksi stress threshold. In addition, a vast majority of samples at a higher 40ksi stress level also pass SCC to 30 days. The lots designated as T7651 temper pass the 25ksi threshold. In addition, they also pass SCC testing at a higher 30ksi stress level, to 30 day duration.

Table 6: SCC testing performance of invention alloy.

					SCC Results		
Alloy	**Plate ID**	**Gauge**	**Temper**	**Stress, ksi**	**Rep1**	**Rep2**	**Rep3**
Invention Alloy	1	1	T7451	35	> 30 day	> 30 day	> 30 day
	5	2	T7451	35	> 30 day	> 30 day	> 30 day
	7	3	T7451	35	> 30 day	> 30 day	> 30 day
	10	4	T7451	35	> 30 day	> 30 day	> 30 day
	11	4	T7451	35	> 30 day	> 30 day	> 30 day
Invention Alloy	2	1	T7651	25	> 30 day	> 30 day	> 30 day
	6	2	T7651	25	> 30 day	> 30 day	> 30 day
	8	3	T7651	25	> 30 day	> 30 day	> 30 day
	12	4	T7651	25	> 30 day	> 30 day	> 30 day
	13	4	T7651	25	> 30 day	> 30 day	> 30 day
Invention Alloy	1	1	T7451	40	> 30 day	> 30 day	> 30 day
	5	2	T7451	40	17	> 30 day	> 30 day
	7	3	T7451	40	> 30 day	> 30 day	> 30 day
	10	4	T7451	40	> 30 day	> 30 day	> 30 day
	11	4	T7451	40	10	> 30 day	> 30 day
Invention Alloy	2	1	T7651	30	> 30 day	> 30 day	> 30 day
	6	2	T7651	30	> 30 day	> 30 day	> 30 day
	8	3	T7651	30	> 30 day	> 30 day	> 30 day
	12	4	T7651	30	> 30 day	> 30 day	> 30 day
	13	4	T7651	30	> 30 day	> 30 day	> 30 day

[0040] In recent years there have been other alloys that have provided superior higher yield strength properties than incumbent alloys such as 7050 and 7075, especially for thicker plate applications. These alloys, however, have proven to be susceptible to a different failure mechanism referred to as Environmentally Assisted Cracking (EAC).

[0041] Table 7 gives the chemical composition of such new high strength 7xxx alloys developed in recent years. The plates were commercial scale plates. The non-invention chemistries, especially Zn content, are significantly different compared with the present invention alloy.

Table 7: The chemical compositions of non-invention new high strength alloy plates for EAC testing

Alloy	**Plate ID**	**Mg**	**Zn**	***Mg/Cu***	***Zn/Mg***	**Cr**	**Zr**	**Ti**	**Si**	**Fe**
Invention Alloy	18	1.96	6.87	1.13	3.50	0.00	0.12	0.02	0.04	0.08
Non Invention Alloy	N7085	1.53	7.32	0.93	4.80	0.00	0.12	0.02	0.03	0.03
	N7449	2.10	7.82	1.10	3.73	0.01	0.10	0.02	0.04	0.07
	N7056	1.70	8.65	1.00	5.09	0.00	0.07	0.03	0.04	0.07
	NT97	1.85	8.19	1.36	4.44	0.00	0.11	0.02	0.03	0.07
	NT99	2.05	7.73	1.18	3.77	0.00	0.09	0.04	0.03	0.05

[0042] Environmentally Assisted Cracking (EAC) resistance was evaluated under the test conditions of Temperature=70°C, relative humidity=85%. The loading stress is at 85% of Rp0.2 at ST direction. The sample is taken at ST direction centered at T/2 (middle of the thickness).

[0043] Three testing coupons (Rep1, Rep2, Rep3) were tested for invention alloy plate #18 along with some new non-invention high strength alloy plates. Table 8 gives the EAC testing results. The results indicate that the aluminum alloy products made from the invention alloy have much better EAC resistance performance than other non-invention high strength alloys. For invention alloy plate ID 18, the three coupons failed at 116, 150 and 159 days. In contrast, all non-invention alloy coupons failed EAC testing in the range from 3 to 21 days.

Table 8: EAC testing performance of alloys, at 70°C and 85% RH

Alloy	Plate ID	EAC Days of Failures		
		Rep1	Rep2	Rep3
Invention Alloy	18	159	150	116
Non Invention Alloy	N7085	15	20	14
	N7449	12	12	12
	N7056	3	1	1
	NT97	3	3	3
	NT99	17	18	21

[0044] 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 high strength and high fracture toughness 7xxx aluminum alloy product comprising,

6.5 to 7.2 wt. % Zn, 1.55 to 1.95 wt. % Cu,
1.75 to 2.15 wt. % Mg, 0.095 to 0.15 wt. % Zr,

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

2. The aluminum alloy product of claim 1 comprising a Mg/Cu ratio of 1.05 to 1.35; and / or comprising a Zn/Mg ratio of 3.2 to 4.0.

3. The aluminum alloy product of claim 1 or 2 further comprising ≤0.12 wt.% Si.

4. The aluminum alloy product of any one of claims 1 to 3 further comprising ≤0.15 wt.% Fe.

5. The aluminum alloy product of any one of claims 1 to 4 further comprising ≤0.04 wt.% Cr; and / or further comprising 0.005 - 0.10 wt.% Ti.

6. The aluminum alloy product of any one of claims 1 to 5 wherein said aluminum alloy product is a 1-10 inches thick plate, extrusion, or forging product.

7. The aluminum alloy product of claim 6 having a yield tensile strength (YTS) in the LT direction ≥ 67 ksi; and / or having a K1c value in the T-L direction of ≥ 28 ksi-in$^{1/2}$.

8. The aluminum alloy product of claim 6 or 7 having a K1c value in the T-L direction of ≥ 28 ksi-in$^{1/2}$ and a yield tensile strength (YTS) in the LT direction ≥ 67 ksi;
and optionally having K_{max}-$_{dev}$ values ≥ 33 MP-m$^{1/2}$; and / or optionally having EAC values ≥ 100 days.

9. The aluminum alloy product of claim 1 consisting of,

6.5 to 7.2 wt. % Zn,	1.55 to 1.95 wt. % Cu,
1.75 to 2.15 wt. % Mg,	0.095 to 0.15 wt. % Zr,
a Mg/Cu ratio of 1.05 to 1.35,	a Zn/Mg ratio of 3.2 to 4.0,
≤0.12 wt.% Si,	≤0.15 wt.% Fe,
≤0.04 wt.% Cr,	0.005 - 0.10 wt.% Ti,

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

10. The aluminum alloy product of claim 1 or 9 comprising ≤0.05 wt.% Si and / or comprising ≤0.10 wt.% Fe.

11. The aluminum alloy product of claim 1 or 9 wherein said aluminum alloy product is a 1-10 inches thick plate, extrusion, or forging product.

12. The aluminum alloy product of claim 11 having a yield tensile strength (YTS) in the LT direction ≥ 67 ksi; and optionally having a K1c value in the T-L direction of ≥ 28 ksi-in$^{1/2}$.

13. The aluminum alloy product of claim 11 or 12 having a K1c value in the T-L direction of ≥ 28 ksi-in$^{1/2}$ and a yield tensile strength (YTS) in the LT direction ≥ 67 ksi; and optionally having K_{max}-$_{dev}$ values ≥ 33 MPa-m$^{1/2}$; and / or optionally having EAC values ≥ 100 days.

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

a. casting stock of an ingot of an AA7xxx-series aluminum alloy comprising the aluminum alloy product of claim 1;
b. homogenizing the cast stock at temperatures from 454 to 491 °C (849 to 916°F);
c. hot working the stock by one or more methods selected from the group consisting of rolling, extrusion, and forging at a temperature of 385 to 450 °C (725 to 842°F);
d. solution heat treating (SHT) of the hot worked stock at temperature range from 454 to 491 °C (849 to 916°F);
e. cold water quenching said SHT stock;
f. optionally stretching the SHT stock at about 1.5 to 3%.; and
h. ageing of the SHT, cold water quenched and optionally stretched stock to a desired temper.

15. The method of claim 14, wherein said step of ageing includes a two-step 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.

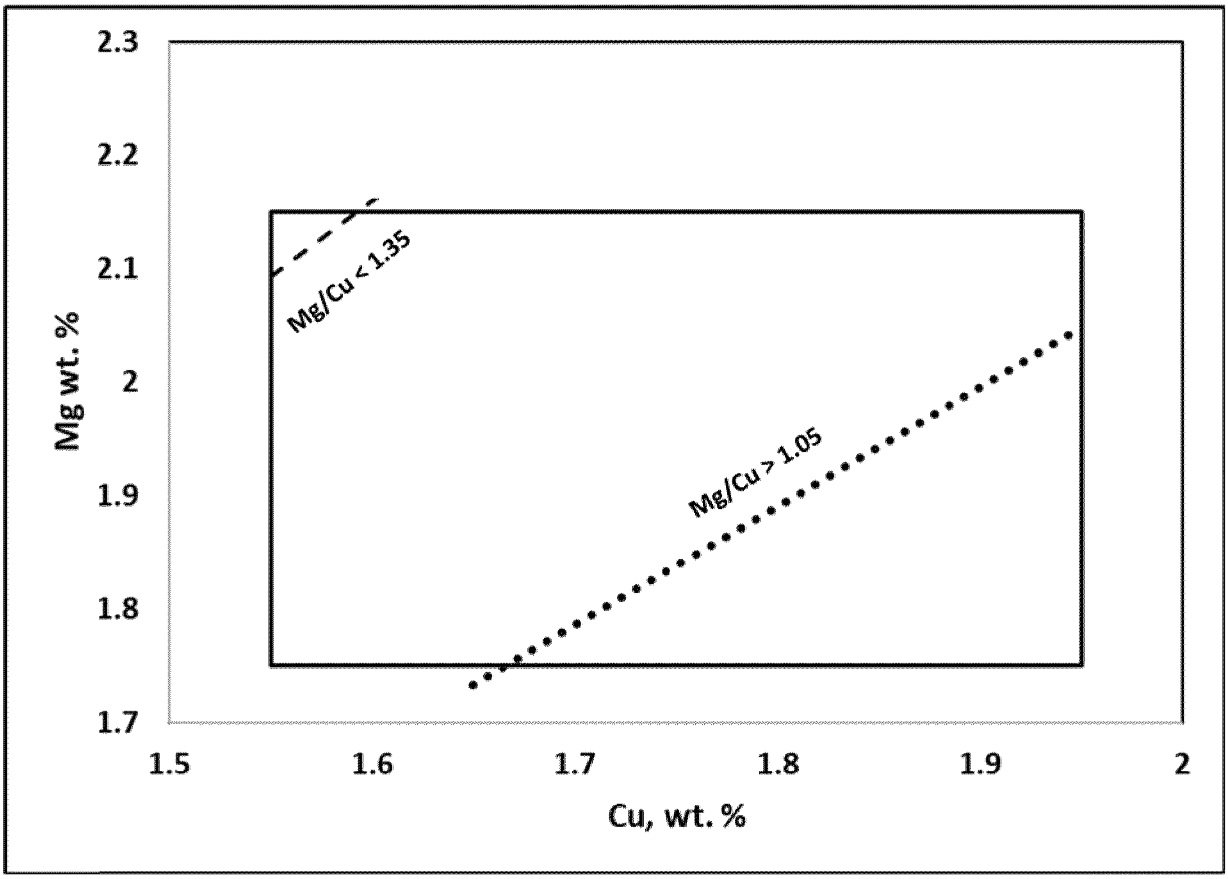

FIG. 1

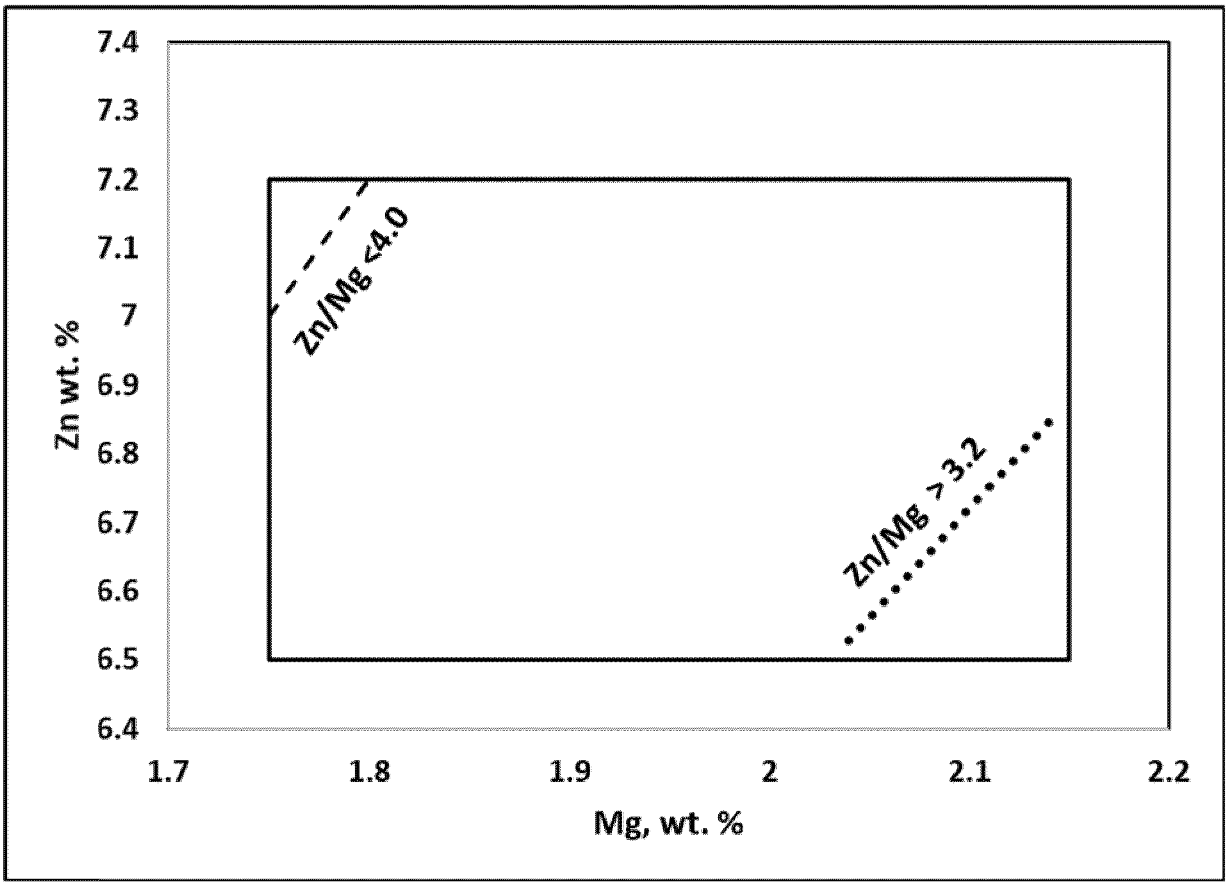
7.4
7.3
7.2
7.1
7
6.9
6.8
6.7
6.6
6.5
6.4
Zn wt. %
Zn/Mg <4.0
Zn/Mg > 3.2
1.7
1.8
1.9
2
2.1
2.2
Mg, wt. %

FIG. 2

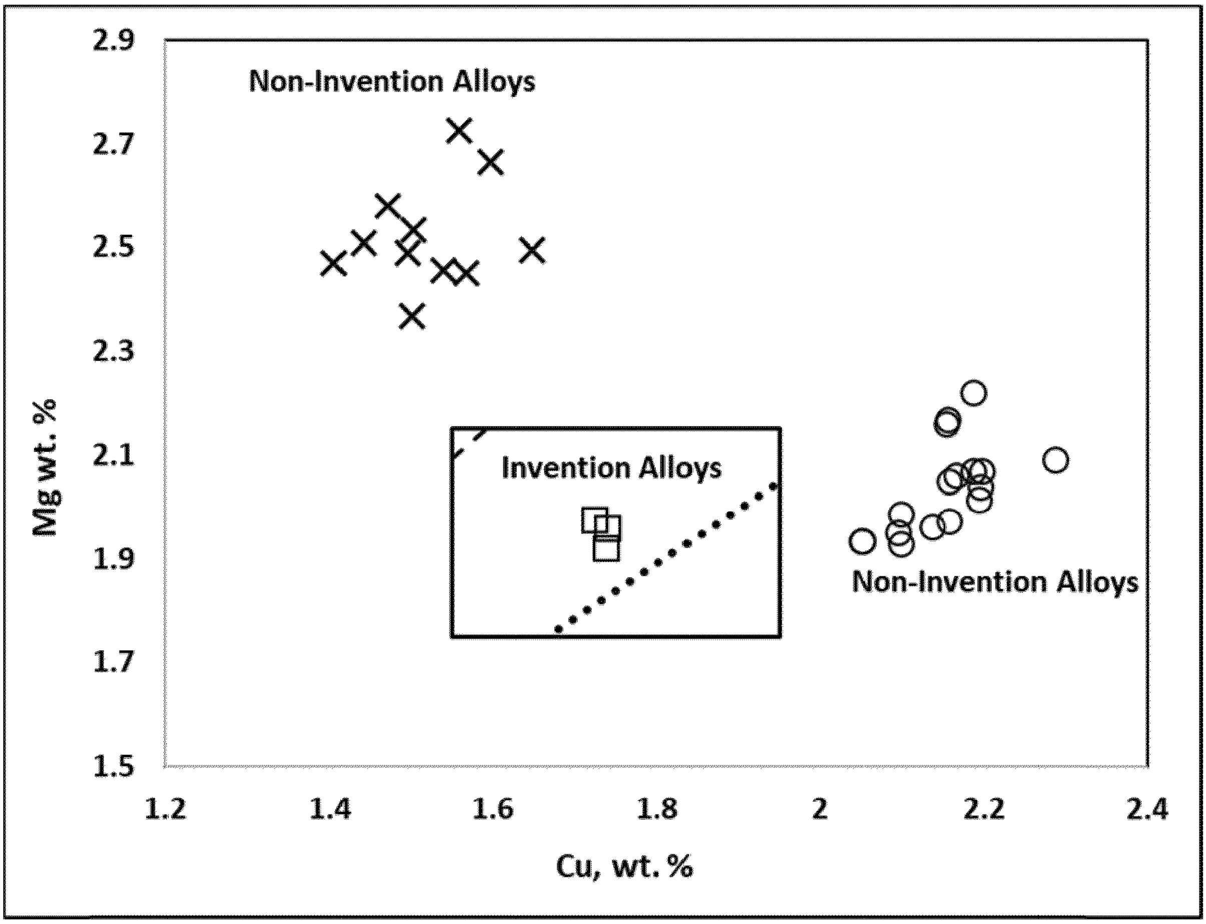
Non-Invention Alloys
Invention Alloys
Non-Invention Alloys
Mg wt. %
Cu, wt. %
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.2
1.4
1.6
1.8
2
2.2
2.4

FIG. 3

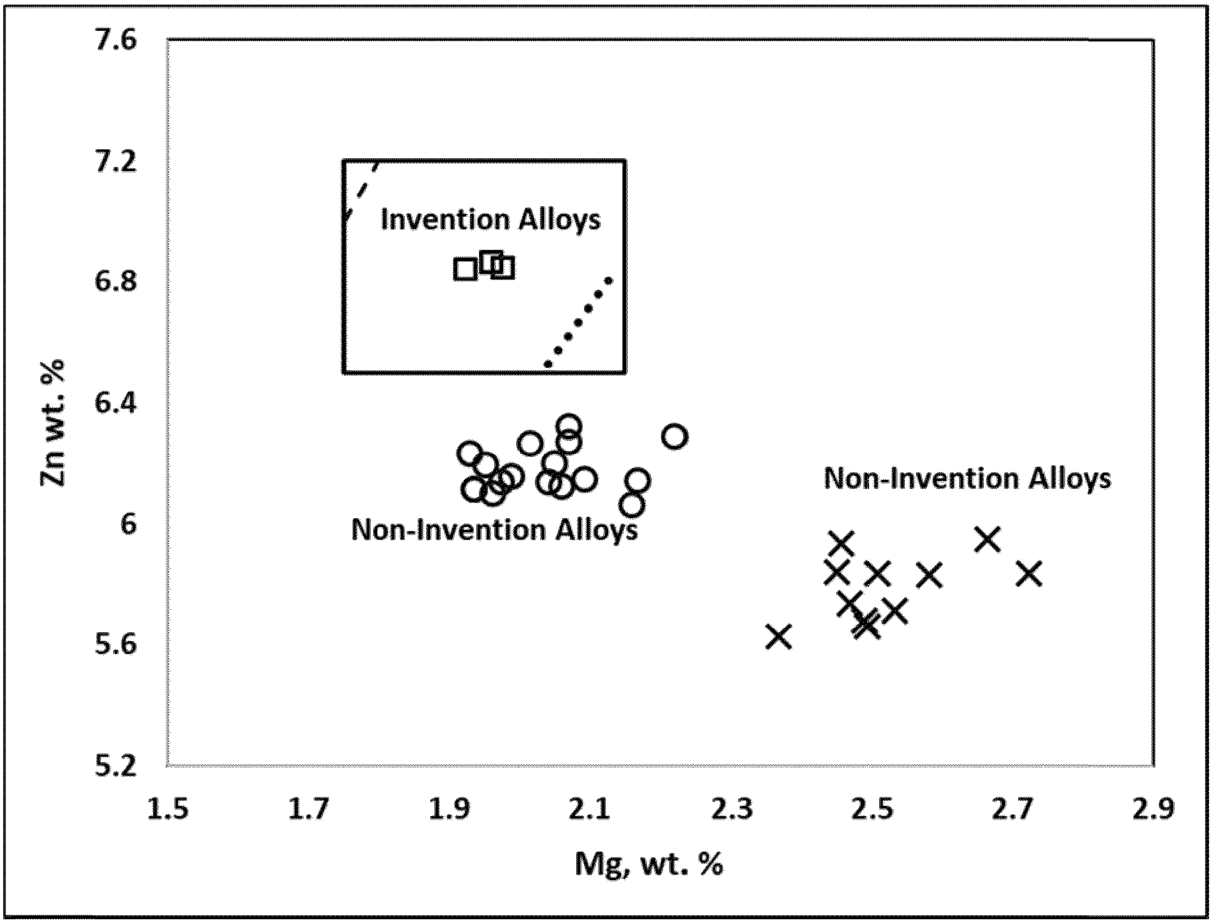
7.6
7.2
6.8
6.4
6
5.6
5.2
Zn wt. %
1.5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
Mg, wt. %
Invention Alloys
Non-Invention Alloys
Non-Invention Alloys

FIG. 4

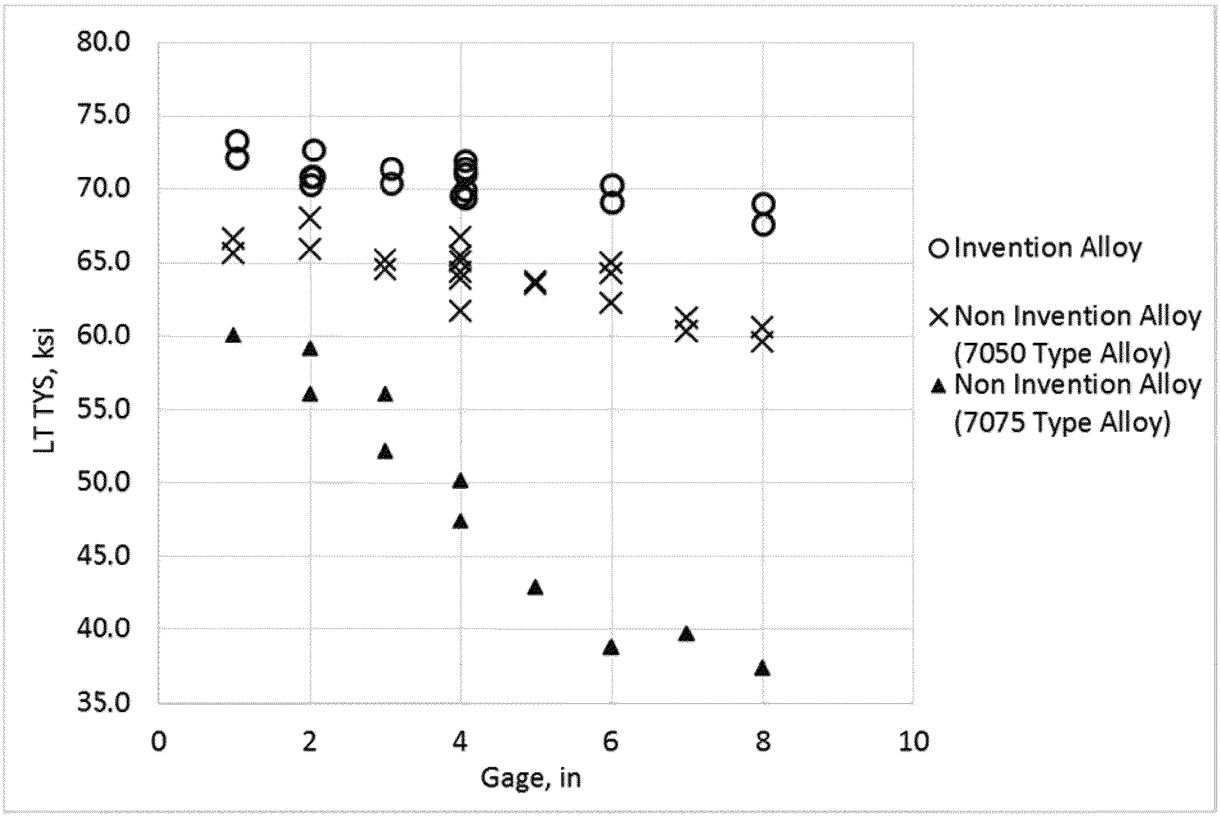
80.0
75.0
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
LT TYS, ksi
0
2
4
6
8
10
Gage, in
Invention Alloy
Non Invention Alloy (7050 Type Alloy)
Non Invention Alloy (7075 Type Alloy)

FIG. 5

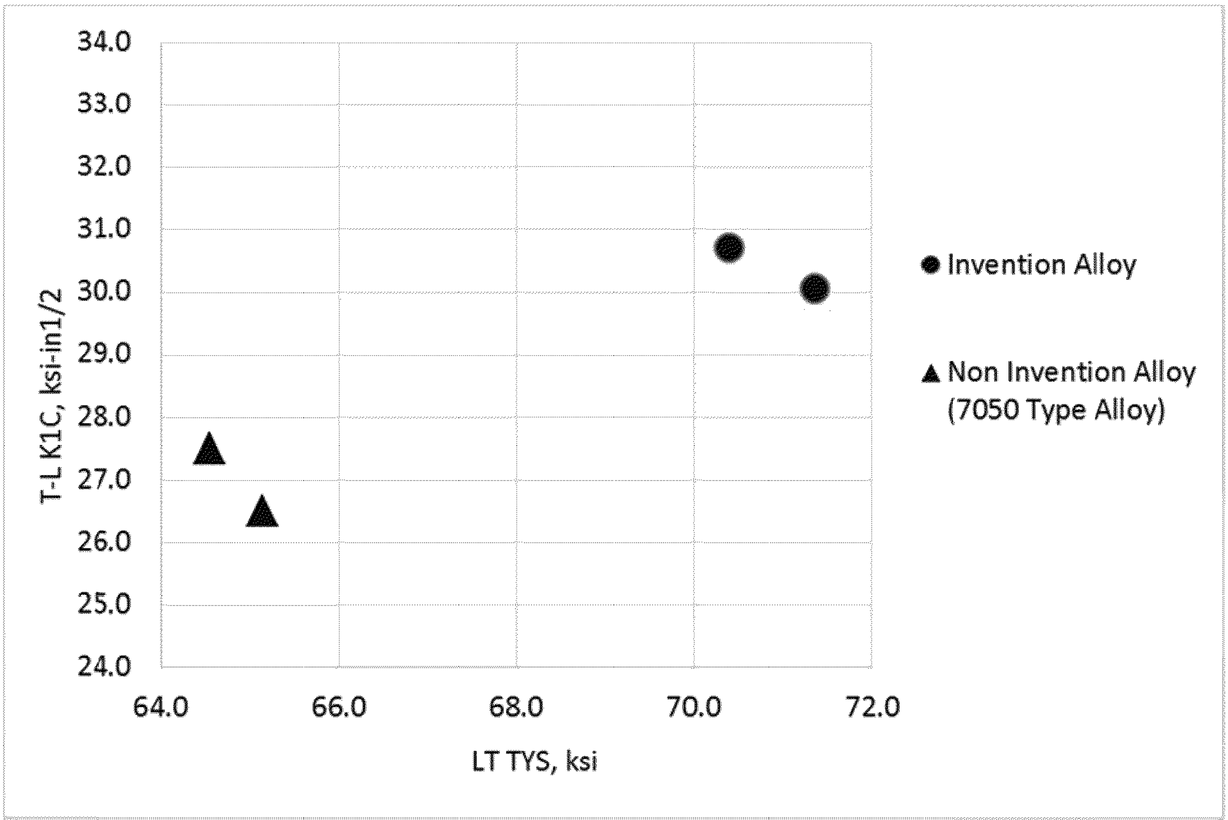
34.0
33.0
32.0
31.0
30.0
29.0
28.0
27.0
26.0
25.0
24.0
T-L K1C, ksi-in1/2
64.0
66.0
68.0
70.0
72.0
LT TYS, ksi
Invention Alloy
Non Invention Alloy
(7050 Type Alloy)

FIG. 6

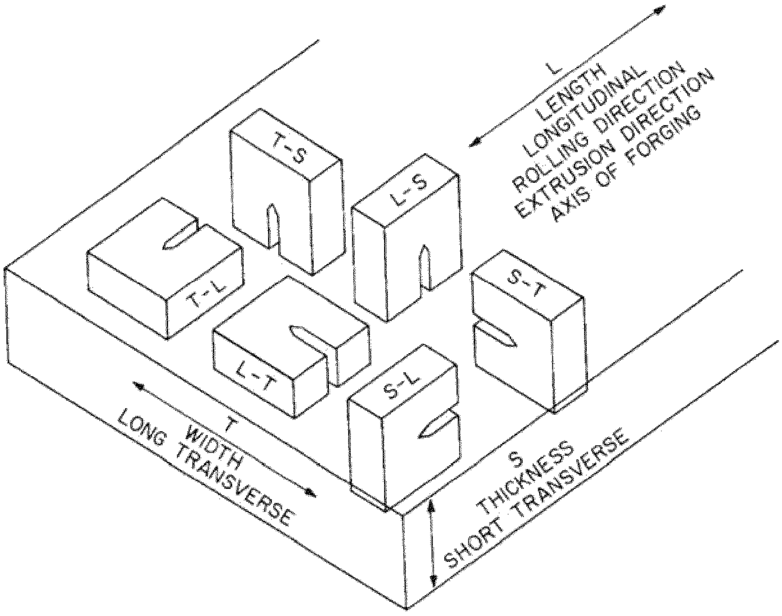
L
LENGTH
LONGITUDINAL
ROLLING DIRECTION
EXTRUSION DIRECTION
AXIS OF FORGING
T-S
L-S
T-L
L-T
S-T
S-L
T
WIDTH
LONG TRANSVERSE
S
THICKNESS
SHORT TRANSVERSE

FIG. 7

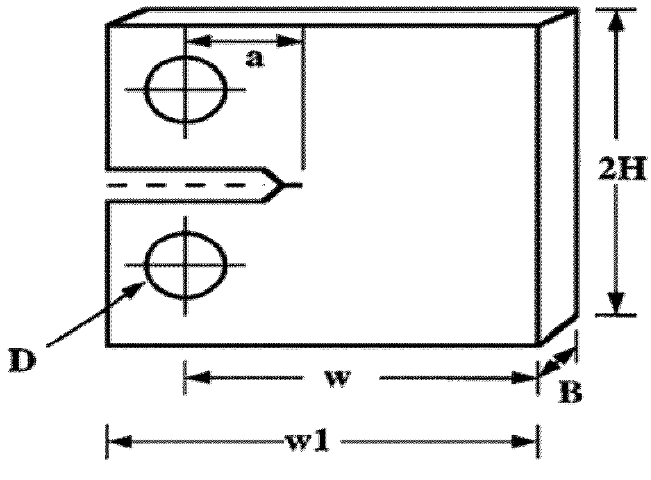
a
2H
D
w
B
w1

FIG. 8

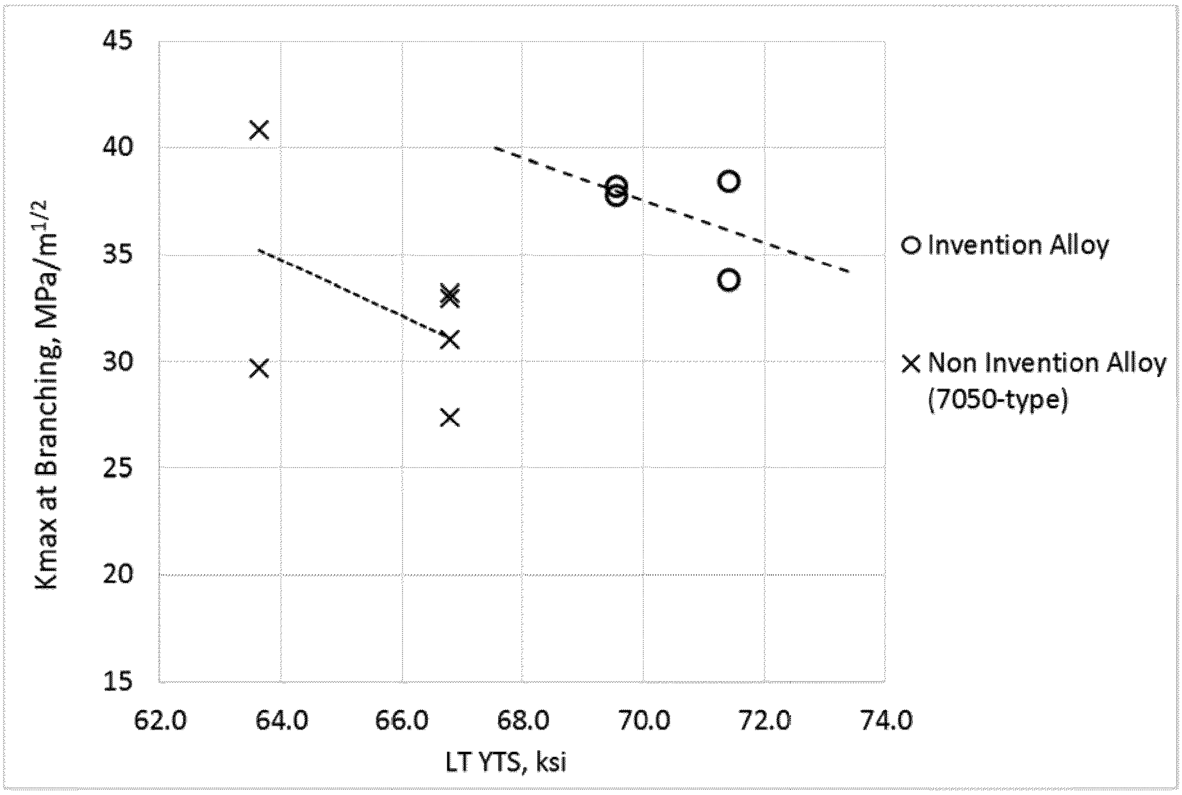
45
40
35
30
25
20
15
Kmax at Branching, MPa/m^1/2
62.0
64.0
66.0
68.0
70.0
72.0
74.0
LT YTS, ksi
Invention Alloy
Non Invention Alloy
(7050-type)

FIG. 9

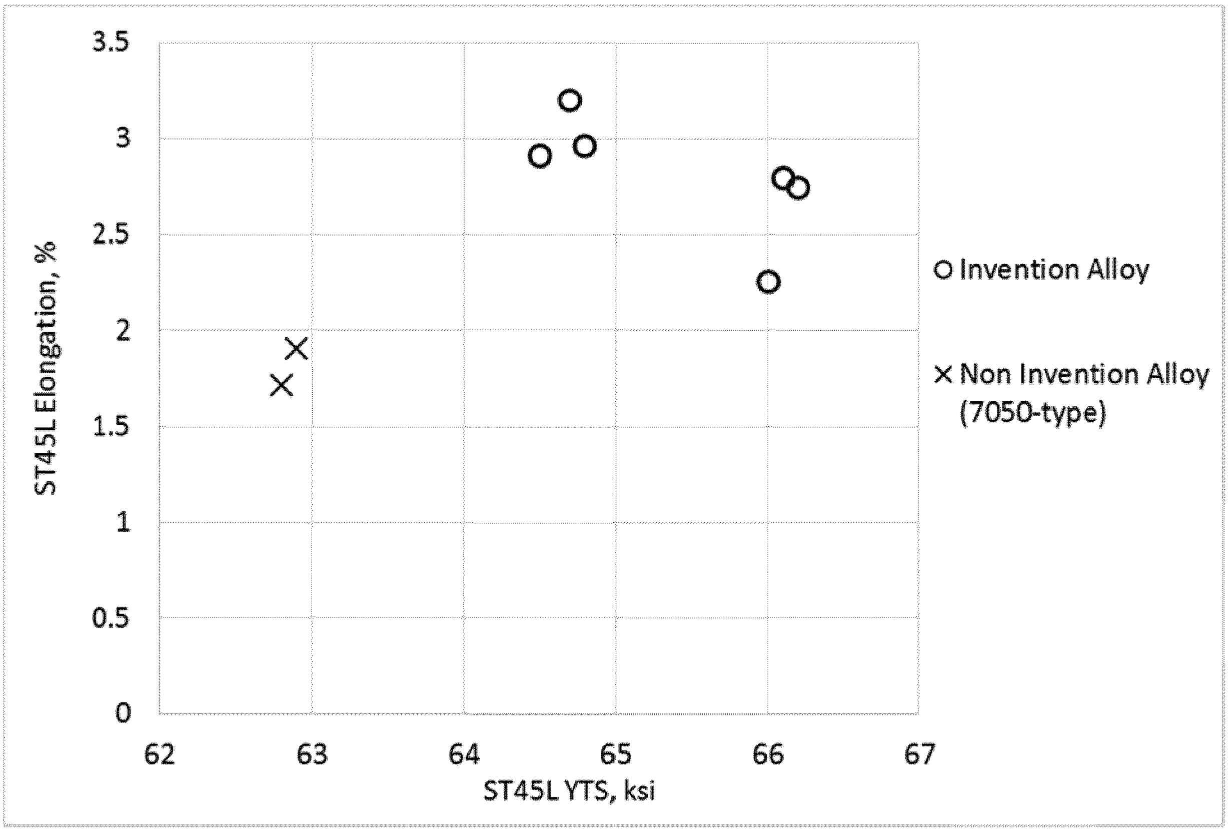
3.5
3
2.5
2
1.5
1
0.5
0
ST45L Elongation, %
62
63
64
65
66
67
ST45L YTS, ksi
Invention Alloy
Non Invention Alloy
(7050-type)

FIG. 10

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 21 20 7643

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2006/086534 A2 (ALCAN ROLLED PRODUCTS RAVENSWOOD LLC [US]; ALCAN RHENALU [FR] ET AL.) 17 August 2006 (2006-08-17) * H (7040); page 14; example 3; tables 6-7 * * J (invention); page 15 - page 16; example 4; tables 8-10 * * page 10 - page 13; example 1 * * claims 1-22 * -----	1-15	INV. C22C21/10 C22F1/00 C22F1/053
X	US 2020/232072 A1 (WHELCHEL RICKY [US] ET AL) 23 July 2020 (2020-07-23) * paragraph [0100] - paragraph [0110] * * Sample C and D; tables 1-3 * * claims 1-14 * -----	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C22C
C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	23 March 2022	Neibecker, Pascal

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 21 20 7643

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-03-2022

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006086534 A2	17-08-2006	AT 453731 T	15-01-2010
		BR PI0606957 A2	28-07-2009
		CA 2596190 A1	17-08-2006
		CN 101115856 A	30-01-2008
		CN 103834837 A	04-06-2014
		EP 1861516 A2	05-12-2007
		ES 2339148 T3	17-05-2010
		JP 5149629 B2	20-02-2013
		JP 2008530365 A	07-08-2008
		US 2006191609 A1	31-08-2006
		WO 2006086534 A2	17-08-2006
US 2020232072 A1	23-07-2020	CA 3074942 A1	04-04-2019
		EP 3688202 A1	05-08-2020
		FR 3071513 A1	29-03-2019
		JP 2020535307 A	03-12-2020
		US 2020232072 A1	23-07-2020
		WO 2019063490 A1	04-04-2019

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 63112294 **[0001]**