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(54) **Ultra-thick high strength 7xxx series aluminum alloy products and methods of making such products**

(57) The present invention is directed to an ultra-thick high strength aluminum alloy, comprising 7.5 to 8.4 wt. % Zn, 1.6 to 2.3 wt. % Mg, 1.4 to 2.1 wt. % Cu, and 0.05 to 0.15 wt. % Zr. This alloy can be fabricated to produce 2-10 inch thick plate, extrusion or forging products, and is especially suitable for aerospace structural components, especially large commercial airplane wing struc-

ture applications. The aluminum product has a minimum yield strength of [75 ksi - 0.8 x (thickness in inch - 3.94 inch)] in LT direction and [76 ksi - 0.8 x (thickness in inch - 3.94 inch)] in L direction for more than 2 inch thick product in T7651 temper. Besides strength, product provides necessary damage tolerance performance as well as corrosion resistance performance suitable for aerospace application.

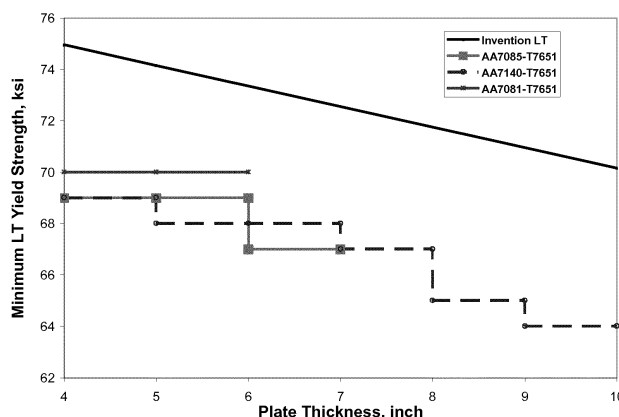


FIG. 1

**Description****BACKGROUND OF THE INVENTION**

## 1. Field of the Invention

**[0001]** The present invention relates to ultra-thick high strength aluminum alloy products and methods for making such products having a Zn content of more than 7.5 wt. %. In one embodiment, the ultra-thick high strength aluminum alloy product is a 7xxx series aluminum alloy used for thick plate, extrusion and forging products applied in aerospace structure applications.

## 2. Description of Related Art

**[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, ultra-thick high strength 7xxx aluminum alloys are being assertively pursued 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. An ultra-thick plate is required for such large monolithic component. However, the combination of high strength and high thickness imposes an extreme metallurgical challenge to produce such ultra-thick high strength aluminum plate for the aluminum manufacturing industry.

**[0003]** 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  $MgZn_2$  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 with Zn in the metastable  $MgZn_2$  phases. In general, Cu has approximately the equivalent effect on strength as the same weight percent of Zn addition.

**[0004]** In order to achieve aging precipitation hardening, 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 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 elements, into solid solution. Therefore, it is an extreme challenge to simultaneously achieve high strength, high fracture toughness, and desirable corrosion resistance for high Zn level 7xxx aluminum alloys.

**[0005]** 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's center significantly decreases, resulting in not only overall lower strength but also a large difference of strength between the plate's center and surface. This phenomenon is also referred to as high strength 7xxx thick plate quench sensitivity, which is believed to be of great concern in high strength 7xxx aluminum alloy.

**[0006]** Another challenge from thick plate high strength 7xxx aluminum alloys is the ductility along through-thickness direction, which is also an indicator for damage tolerance performance. The ductility is normally evaluated by tensile elongation along thickness direction (also called Short-Transverse, or ST, direction). It is well known that a higher strength alloy has lower elongation than a lower strength 7xxx aging hardening alloy. Therefore, the solution, although not desirable, to achieve required elongation for aerospace application is to sacrifice strength by using longer aging temper T7451 instead of higher strength T7651 temper.

**[0007]** Due to the extreme challenge from quench sensitivity, 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 "Aluminum Standard and Data 2009", only AA7140, AA7081, and AA7085 are registered to provide equal or thicker than 4 inch commercial scale aerospace application plates with high strength T7651 temper. It should be noticed that higher Zn (i.e. above 7.5%) alloy 7449 T7651 is limited to 4" maximum gauge. AA7140, the only alloy without restricting 7.0 inch gauge, has a low Zn level in the range of 6.2 to 7.0 wt. %. No fracture toughness values are specified for AA7081-T7651 in "Aluminum Association: 2011 Yellow/Tan Sheets".

**[0008]** AA7085 is an alloy registered at the Aluminum Association. This alloy was claimed to be capable of producing more than 4.0" thick high strength 7xxx alloy plate for aerospace application. It is worth noting that a very low content of Mg (preferred range of 1.2-1.7 wt. %), and lower Cu and Zn amounts were used to improve quench sensitivity. Meanwhile, others have addressed the concerns related to a low Mg content, such as providing for the condition of " $Mg \leq (Cu+0.3)$ ". The chemistry with lower alloying elements of Mg, Cu and Zn usually has lower strength, which is not desirable for weight reduction of aerospace application.

**[0009]** A high strength 7xxx aluminum alloy used for aerospace application having a high Zn in the range of 7.6 to 8.4 wt. %, a higher Cu level (2.0 - 2.6 wt. % Cu), and very high Cu/Mg ratio (1.15) is known. However, this alloy is generally not capable of producing thick cross section products as said thickness ranges from about 0.3 or 0.35 inch up to about 1.5", 2" or even 3" inches. Also, the maximum thickness of the examples provided in the prior art is about 1.5". It indirectly

implicates that thick plate quench sensitivity is an extreme challenge for such alloy with normal plate processing process. **[0010]** A modified 7050 alloy with very low Fe and Si contents and a Zn content of 5.2 to 6.8 wt%, which is basically a low Zn level alloy, is also known. In addition, a higher Cu than Mg strategy is used in this alloy. More importantly, the plate thickness is related to low gauge products as within around from about 0.35 or 0.4 or 0.45 or 0.5 to about 1.9 or 2.0 or 2.1 inches. Even for rather low thickness products the moderate level of Zn, Cu and Mg along with high purity has to be used to improve damage tolerance properties. However, the challenge of quench sensitivity on high gauge product suitable for aerospace application still exists.

**[0011]** Also known is a high strength 7xxx alloy to improve exfoliation through an aging process consisting of 5.9-6.9 wt. % Zn, 1.5-4.0 wt. % Mg, and 1.5-3.0 % wt. Cu. This alloy is basically a low Zn version 7xxx alloy. Also, Mg and Cu levels are so wide that they almost include all existing 7xxx alloys. The chemistry is exactly the same as Aluminum Association registered 7150 alloy chemistry range. Therefore, this alloy is basically for 7050 type alloy, not for high Zn high strength alloys. Also, this alloy is mainly for lower gage products such as the lower gage, 0.156", 0.25" and 0.8" inch plate.

**[0012]** Another known aerospace 7xxx aluminum alloy has a suitable alloy temper condition for aerospace application, which requires damage tolerance performance, and includes a low strength condition as specified as T7451 temper. It is well known in the art that damage tolerance property can be improved by lower strength aging temper for 7xxx aluminum alloys. In addition, no elongation along through-thickness direction has been shown. It is known that ductility along through-thickness direction is another critical indicator for damage tolerance performance. It is also well known that higher strength has lower elongation for 7xxx age hardening alloys. The maximum Zn in such prior art examples for the temper is only 6.4 wt. %. It is also known that the chemistry of 5.7-8.7 Zn, 1.7-2.5 Mg, 1.2-2.2 Cu is essentially the base for Aluminum Association registered AA7040 alloy (5.7-6.7 Zn, 1.7-2.4 Mg, 1.5-2.3 Cu), which is well known to be the lean version of 7050 alloy (6.0-6.4 Zn, 2.0-2.3 Mg, 2.0-2.3 Cu). Considering the relationship between elongation and strength, there is an indirect indication that there exists a strong challenge for high strength thick plate production for aerospace application.

**[0013]** In general, the current related prior art teaches that: 1) for ultra-thick high strength 7xxx aluminum alloys, a moderate amount of Zn, Mg, and Cu alloying elements, especially Zn, has to be used in order to reduce their adverse effects on quench sensitivity; 2) the strong challenge from thick plate damage tolerance related properties in the critical ST direction is mainly through sacrificing strength by using T7451 temper to improve these damage tolerance related properties, as is well-known by those with skills in the art; and 3) there still is a strong need for an ultra-thick high strength 7xxx aluminum alloy product with good damage tolerance properties and corrosion resistance for aerospace application, especially for large size commercial aircraft.

#### BRIEF SUMMARY OF THE INVENTION

**[0014]** Ultra-thick high strength aluminum alloy products, such as plates, forgings and extrusions, suitable for use in making aerospace structural components like large commercial airplane wing components, comprise 7.5 to 8.4 wt. % Zn, 1.6 to 2.3 wt. % Mg, 1.4 to 2.1 wt. % Cu, one or more elements selected from the group consisting of up to 0.2 wt. % Zr, up to 0.2 wt. % Sc, up to 0.2 wt. % Hf, and the balance Al, incidental elements and impurities.

**[0015]** Preferably, the alloy has a thickness of 2-10 inch, more preferably 4-10 inch, more preferably 4-8 inches and even more preferably 2-6 inch for producing plates, extrusions, and forging products. The aluminum alloy product has a minimum yield strength of [75 ksi - 0.8 x (thickness in inch - 3.94 inch)] in LT direction and [76 ksi - 0.8 x (thickness in inch - 3.94 inch)] in L direction. 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 application.

**[0016]** It has been surprisingly discovered that an aluminum alloy having a high Zn chemistry, associated with precise Mg and Cu content, along with deliberately controlled thermal mechanical processing, is capable of producing 2 to 10" gauge thick products with high strength, better damage tolerance, and corrosion properties never achieved before.

**[0017]** In one embodiment, the high strength 7xxx ultra-thick 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 ST tensile ductility, damage tolerance, corrosion resistance performance, such as exfoliation and stress corrosion resistance, and fatigue crack growth resistance.

BRIEF DESCRIPTION OF DRAWINGS

**[0018]** 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 minimum yield strength in long transverse direction (LT) as a function of the product thickness for the ultra-thick high strength aluminum alloy product of the present invention and known aluminum alloy products (the testing location is quarter thickness (T/4));

FIG. 2 is a graph showing the minimum yield strength in rolling direction (L) as a function of product thickness for the ultra-thick high strength aluminum alloy product of the present invention and known aluminum alloy products (the testing location is quarter thickness (T/4));

FIG. 3 is a graph showing the comparison of average Zn level and maximum gauge capacity between currently available T7651 high strength alloys and the ultra-thick high strength aluminum alloy product of the present invention;

FIG. 4 is a graph showing a comparison of Cu and Mg range between the ultra-thick high strength aluminum alloy product of the present invention and the preferred range in U.S. Patent 6,972,100; and

FIG. 5 is a graph showing L-T and T-L orientation fatigue crack growth rates of 5.9 inch aluminum alloy plate in accordance with the ultra-thick high strength aluminum alloy product of the present invention. The test was in accordance with ASTM E647 having a specimen that is 4" wide x 12" long x 0.25" thick. The stress ratio is 0.10 and frequency is 5 Hz.

DETAILED DESCRIPTION OF THE INVENTION

**[0019]** An ultra-thick high strength aluminum alloy product is produced using a precise chemistry range, along with proper thermal mechanical processes. In one embodiment, this ultra-thick high strength aluminum alloy product is used in aerospace applications. The ultra-thick high strength aluminum alloy product comprises about 7.5 to 8.4 wt. % Zn, 1.6 to 2.3 wt. % Mg, 1.4 to 2.1 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, and the balance Al, incidental elements and impurities. Preferably, the ultra-thick high strength aluminum alloy product, such as plates, forgings and extrusions, is suitable for use in making aerospace structural components like large commercial airplane wing components. Preferably, the alloy has a thickness of 2-10 inch, more preferably 4-10 inch, more preferably 4-8 inch, and even more preferably 2-6 inches for producing plates, extrusion, and forging products. The aluminum alloy product has a minimum yield strength of [75 ksi - 0.8 x (thickness in inch - 3.94 inch)] in LT direction and [76 ksi - 0.8 x (thickness in inch - 3.94 inch)] in L direction. 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 application.

**[0020]** In one embodiment, the ultra-thick high strength aluminum alloy product includes  $\leq 0.12$  wt. % Si, preferably  $\leq 0.05$  wt. % Si. In one embodiment, the ultra-thick high strength aluminum alloy product includes  $\leq 0.15$  wt. % Fe, preferably  $\leq 0.08$  wt. % Fe. In one embodiment, the ultra-thick high strength aluminum alloy product includes  $\leq 0.04$  wt. % Mn, preferably no Mn is added to the alloy other than that provided as an incidental impurity or element. In one embodiment, the ultra-thick high strength aluminum alloy product includes  $\leq 0.04$  wt. % Cr, preferably no Cr is added to the alloy other than that provided as an incidental impurity or element. In one embodiment, the ultra-thick high strength aluminum alloy product includes  $\leq 0.06$  wt. % Ti. In one embodiment, the ultra-thick high strength aluminum alloy product includes about 7.5 to 8.4 wt. % Zn, 1.6 to 2.3 wt. % Mg, 1.4 to 2.1 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,  $\leq 0.12$  wt. % Si,  $\leq 0.15$  wt. % Fe,  $\leq 0.04$  wt. % Mn,  $\leq 0.04$  wt. % Cr, and  $\leq 0.06$  wt. % Ti and the balance Al, incidental elements and impurities.

**[0021]** In one embodiment, the ultra-thick high strength aluminum alloy product includes 7.65-7.95 wt. % Zn, 2.00-2.20 wt. % Mg, 1.55-1.75 wt. % Cu, 0.08-0.11 wt. % Zr,  $\leq 0.05$  wt. % Si,  $\leq 0.08$  wt. % Fe, with the balance Al, incidental elements and impurities. In one aspect of this preferred embodiment, the ultra-thick high strength aluminum alloy product does not contain any additional Mn, Cr, or Ti, other than an amount that would be an incidental impurity or element. In another aspect of this preferred embodiment, the ultra-thick high strength aluminum alloy product would consist essentially of 7.65-7.95 wt. % Zn, 2.00-2.20 wt. % Mg, 1.55-1.75 wt. % Cu, 0.08-0.11 wt. % Zr,  $\leq 0.05$  wt. % Si,  $\leq 0.08$  wt. % Fe, with the balance Al, incidental elements and impurities.

**[0022]** In another embodiment, the ultra-thick high strength aluminum alloy product includes 7.78-7.94 wt. % Zn, 2.06-2.10 wt. % Mg, 1.65-1.70 wt. % Cu, 0.08-0.09 wt. % Zr, 0.03-0.04 wt. % Si, 0.06-0.07 wt. % Fe, about 0.03 wt. % Ti, with the balance Al, incidental elements and impurities. In one aspect of this preferred embodiment, the ultra-thick high strength aluminum alloy product does not contain any additional Mn or Cr other than an amount that would be an incidental impurity or element. In another aspect of this preferred embodiment, the ultra-thick high strength aluminum alloy product would consist essentially of 7.78-7.94 wt. % Zn, 2.06-2.10 wt. % Mg, 1.65-1.70 wt. % Cu, 0.08-0.09 wt. % Zr, 0.03-0.04 wt. % Si, 0.06-0.07 wt. % Fe, about 0.03 wt. % Ti, with the balance Al, incidental elements and impurities.

**[0023]** The ultra-thick high strength aluminum alloy product may be used to produce plates, extrusions, and forging products. In one embodiment, the ultra-thick high strength 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, heat solution treatments and ageing treatments.

**[0024]** In one embodiment, ingots of the ultra-thick high strength 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 ultra-thick high strength aluminum alloy is a plate subjected to a final T7651 temper in the thickness range from 2 inch to 6 inch. The ingots may be homogenized at temperatures from 454 to 491 °C (850 to 915°F). The hot rolling start temperature may be from 399 to 443 °C (750 to 830°F). The exit temperature may be in a similar range as the start temperature. The rolling reduction of each pass may be deliberately controlled to achieve target temperature during hot rolling process. The plates may be solution heat treated at temperature range from 454 to 491 °C (850 to 915°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 subjected 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 150 to 200 °C (212 to 392 °F) for 5 to 20 hours.

**[0025]** FIG. 1 and FIG. 2 are graphs showing the minimum strength as a function of plate thickness provided in an ultra-thick high strength aluminum alloy product in accordance with the present invention compared with other aluminum alloy products currently available based on the most recent "Aluminum Association: 2011 Yellow/Tan Sheets" and "Aluminum Standard and Data 2009". The minimum strength of the ultra-thick high strength aluminum alloy product in accordance with the present invention is based on a significant number of commercial production trial lots and calculated based on the statistical method outlined in MMPDS-06. It should be mentioned that no fracture toughness values are specified for AA7081-T7651 in "Aluminum Association: 2011 Yellow/Tan Sheets". AA7140, the only alloy without restricting gauge, has a low Zn level in the range of 6.2 to 7.0 wt. %.

**[0026]** The ultra-thick high strength aluminum alloy product in accordance with the present invention is based on a fundamental understanding of how chemistry affects large cross section quench sensitivity of 7xxx alloys. The quench sensitivity is affected by the thermodynamic behavior of precipitations during quenching. The thermodynamic driving force of precipitation is strongly affected by chemical composition. This is the reason that chemical composition optimization is very important for high strength 7xxx production.

**[0027]** The favorable sites for precipitation include large and small angle grain boundaries as well as particles with preference to fine size dispersoid particles. The fine dispersoid particles form due to the addition of grain refiner elements such as Zr, Cr, Sc, and Mn. The fine dispersoid particles are preferred sites for precipitation during quenching. Meanwhile, the dispersoid particles significantly retard grain recrystallization, resulting in less large angle grain boundaries, which are also favorable sites for precipitation.

**[0028]** The recrystallization is also affected by rolling history. It is also well known that hot rolling processes strongly affects aluminum crystallographic texture and subsequently final product anisotropy mechanical property, through thickness properties and quench sensitivity as discussed in the paper "A Study of Through-Thickness Texture Gradients in Rolled Sheets" by O. Engler et al. published in "Metallurgical and Materials Transaction A" in September 2000 and another paper "Through Thickness Property Variations in 7050 Plate" by D.J. Chakrabakti et al., published in "Materials Science Forum Vols., 217 - 211" in 1996. The thermomechanical processing, especially hot rolling, must be precisely controlled in order to achieve appropriate microstructure including crystallographic texture for desirable static mechanical properties and damage tolerance related properties.

**[0029]** The present invention is directed to an ultra-thick high strength aluminum alloy product with a high content of Zn in the range of 7.5 - 8.4 wt. % to increase strength. With a precise content of Mg in the range of 1.6 to 2.3 wt. % and Cu in the range of 1.4 to 2.1wt. %, this ultra-thick high strength aluminum alloy product is surprisingly capable of use as a high strength thick plate for aerospace application. Compared with previously known technologies of available high strength thick plates, the present invention has a much higher Zn content and higher gauge capability as demonstrated in FIG 3.

**[0030]** As seen in the graph provided for FIG. 3, the closest product is AA7085-T7651, in which Zn is at the average of 7.5 wt. % with maximum of 7" gauge capacity. AA7085 was registered by Alcoa and provided in US Patent No. 6,972,100. This patent generally provides that a preferred chemistry range, as shown in FIG. 4, can produce more than 4.0" thick high strength 7xxx alloy plate for aerospace application. Surprisingly, the ultra-high strength aluminum alloy product in accordance with the present invention, with distinctive chemistry characterized by higher Zn and Mg, is capable of producing even higher strength thick plates, while keeping a good short transverse ductility and damage tolerance.

**[0031]** The selected content range of Mg and Cu in the ultra-thick high strength aluminum alloy product in accordance with the present invention is especially important for alloys with a high Zn range of 7.5 to 8.4 wt. % as specified for the present invention. Although 7040 has similar Mg and Cu composition ranges as the present invention, it has much lower

Zn level. The yield strengths, as shown in FIG. 1 and FIG. 2, between the ultra-thick high strength aluminum alloy product of the present invention and the alloys generally provided in US Patent 6,027,582 are significantly different partially due to different Zn levels.

**[0032]** Although the following examples demonstrate various embodiment of the present invention, one of skill in the art should understand how additional ultra-thick high strength aluminum alloy products may 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. Unless otherwise indicated herein, all percentage amounts are % by weight.

#### Examples (Plant Trial)

**[0033]** More than 20 industrial scale 508mm (20 inch) thick ingots were cast by DC (Direct Chill) casting process and processed to different gauge plates. Those plates provided a sufficient material properties database to establish the minimum strength of the ultra-thick high strength aluminum alloy product in accordance with the present invention based on the statistical method outlined in MMPDS-06. Table 1 gives the typical chemical compositions of selected plates with different gauges.

Table 1: Chemical compositions of industrial scale ingots

| Batch    | Thickness (mm) | Thickness (in) | Si   | Fe   | Cu   | Mg   | Zn   | Ti   | Zr   |
|----------|----------------|----------------|------|------|------|------|------|------|------|
| 537101A8 | 50             | 2.0            | 0.04 | 0.06 | 1.65 | 2.09 | 7.93 | 0.03 | 0.09 |
| 537041A6 | 75             | 3.0            | 0.03 | 0.06 | 1.66 | 2.06 | 7.78 | 0.03 | 0.09 |
| 537017A6 | 100            | 3.9            | 0.03 | 0.06 | 1.66 | 2.06 | 7.78 | 0.03 | 0.09 |
| 537204A0 | 125            | 4.9            | 0.04 | 0.06 | 1.65 | 2.09 | 7.93 | 0.03 | 0.09 |
| 537232A1 | 140            | 5.5            | 0.04 | 0.06 | 1.65 | 2.08 | 7.94 | 0.03 | 0.09 |
| 537131A5 | 150            | 5.9            | 0.04 | 0.07 | 1.70 | 2.10 | 7.87 | 0.03 | 0.08 |

**[0034]** Ingots were homogenized, hot rolled, solution heat treated, quenched, stretched and aged to final T7651 temper plates in the thickness range from 2 inch to 6 inch. The ingots were homogenized at temperature from 454 to 491 °C (850 to 915°F). The hot rolling start temperature is from 399 to 443 °C (750 to 830°F). The exit 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.

**[0035]** The plates were solution heat treated at temperature range from 454 to 491 °C (850 to 915°F). The plates were stretched at about 1.5 to 3% and cold water quenched to room temperature. A two-step aging practice was used to produce final T7651 temper. The first stage temperature is in the range of 100 to 140 °C (212 to 284 °F) for 4 to 24 hours and the second stage temperature is in the range of 150 to 200 °C (212 to 392 °F) for 5 to 20 hours.

**[0036]** Tables 2 and 3 give tensile and fracture toughness properties. The 0.2% offset yield strength (TYS) along rolling direction (L) and transverse direction (LT) were measured at both quarter thickness (a/4) and center thickness (a/2) under ASTM B557 specification. The plane strain fracture toughness ( $K_{IC}$ ) in L-T and T-L orientations at both quarter thickness (T/4) and center thickness (T/2) were measured under ASTM E399 using CT specimens.

**[0037]** As described previously, the ST elongation property is one important indicator for product damage tolerance performance. The ST elongation of the samples provided in this examples is about 4 to 6 %, which is very good compared with those alloys previous known in the art. The prior art with the closest, but not the same, chemistry is AA7449. Unfortunately, AA7449 is not capable of being produced as more than a 4" plate based on "Aluminum Association: 2011 Aluminum Standard and Data Yellow/Tan Sheets". The minimum ST yield strength and elongation of 4" thick T7651 temper plate is 67ksi and 1% elongation. The 4" thickness is the maximum thickness that 7449-T7651 can offer as provided in "Aluminum Association: 2011 Aluminum Standard and Data Yellow/Tan Sheets". With the same thickness of 4", the samples provided herein for the ultra-thick high strength aluminum alloy product in accordance with the present invention have 72 ksi ST yield strength and 4% elongation, which are much higher than AA7449 alloy. It is also well-known by those skilled in the art that with the same 7449 chemistry, at higher thickness, ST elongation would be further reduced. However, the ultra-thick high strength aluminum alloy products in accordance with the present invention at 5.9" thickness has a ST elongation measured at 4.0%.

**[0038]** Stress corrosion resistance is critical for aerospace application. The standard stress corrosion 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 60 days testing without

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failing under 200MPa 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.

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Table 2: Tensile properties of final product T7651 temper plates

|  | Batch    | LT a/2        |              |              | LT a/4     |              |              | L a/2      |              |              | L a/4      |              |              | ST a/2     |              |              |
|--|----------|---------------|--------------|--------------|------------|--------------|--------------|------------|--------------|--------------|------------|--------------|--------------|------------|--------------|--------------|
|  |          | Gauge<br>(in) | TYS<br>(ksi) | UTS<br>(ksi) | EL.<br>(%) | TYS<br>(ksi) | UTS<br>(ksi) | EL.<br>(%) | TYS<br>(ksi) | UTS<br>(ksi) | EL.<br>(%) | TYS<br>(ksi) | UTS<br>(ksi) | EL.<br>(%) | TYS<br>(ksi) | UTS<br>(ksi) |
|  | 537041A6 | 2.0           | 78.6         | 83.5         | 12.8       | 80.5         | 85.6         | 11.6       | 80.7         | 85.4         | 14.4       | 81.7         | 85.8         | 13.0       | 76.4         | 85.7         |
|  | 537245A3 | 3.0           | 76.2         | 81.7         | 11.4       | 77.5         | 83.9         | 9.1        | 79.2         | 84.2         | 12.4       | 79.4         | 84.0         | 11.6       | 75.3         | 81.3         |
|  | 537017A6 | 3.9           | 75.6         | 81.2         | 10.1       | 77.9         | 84.3         | 8.6        | 79.4         | 84.1         | 11.4       | 78.7         | 82.0         | 11.7       | 73.9         | 80.5         |
|  | 537204A0 | 4.9           | 72.5         | 78.6         | 9.4        | 75.4         | 81.9         | 8.3        | 75.8         | 81.3         | 11.6       | 75.9         | 79.7         | 12.4       | 70.1         | 78.2         |
|  | 537232A1 | 5.5           | 71.4         | 78.3         | 8.0        | 74.5         | 81.2         | 7.2        | 75.1         | 80.6         | 10.7       | 75.4         | 79.9         | 11.1       | 69.4         | 78.0         |
|  | 537131A5 | 5.9           | 72.5         | 79.0         | 6.5        | 76.2         | 82.2         | 6.1        | 77.7         | 82.9         | 10.2       | 76.9         | 80.7         | 10.3       | 71.8         | 79.6         |

Table 3: Fracture toughness properties of final product T7651 temper plates

|          | Gauge | L-T K <sub>IC</sub> at a/2 | L-T K <sub>IC</sub> at a/4 | T-L K <sub>IC</sub> at a/2 | T-L K <sub>IC</sub> at a/4 | S-L K <sub>IC</sub> at a/2 |
|----------|-------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Batch    | in    | (ksi*in <sup>1/2</sup> )   | (ksi*in <sup>1/2</sup> )   | (ksi*in <sup>1/2</sup> )   | (ksi*in <sup>1/2</sup> )   | (ksi*in <sup>1/2</sup> )   |
| 537041A6 | 2.0   | 29.1                       | 29.7                       | 25.5                       | 25.6                       | 25.6                       |
| 537245A3 | 3.0   | 28.5                       | 24.6                       | 24.3                       | 22.3                       | 24.2                       |
| 537017A6 | 3.9   | 28.2                       | 24.4                       | 23.7                       | 21.8                       | 20.7                       |
| 537204A0 | 4.9   | 29.8                       | 25.7                       | 23.9                       | 22.2                       | 23.3                       |
| 537232A1 | 5.5   | 30.3                       | 25.8                       | 24.1                       | 21.9                       | 22.2                       |
| 537131A5 | 5.9   | 29.1                       | 24.2                       | 22.8                       | 20.5                       | 21.9                       |

**[0039]** Smooth fatigue property was tested in accordance with the requirements of ASTM E466. Four LT specimens were tested from each plate at plate thickness center along transverse direction. Specimen was tested at 240MPa (35 ksi). All plates met the common industrially accepted criterion, i.e. 120,000 cycles of logarithm average of four specimens.

**[0040]** Crack propagation was tested in accordance with the testing methods established in ASTM E647. Test specimens were prepared in the L-T and T-L orientations. The test specimen geometry was 101 mm (4") wide x 305 mm (12") long (minimum) x 6.35 mm (0.25") thick. The stress ratio of 0.10 and frequency of 5 Hz was used in the testing. By way of example, FIG. 5 is a graph showing L-T and T-L orientation sample fatigue crack growth rates for a 5.9" gauge plate using the ultra-thick high strength aluminum alloy product of the present invention.

**[0041]** 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. An ultra-thick high strength aluminum alloy product comprising  
7.5 to 8.4 wt. % Zn,  
1.6 to 2.3 wt. % Mg,  
1.4 to 2.1 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 Al, incidental elements and impurities, wherein said aluminum alloy product is a 2-10 inches thick plate, extrusion, or forging product and has a minimum yield strength of [75ksi - 0.8 x (thickness in inch - 3.94 inch)] in LT direction and [76ksi - 0.8 x (thickness in inch - 3.94inch)] in L direction.
2. The ultra-thick high strength aluminum alloy product of claim 1 comprising  $\leq 0.12$  wt. % Si; optionally comprising  $\leq 0.05$  wt. % Si.
3. The ultra-thick high strength aluminum alloy product of claim 1 or 2 comprising  $\leq 0.15$  wt. % Fe; optionally comprising  $\leq 0.08$  wt. % Fe.
4. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 3 comprising  $\leq 0.04$  wt. % Mn and / or  $\leq 0.04$  wt. % Cr and / or  $\leq 0.06$  wt. % Ti.
5. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 4 consisting essentially of  
7.5 to 8.4 wt. % Zn,  
1.6 to 2.3 wt. % Mg,  
1.4 to 2.1 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,  
 $\leq 0.12$  wt. % Si,  
 $\leq 0.15$  wt. % Fe,

≤0.04 wt. % Mn,  
 ≤0.04 wt. % Cr,  
 and ≤0.06 wt. % Ti  
 with the balance Al, incidental elements and impurities.

6. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 4 consisting essentially of

|                    |                    |                    |
|--------------------|--------------------|--------------------|
| 7.65-7.95 wt. % Zn | 2.00-2.20 wt. % Mg | 1.55-1.75 wt. % Cu |
| 0.08-0.11 wt. % Zr | ≤0.05 wt. % Si     | ≤0.08 wt. % Fe     |

with the balance Al, incidental elements and impurities.

7. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 4 consisting essentially of

|                     |                    |                    |
|---------------------|--------------------|--------------------|
| 7.78-7.94 wt. % Zn  | 2.06-2.10 wt. % Mg | 1.65-1.70 wt. % Cu |
| 0.08-0.09 wt. % Zr  | 0.03-0.04 wt. % Si | 0.06-0.07 wt. % Fe |
| about 0.03 wt. % Ti |                    |                    |

with the balance Al, incidental elements and impurities.

8. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 7 wherein said aluminum alloy product is a 4-10 inches thick plate, extrusion, or forging product;  
 wherein, optionally, said aluminum alloy product is a 4-8 inches thick plate, extrusion, or forging product;  
 wherein, further optionally, said aluminum alloy product is a 2-6 inches thick plate, extrusion, or forging product.

9. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 8 having a minimum short transvers (ST) stress corrosion cracking (SCC) of 25 ksi;  
 optionally having a minimum short transverse (ST) stress corrosion cracking (SCC) of 30 ksi.

10. The ultra-thick high strength aluminum alloy product of any one of claims 1 to 9 having a minimum short transverse elongation of 2%;  
 optionally having a minimum short transverse elongation of 3%.

11. A method of manufacturing an ultra-thick high strength aluminum alloy product of an AA7xxx-series alloy, the method 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;
- 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.

12. The method of claim 11, wherein said step of homogenizing includes homogenizing at temperatures from 454 to 491 °C (850 to 915°F).

13. The method of claim 11 or 12, wherein said step of hot working includes hot rolling at a temperature of 399 to 443 °C (750 to 830°F).

14. The method of any one of claims 11 to 13, wherein said step of solution heat treating includes solution heat treated at temperature range from 454 to 491 °C (850 to 915°F).

15. The method of any one of claims 11 to 14, wherein said step of optionally stretching includes stretching at about 1.5 to 3%.

16. The method of any one of claims 11 to 15, 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 150 to 200 °C (212 to 392 °F) for 5 to 20 hours.

5 17. The method of any one of claims 11 to 15, wherein

b. said step of homogenizing includes homogenizing at temperatures from 454 to 491 °C (850 to 915°F);

c. said step of hot working includes hot rolling at a temperature of 399 to 443 °C (750 to 830°F);

10 d. said step of solution heat treating includes solution heat treated at temperature range from 454 to 491 °C (850 to 915°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%;

15 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 150 to 200 °C (212 to 392 °F) for 5 to 20 hours.

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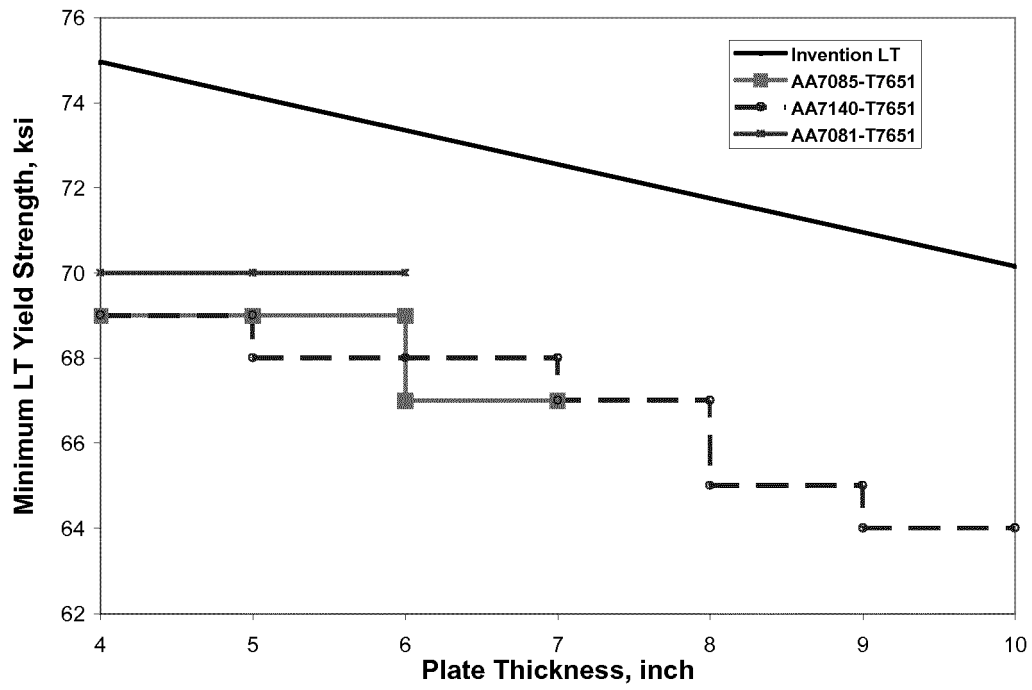


FIG. 1

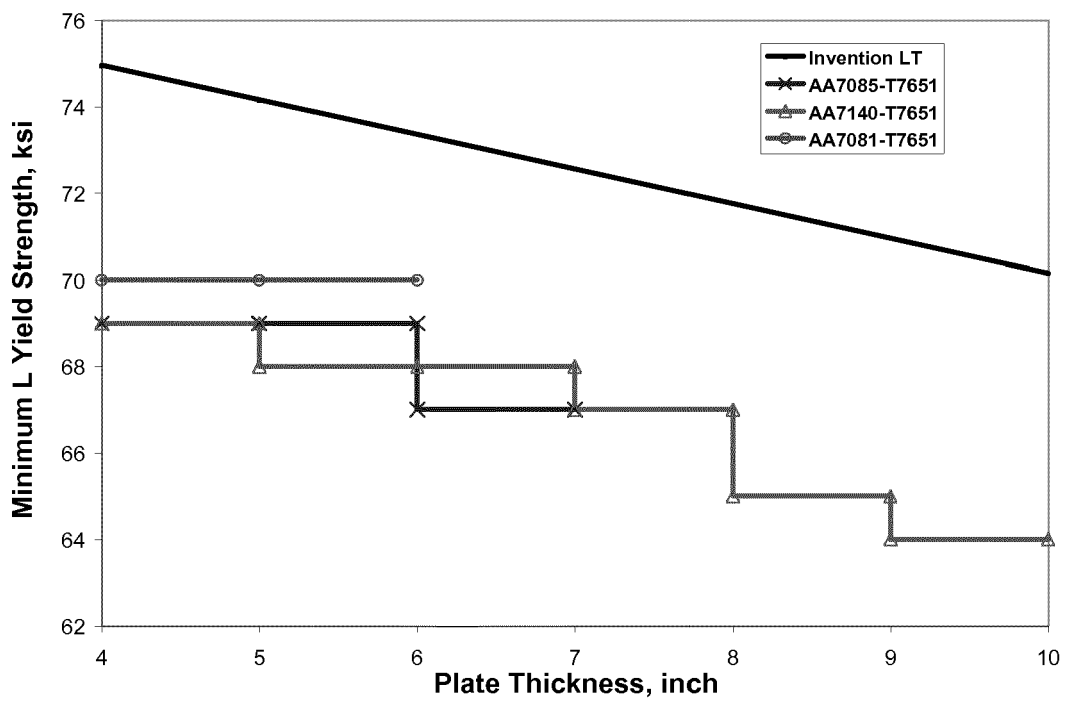


FIG. 2

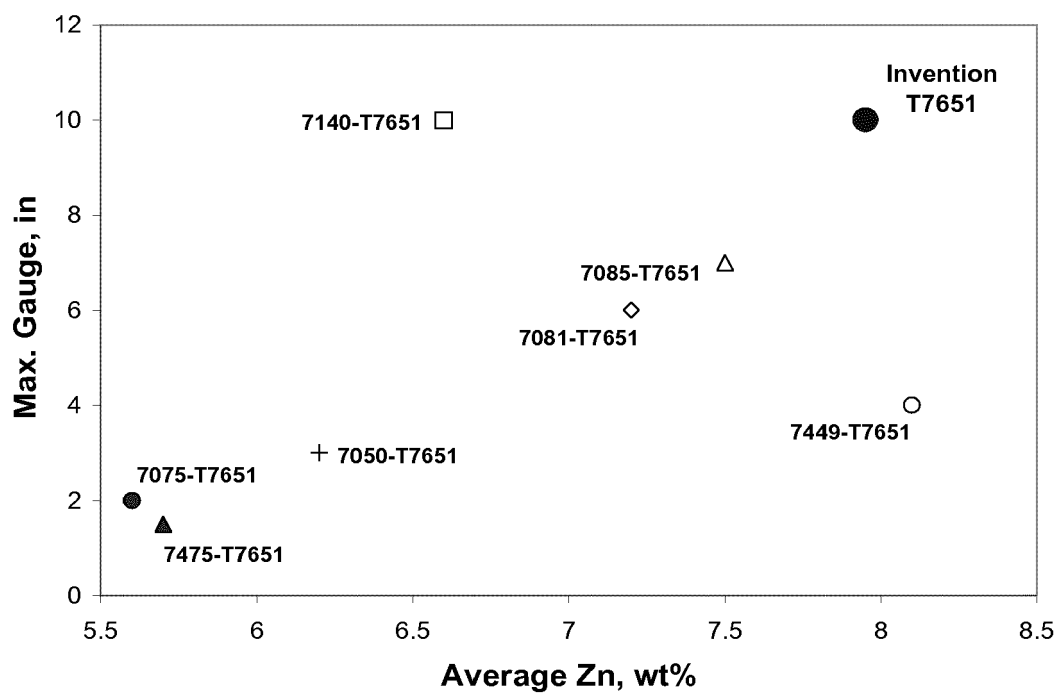


FIG. 3

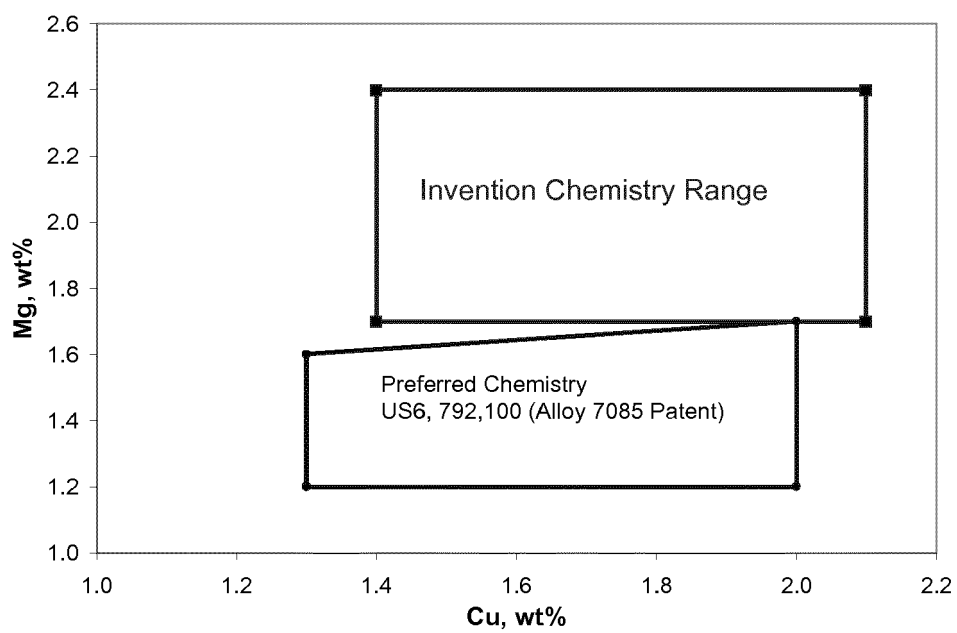


FIG. 4

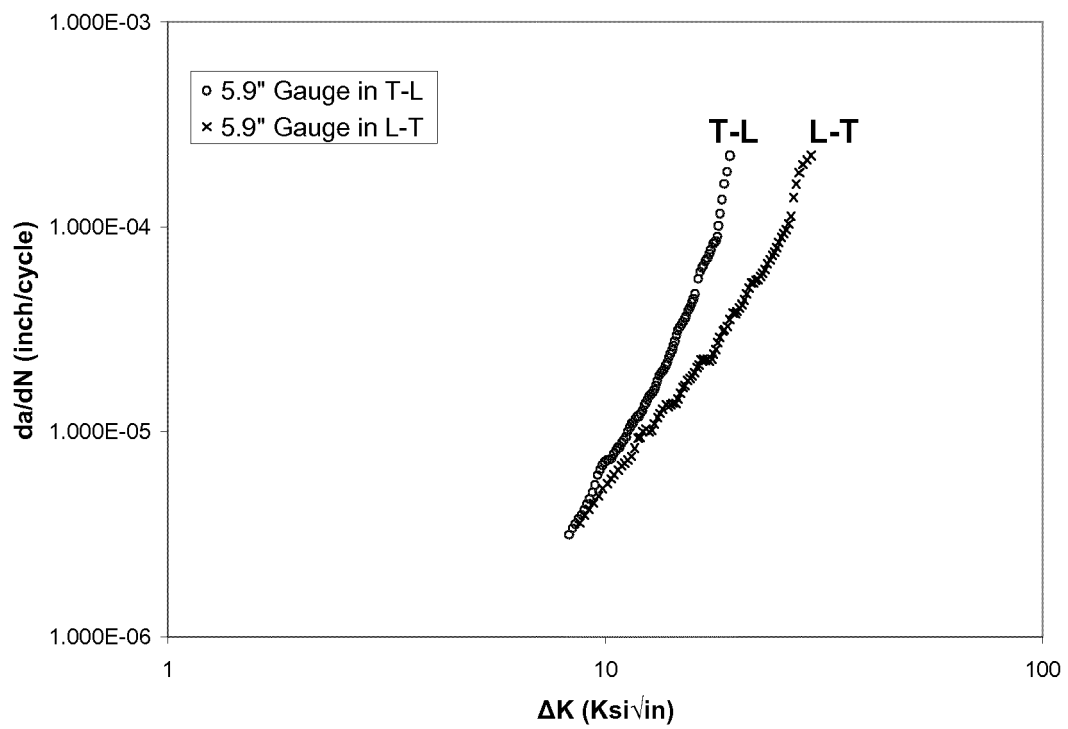


FIG. 5



## EUROPEAN SEARCH REPORT

Application Number  
EP 13 16 4525

| 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                                                                                                                                                                                                                                                      | US 2005/006010 A1 (BENEDICTUS RINZE [NL] ET AL) 13 January 2005 (2005-01-13)<br>* paragraphs [0001], [0017], [0028] - [0031], [0033], [0034], [0039], [0042]<br>*<br>-----                                                  | 1-5,8-17                                                                                                                                                                                                                                                                              | INV.<br>C22C21/10<br>C22C21/12<br>C22C21/16<br>C22F1/053 |
| X                                                                                                                                                                                                                                                      | EP 2 386 667 A1 (GEN RES INST FOR NONFERROUS METALS [CN])<br>16 November 2011 (2011-11-16)<br>* paragraphs [0001], [0010], [0014], [0021], [0025], [0037] - [0043] *<br>-----                                               | 1-5,8-17                                                                                                                                                                                                                                                                              |                                                          |
| X                                                                                                                                                                                                                                                      | US 2002/150498 A1 (CHAKRABARTI DHRUBA J [US] ET AL) 17 October 2002 (2002-10-17)<br>* paragraphs [0002], [0010], [0018], [0019], [0032], [0036], [0042], [0043], [0045], [0048], [0050], [0061], [0063]; table 1 *<br>----- | 1-5,8-17                                                                                                                                                                                                                                                                              |                                                          |
|                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                       | TECHNICAL FIELDS SEARCHED (IPC)                          |
|                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                       | C22C<br>C22F                                             |
| The present search report has been drawn up for all claims                                                                                                                                                                                             |                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                       |                                                          |
| Place of search<br><b>Munich</b>                                                                                                                                                                                                                       |                                                                                                                                                                                                                             | Date of completion of the search<br><b>30 September 2013</b>                                                                                                                                                                                                                          | Examiner<br><b>Brown, Andrew</b>                         |
| CATEGORY OF CITED DOCUMENTS<br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |                                                                                                                                                                                                                             | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>-----<br>& : member of the same patent family, corresponding document |                                                          |

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 13 16 4525

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  
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30-09-2013

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) |            |    | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|------------|----|---------------------|
| US 2005006010                             | A1 | 13-01-2005          | AU                         | 2003277929 | A1 | 06-01-2004          |
|                                           |    |                     | BR                         | 0312101    | A  | 29-03-2005          |
|                                           |    |                     | CA                         | 2485524    | A1 | 31-12-2003          |
|                                           |    |                     | CN                         | 1656240    | A  | 17-08-2005          |
|                                           |    |                     | DE                         | 10392805   | T5 | 02-06-2005          |
|                                           |    |                     | FR                         | 2841264    | A1 | 26-12-2003          |
|                                           |    |                     | GB                         | 2402943    | A  | 22-12-2004          |
|                                           |    |                     | US                         | 2005006010 | A1 | 13-01-2005          |
|                                           |    |                     | WO                         | 2004001080 | A1 | 31-12-2003          |
| -----                                     |    |                     |                            |            |    |                     |
| EP 2386667                                | A1 | 16-11-2011          | AU                         | 2010310912 | A1 | 18-08-2011          |
|                                           |    |                     | CN                         | 102108463  | A  | 29-06-2011          |
|                                           |    |                     | EP                         | 2386667    | A1 | 16-11-2011          |
|                                           |    |                     | JP                         | 2013518184 | A  | 20-05-2013          |
|                                           |    |                     | US                         | 2011297278 | A1 | 08-12-2011          |
|                                           |    |                     | WO                         | 2011091645 | A1 | 04-08-2011          |
| -----                                     |    |                     |                            |            |    |                     |
| US 2002150498                             | A1 | 17-10-2002          | NONE                       |            |    |                     |
| -----                                     |    |                     |                            |            |    |                     |

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- US 6972100 B [0018] [0030]
- US 6027582 A [0031]

**Non-patent literature cited in the description**

- **O. ENGLER et al.** A Study of Through-Thickness Texture Gradients in Rolled Sheets. *Metallurgical and Materials Transaction A*, September 2000 [0028]
- **D.J. CHAKRABAKTI et al.** Through Thickness Property Variations in 7050 Plate. *Materials Science Forum*, 1996 [0028]