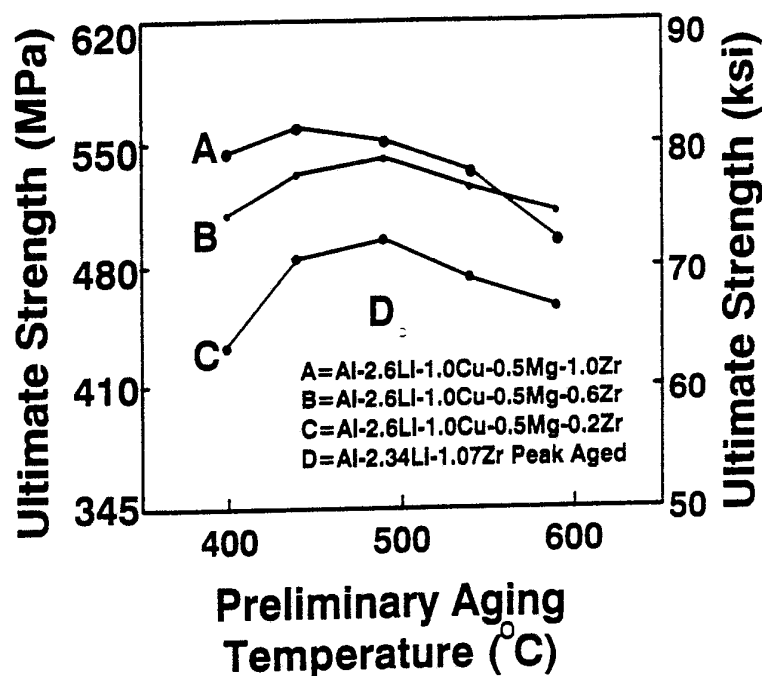




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C22F 1/04, C22C 21/00	A1	(11) International Publication Number: WO 91/17281 (43) International Publication Date: 14 November 1991 (14.11.91)
(21) International Application Number: PCT/US91/00549 (22) International Filing Date: 25 January 1991 (25.01.91) (30) Priority data: 517,774 2 May 1990 (02.05.90) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07960 (US). (72) Inventors: LASALLE, Jerry, C. ; 6 Valley Place, Upper Montclair, NJ 07043 (US). RAMANAN, V., R., V. ; 111 Richard Street, Dover, NJ 07801 (US). SKINNER, David, J. ; 14 Windswept Way, Long Valley, NJ 07853 (US).		(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>

(54) Title: DOUBLE AGED RAPIDLY SOLIDIFIED ALUMINUM-LITHIUM ALLOYS



(57) Abstract

A component consolidated from a rapidly solidified aluminum-lithium alloy containing copper, magnesium and zirconium is subjected to a preliminary aging treatment at a temperature of about 400 °C to 500 °C for a time period of about 0.5 to 10 hours; quenched in a fluid bath; and subjected to a final aging treatment at a temperature of about 100 °C to 250 °C for a time period ranging up to about 40 hours. The component exhibits increased strength and elongation, and is especially suited for use in lightweight structural parts for land vehicles and aerospace applications.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

Double aged rapidly solidified aluminium-lithium alloys.

5 1. Field of Invention

The invention relates to rapidly solidified aluminum-lithium-copper-magnesium-zirconium powder metallurgy components having a combination of high ductility and high tensile strength; and more particularly to a process wherein the components are subjected to thermal treatment which improves yield and ultimate strengths thereof with minimal loss in tensile ductility.

15 2. Brief Description of the Prior Art

The need for structural aerospace alloys of improved specific strength and specific modulus has long been present. It is known that the elements lithium, beryllium, boron, and magnesium can be added to an aluminum alloy to decrease its density. Conventional methods for producing aluminum alloys, such as direct chill (DC), continuous and semi-continuous casting, yield aluminum alloys having up to 5 wt% magnesium or beryllium; but such alloys are inadequate for use in applications requiring a combination of high strength and low density. Lithium contents of about 2.5 wt% have been satisfactorily incorporated into the lithium-copper-magnesium family of aluminum alloys, including those alloys designated 8090, 8091, 2090 and 2091. These alloys have copper and magnesium additions in the 1 to 3 wt% and 0.25 to 1.5 wt% range, respectively. In addition, zirconium is also added at levels up to 0.16 wt%.

35 The above alloys derive strength and toughness through the formation of several precipitate phases, which are described in detail in the Conference Proceedings of Aluminum-Lithium V, edited by T.H.

- 2 -

Sanders and E.A. Starke, pub. MCE, (1989). An important strengthening precipitate in aluminum-lithium alloys is the metastable δ phase which has a well defined solvus line. Thus, aluminum-lithium alloys are heat treatable, their strength increasing as δ' homogeneously nucleates from the supersaturated aluminum matrix.

The δ' phase consists of the ordered $L1_2$ crystal structure and the composition Al_3Li . The phase has a very small lattice misfit with the surrounding aluminum matrix and thus a coherent interface with the matrix. Dislocations easily shear the precipitates during deformation, resulting in the buildup of planar slip bands. This, in turn, reduces the toughness of aluminum lithium alloys. In binary aluminum-lithium alloys where this is the only strengthening phase employed, the slip planarity results in reduced toughness.

The addition of copper and magnesium to aluminum-lithium alloys has two beneficial effects. First, the elements reduce the solubility of lithium in aluminum, increasing the amount of strengthening precipitates available. More importantly, however, the copper and magnesium allow the formation of additional precipitate phases, most importantly the orthorhombic S' phase (Al_2MgLi) and the hexagonal T_1 phase (Al_2CuLi). Unlike δ' , these phases are resistant to shearing by dislocations and are effective in minimizing slip planarity. The resulting homogeneity of the deformation results in improved toughness, increasing the applicability of these alloys over binary aluminum-lithium. Unfortunately, these phases form sluggishly, precipitating primarily on heterogeneous nucleation sites such as dislocations. In order to generate these nucleations sites, the alloys must be cold worked prior to aging.

- 3 -

Zirconium, at levels under approximately 0.15 wt%, is typically added to the alloys to form the metastable Al_3Zr phase for grain size control and to retard recrystallization. Metastable Al_3Zr consists of an Ll_2 crystal structure which is essentially isostructural with δ' (Al_3Li). Additions of zirconium to aluminum beyond 0.15 wt% using conventional casting practice result in the formation of relatively large dispersoids of equilibrium Al_3Zr having the tetragonal DO_{23} structure which are detrimental to toughness.

Much work has been done to develop the aforementioned alloys, which are currently near commercialization. However, the processing constraint imposed by the need for cold deformation has limited the application of these alloys to thin, low dimensional shapes such as sheet and plate. Complex, shaped components such as forgings are not amenable to such processing. Hence, conventional aluminum-lithium alloy forgings lack the combination of strength, ductility, and low density required for aerospace structural applications.

Summary of the Invention

The invention provides a method for increasing the tensile strength of a component composed of a rapidly solidified aluminum-lithium-copper-magnesium-zirconium alloy by subjecting the component to a multi-step aging treatment. Generally stated, the component is a consolidated article, formed from an alloy that is rapidly solidified and consists essentially of the formula $\text{Al}_{ba}\text{Li}_a\text{Cu}_b\text{Mg}_c\text{Zr}_d$ wherein "a" ranges from about 2.1 to 3.4 wt%, "b" ranges from 0.5 to 2.0 wt%, "c" ranges from 0.2 to 2.0 wt%, and "d" ranges from about 0.4 to 1.8 wt%, the balance being aluminum. The aging treatment to which the component is subjected comprises the steps of subjecting the

- 4 -

component to a preliminary aging treatment at a temperature of about 400°C-500°C for a time period ranging from about 0.5 to 10 hours; quenching the component in a fluid bath; and subjecting the component to a final aging treatment at a temperature of about 100°C-250°C for a time period ranging up to about 40 hours.

In addition, the invention provides a component consolidated from a rapidly solidified aluminum-lithium alloy of the type delineated, which component has been subjected to the multi-step aging treatment specified hereinabove.

It has been found that when specific components consolidated from rapidly solidified alloys of the composition delineated are subjected to the multi-step aging treatment specified, they exhibit increased strength and elongation, as compared with components that are thermally processed in a conventional manner. The improved combination of properties afforded by components of the invention renders them especially suited for lightweight structural parts used in automobile, aircraft or spacecraft applications.

Brief Description of the Drawings

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiment of the invention and the accompanying drawings in which:

FIG. 1 is a graph depicting the heat evolution/absorption vs. temperature as measured by differential scanning calorimetry for an Al-2.6Li-1.0Cu-0.5Mg-1.0Zr alloy aged at 590°C for 2 hours and ice water quenched;

FIG. 2 is a graph of the yield strength vs. aging temperature of a transverse specimen cut from an extruded bar aged for 2 hrs. followed by an ice water quench and subsequent aging for 16 hrs. at

- 5 -

135°C, the open rectangle providing data for a transverse specimen cut from an Al-2.34Li-1.07Zr extruded bar; the specimen being aged at 500°C for 1 hr. was water quenched and subsequently aged at 190°C for 2 hours;

FIG. 3 is a graph of the ultimate tensile strength vs. aging temperature for specimens aged in the manner of the specimens of Fig. 2;

FIG. 4 is a graph of the tensile elongation vs. aging temperature for specimens aged in the manner of the specimens of Fig. 2; and

FIG. 5 is a graph depicting the ultimate strength vs. elongation for the alloys of Fig. 2 illustrating the improvement in properties extant along the diagonal away from the origin.

Description of the Preferred Embodiment

The invention provides a thermal treatment that increases the tensile strength of a low density rapidly solidified aluminum-base alloy, consisting essentially of the formula $Al_{bal}Li_aCu_bMg_cZr_d$ wherein "a" ranges from 2.1 to 3.4 wt%, "b" ranges from about 0.5 to 2.0 wt%, "c" ranges from 0.2 to 2.0 wt%, "d" ranges from about 0.4 to 1.8 wt% and the balance is aluminum.

In accordance with the invention, the compacted alloy or component is subjected to a preliminary thermal treatment at temperatures ranging from about 400°C to 500°C for a period of approximately 0.5 to 10 hours. While not being bound by theory, it is believed that this treatment dissolves elements such as Cu, Mg, and Li which may be microsegregated in precipitated phases such as δ' , δ , T, and S. In addition, the thermal treatment produces an optimized distribution of cubic $L1_2$ particles ranging from about 5 to 50 nanometers in size. The alloy article is then quenched in a fluid bath, preferably held between 0° and 60°C. As used

- 6 -

hereinafter in the specification and claims, the term "preliminary aging" is intended to define the thermal treatment described in the first sentence of this paragraph. The compacted article is then aged at a temperature ranging from about 100°C to 250°C. for a time period ranging up to about 40 hours to provide selected strength/toughness tempers. No cold deformation step is required during this thermal processing, with the result that complex shaped components such as forgings produced from the aged component have excellent mechanical properties.

Preliminary aging below approximately 400°C results in a deleterious drop in tensile properties due to the formation of undesirable phases such as the δ (AlLi) phase. Preliminary aging above approximately 500°C results in an acceptable combination of tensile properties but does not result in the attainment of the optimum tensile strength since the volume fraction of precipitates is reduced. Grain coarsening may also occur at temperature beyond 550°C, further reducing strength.

Consolidated articles aged in accordance with the invention exhibit tensile yield strength ranging from about 400 MPa (58 ksi) to 545 MPa (79 ksi), ultimate tensile strength ranging from about 510 MPa (74ksi) to MPa (83 ksi) and elongation to fracture ranging from about 4 to 9 % when measured at room temperature (20°C).

The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of the invention.

- 7 -

EXAMPLES 1-3

Thermal processing in accordance with the invention was carried out on extruded bar made from rapidly solidified alloys having compositions (in wt%) listed in Table I.

TABLE I

	1. Al-2.1Li-1.0Cu-0.5Mg-0.2Zr
	2. Al-2.6Li-1.0Cu-0.5Mg-0.6Zr
10	3. Al-2.6Li-1.0Cu-0.5Mg-1.0Zr

EXAMPLE 4

Al-2.6Li-1.0Cu-0.5Mg-1.0Zr, made via rapid solidification and formed into an extrusion, was given a preliminary age at 590°C for 2 hours and ice water quenched. The heat evolution/absorption as a function of temperature was then measured using the technique of differential scanning calorimetry (DSC), shown in Figure 1. The peaks in Figure 1 represent the dissolution of precipitate phases during heating while the troughs represent precipitation. A precipitation reaction is represented by the trough centered at 450°C. It is this precipitation reaction which is responsible for the enhanced strength resulting from the preliminary aging treatment.

EXAMPLE 5

The tensile properties of consolidated articles formed by extrusion of the alloys listed in Table I and thermally processed in accordance with the method of the invention are listed in Table II. The extruded bars were given a preliminary age for 2 hours at temperatures between 400°C and 600°C and quenched into an ice water bath; subsequently, they were aged at 135°C for 16 hours. Transverse specimens were then cut and machined into round tensile specimens having a gauge diameter of 3/8

- 8 -

inches and a gauge length of 3/4 inches. Tensile testing was performed at room temperature at a strain rate of $5.5 \times 10^{-4} \text{sec}^{-1}$.

TABLE II

5	Composition (wt%)		0.2% YS	UTS	Elong. to
	Aging Temp.		(MPa)	(MPa)	fract. (%)
10	Al-2.6Li-1.0Cu-0.5Mg-0.2Zr				
	400°C		400	435	4.9
	440°C		410	495	7.2
	490°C		395	500	6.3
	540°C		350	470	8.0
15	Al-2.6Li-1.0Cu-0.5Mg-0.6Zr				
	400°C		500	510	5.2
	440°C		490	535	6.9
	490°C		470	540	7.7
	540°C		440	520	5.8
20	Al-2.6Li-1.0Cu-0.5Mg-1.0Zr				
	400°C		540	555	3.7
	440°C		535	570	7.1
	490°C		510	560	6.3
	540°C		465	545	8.4
25	Al-2.6Li-1.0Mg-0.6Zr		405	505	7.3

Figures 2, 3, and 4 are graphs of the data listed in Table II. The graphs illustrate that the peak ultimate tensile strength (UTS) is a function of both zirconium content and temperature of the first aging treatment. For example, a peak UTS of 570 MPa is obtained for 440°C preliminary aged Al-2.6Li-1.0Cu-0.5Mg-1.0Zr while a peak UTS of 540 MPa is obtained for a 490°C preliminary aged Al-2.6Li-1.0Mg-0.6Zr.

Also included for reference in the Figures 2, 3, and 4 is the transverse tensile data for an

- 9 -

Al-2.34Li-1.07Zr extrude bar processed in the manner disclosed by U.S.P. 4,747,884 to Gayle et al. It is clear that the tensile properties of materials processed in accordance with the present invention are superior to those of conventionally processed alloy chemistries. Gayle et al. have also included data on rod produced from this alloy which displays, qualitatively, a similar strength behavior with preliminary aging temperature. The rod, due to enhanced deformation compared with bar, displays a strength somewhat higher than the bar stock, as shown in the data of Gayle et al. It will be appreciated by those skilled in the art that similar comparative gains in strength induced by enhanced deformation will be achieved in rod made from Al-Li-Cu-Mg-Zr alloys. Data is also included for the ingot aluminum-lithium alloy 8090, is taken from Damerval et. al., "4th International Aluminum-Lithium Conference", J. de Physique, pg. C3-661, (1987), for transverse sections of extruded bar. The bar was solutionized at 540°C-1 hr; cold water quenched, given a 2% cold stretch, and peak aged at 190°C for 12 hours. It will be seen that the properties of RS Al-Li-Cu-Mg-Zr bar stock given a preliminary age in accordance with the invention are superior to those of the alloy 8090, without the cold deformation commonly employed on ingot aluminum-lithium alloys.

EXAMPLE 6

This example illustrates that the enhanced strength resulting from control of the preliminary age is greater than and thus distinct from merely extending the aging time of the second low temperature aging treatment. The tensile yield strengths for an Al-2.6Li0.10Cu-0.5Mg-0.6Zr extrusion measured in the manner set forth in Example 5 are listed in Table III. Reducing the preliminary aging temperature from 540°C to 400°C results in a 14%

- 10 -

increase in tensile strength compared with only 4% increase in strength when a 540°C preliminary aged specimen is aged for double the time 135°C.

Table III

5

	<u>Thermal Treatment</u>	<u>YS(MPa)</u>
	400°C-2hr ice WQ;135°C-16hr	500
	540°C-2hr ice WQ;135°C-16hr	440
10	540°C-2hr ice WQ;135°C-32hr	460

Having thus described the invention in rather full detail, it will be understood that these details need not be strictly adhered to but that various
15 changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

20

25

30

35

- 11 -

What is claimed is:

1. A process for increasing the strength of a rapidly solidified aluminum-lithium alloy component, comprising the steps of:

5 a. subjecting the component to a preliminary aging treatment at a temperature of about 400°C to 500°C for a time period from about 0.5 to 10 hours;

 b. quenching the component in a fluid bath; and,

10 c. subjecting the component to final treatment at a temperature of about 100°C to 250°C for a time period ranging up to about 40 hours, said component being a consolidated article formed from an aluminum-lithium alloy that is rapidly solidified and
15 consists essentially of the formula $Al_{ba}Li_aCu_bMg_cZr_d$ wherein "a" ranges from about 2.1 to 3.4 wt%, "b" ranges from about 0.5 to 2.0 wt%, "c" ranges from about 0.2 to 2.0 wt% and "d" ranges from about 0.4 to 1.8 wt%, the balance being aluminum.

20 2. A process as recited by claim 1, wherein said component has the composition 2.6 wt% lithium, 1.0 wt% copper, 0.5 wt% magnesium and 0.6 wt% zirconium, the balance being aluminum.

 3. A process as recited by claim 2, wherein
25 said component, after final aging, has a 0.2% tensile yield strength of 440 MPa, ultimate tensile strength of 530 MPa, and elongation to fracture of 7%.

 4. A process as recited by claim 1, wherein said component has the composition 2.6 wt% lithium,
30 1.0 wt% copper, 0.5 wt% magnesium and 1.0 wt% zirconium, the balance being aluminum.

 5. A process as recited by claim 4, wherein said component, after final aging, has 0.2% tensile
35 yield strength of about 535 MPa, ultimate tensile strength of 570 MPa, and elongation to fracture of 7%.

 6. A component consolidated from an alloy that is rapidly solidified and consists essentially

- 12 -

of the formula $Al_{bal}Cu_bMg_cZr_d$ wherein "a" ranges from about 2.1 to 3.4 wt%, "b" ranges from about 0.5 to 2.0 wt%, "c" ranges from about 0.2 to 2.0 wt%, and "d" ranges from about 0.4 to 1.8 wt%, the balance being aluminum, said component having been subjected to a preliminary aging treatment at a temperature of about 400°C to 500°C for a time period of about 0.5 to 10 hours, quenched in a fluid bath and subjected to a final aging treatment at a temperature of about 100°C to 250°C for a time period ranging up to about 40 hours.

7. A component as recited by claim 6, wherein said alloy has the composition 2.6 wt% lithium, 1.0 wt% copper, 0.5 wt% magnesium and 0.6 wt% zirconium, the balance being aluminum.

8. A component as recited by claim 7, having a 0.2% tensile yield strength of 440 MPa, ultimate tensile strength of 530 MPa, and elongation to fracture of 7%.

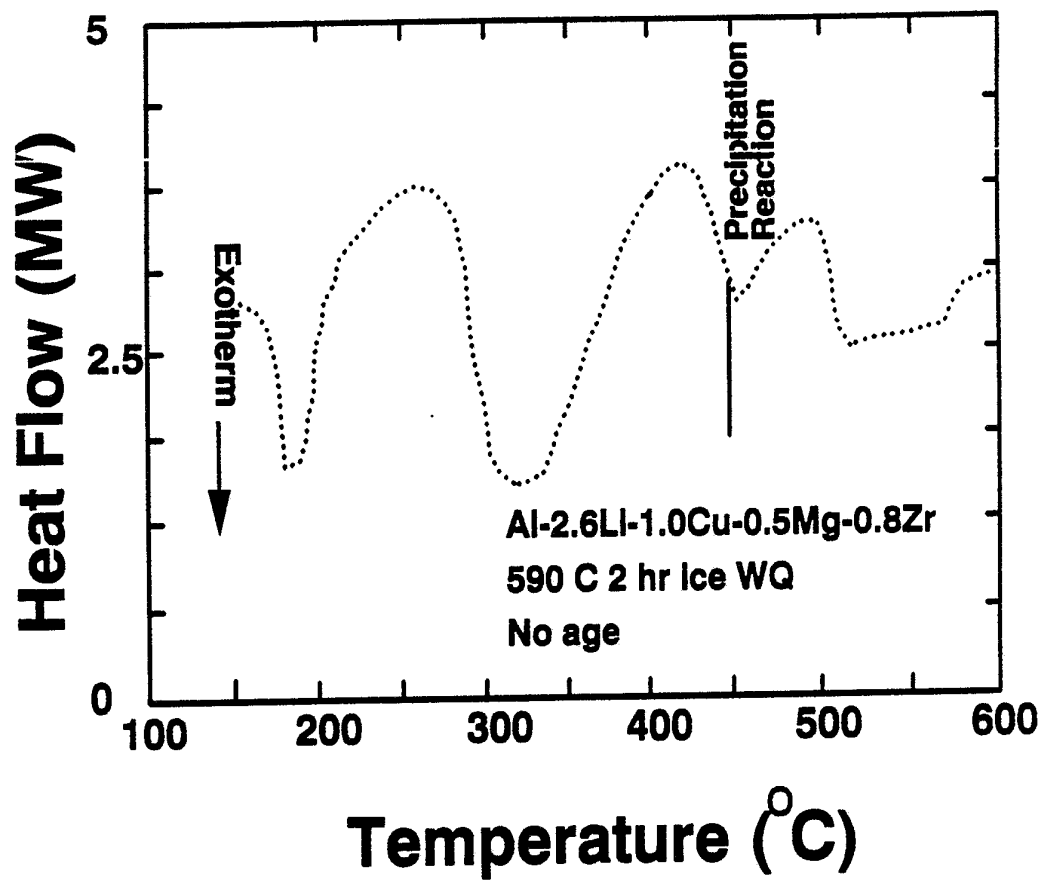
9. A component as recited by claim 6, wherein said alloy has the composition 2.6 wt% lithium, 1.0 wt% copper, 0.5 wt% magnesium and 1.0 wt% zirconium, the balance being aluminum.

10. A component as recited by claim 9, having 0.2% tensile yield strength of 535 MPa, ultimate tensile strength of 570 MPa and elongation to fracture of 7%.

30

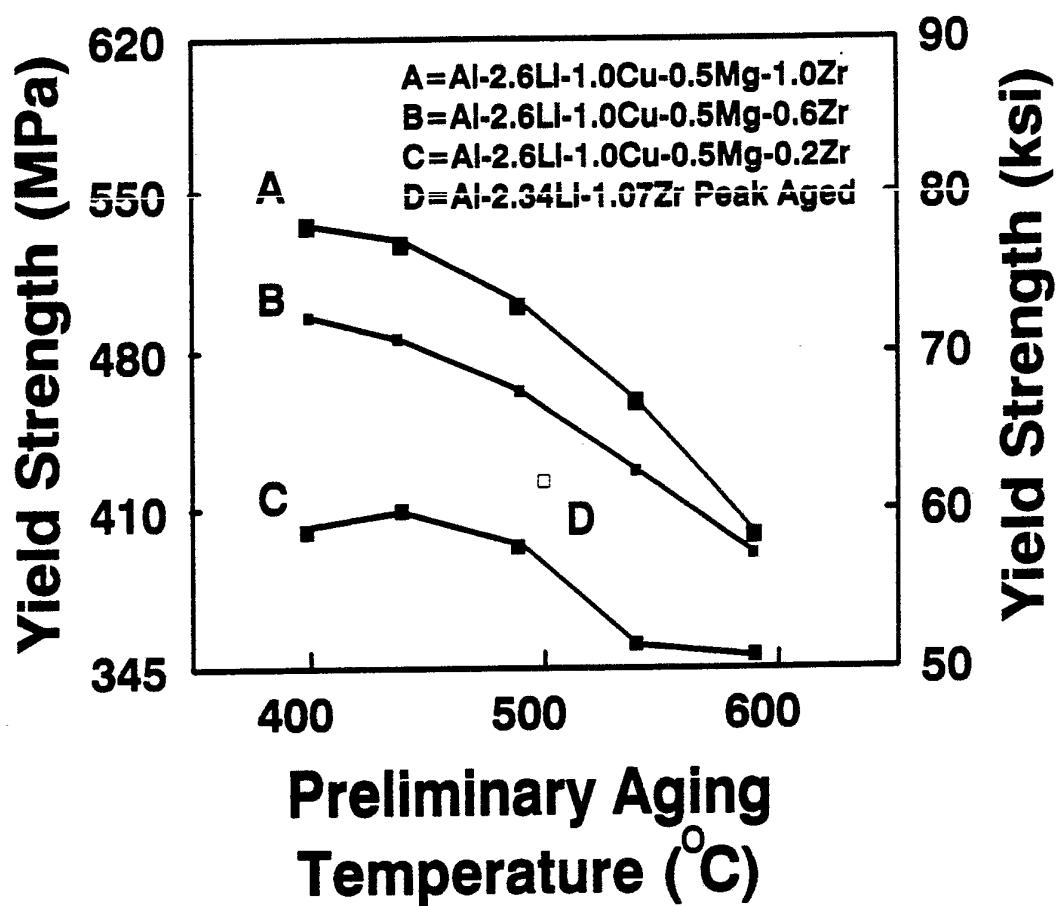
35

1/5

Fig. 1

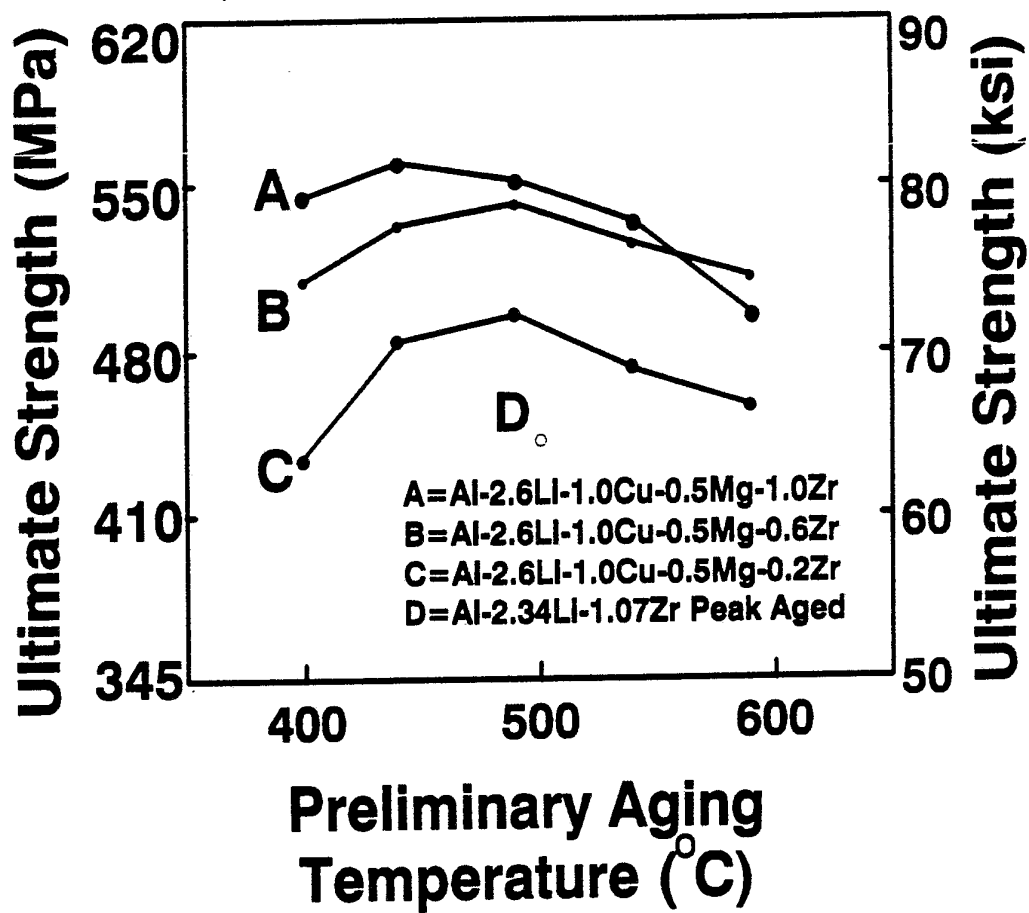
SUBSTITUTE SHEET

2/5

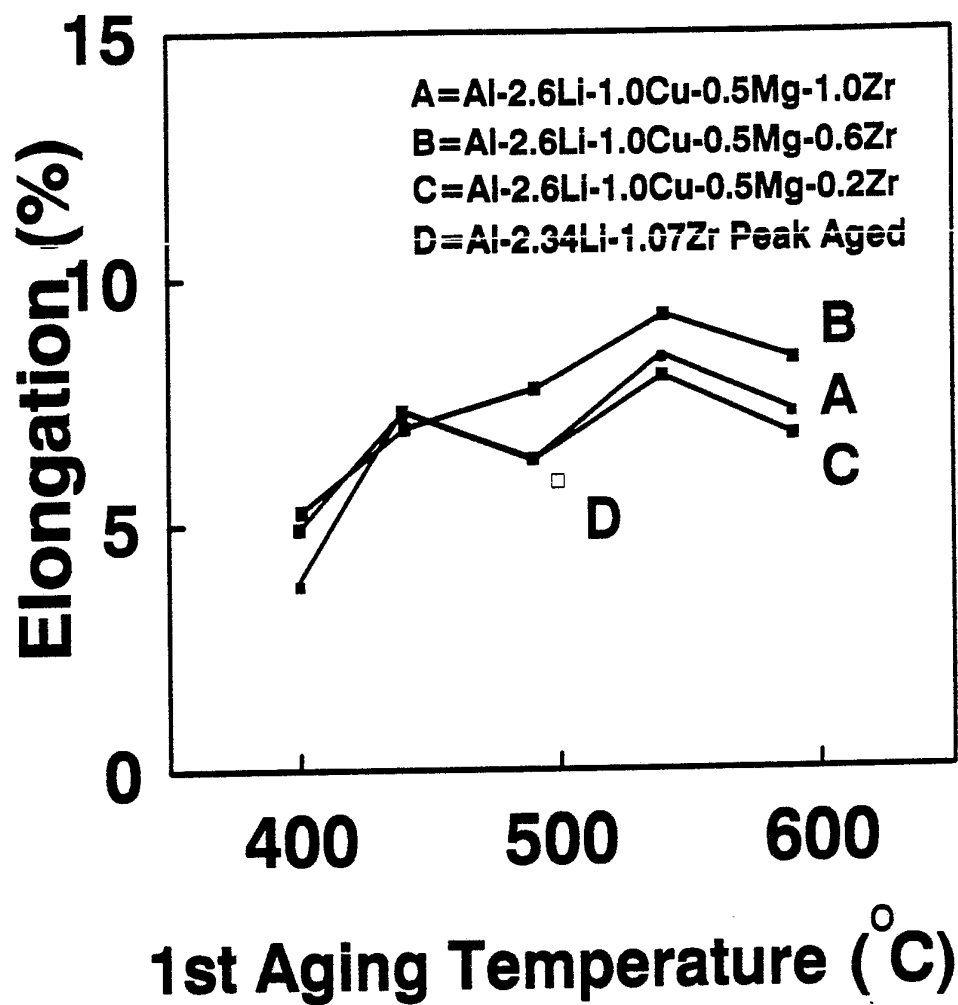
Fig. 2

SUBSTITUTE SHEET

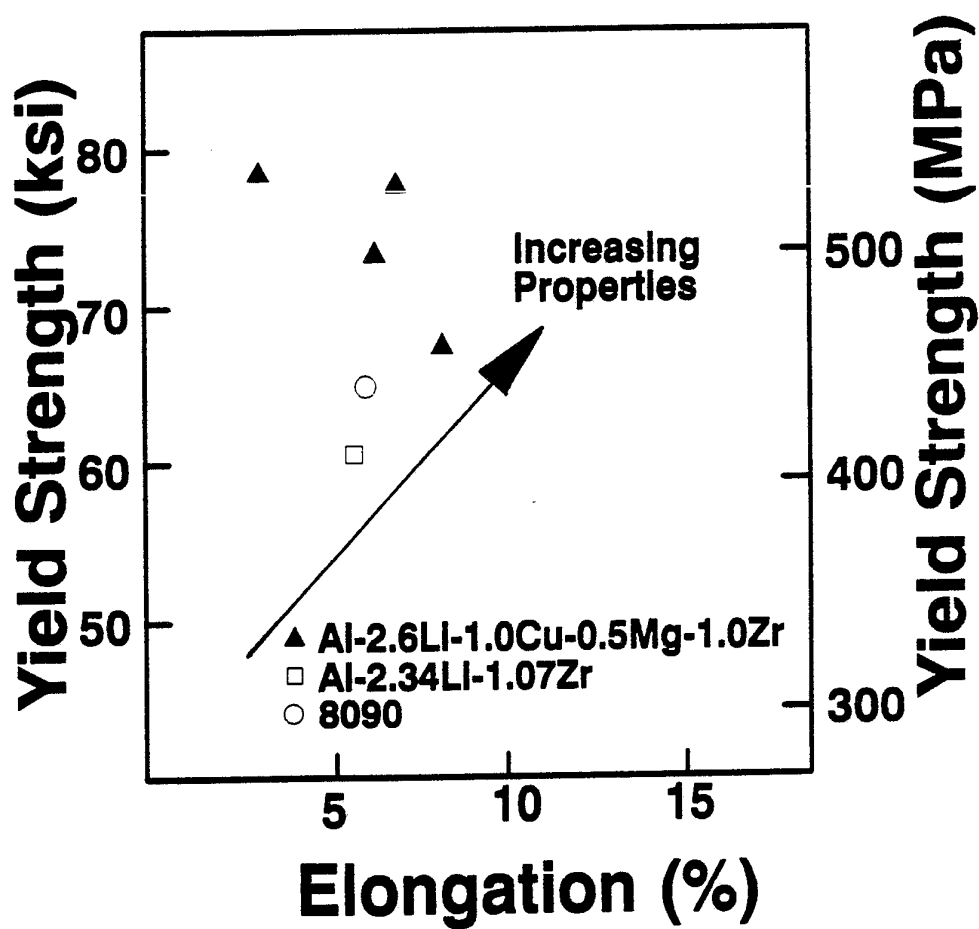
3/5

Fig. 3

4/5

Fig. 4

5/5

Fig. 5

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/00549

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 22 F 1/04, C 22 C 21/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 22 F, C 22 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4747884 (F.W. GAYLE et al.) 31 May 1988 see example 2; claim 1 cited in the application --	1,6
A	WO, A, 8703011 (ALUMINIUM CO. OF AMERICA) 21 May 1987 see claims 21,33-35; example 8 --	1,6
A	US, A, 4721537 (A.K. GHOSH) 26 January 1988 see claim 9; example 4 --	1,6
A	Proceedings of the International Aluminium Lithium Conference, Williamsburg, 27-31 March 1989, vol. 1, conf. 5, MCEP Ltd, (Birmingham, GB), Y.C. Zhang et al.: "Structure and properties of two rapidly solidified Al-Li-Cu-Mg-Zr alloys produced by liquid dynamic compaction", pages 95- 104 ./.	1,6
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2nd May 1991	28 JUN 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	see tabels 1,2,4 cited in the application -- Proceedings of the International Aluminium Lithium Conference, Williamsburg, 27-31 March 1989, vol. 1, conf. 5, MCEP Ltd, (Birmingham, GB), H.B. McShane et al.: "Extrusion processing of Al-Li-Zr RSP alloys with differing lithium and zirconium contents", pages 287-303 see page 288, paragraph 1 - page 289, paragraph 2 cited in the application -----	1,6

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9100549

SA 44816

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/06/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4747884	31-05-88	None	
WO-A- 8703011	21-05-87	US-A- 4806174	21-02-89
		AU-A- 6838187	02-06-87
		EP-A- 0247181	02-12-87
		JP-T- 63501883	28-07-88
US-A- 4721537	26-01-88	None	