

(19)



(11)

**EP 2 112 242 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**28.10.2009 Bulletin 2009/44**

(51) Int Cl.:

**C22C 21/04 (2006.01)**

**C22F 1/043 (2006.01)**

(21) Application number: **09251012.2**

(22) Date of filing: **31.03.2009**

(84) Designated Contracting States:

**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 SE SI SK TR**

Designated Extension States:

**AL BA RS**

(72) Inventor: **Pandey, Awadh B.**

**Jupiter  
Florida 33458 (US)**

(74) Representative: **Hall, Matthew Benjamin**

**Frank B. Dehn & Co.  
St Bride's House  
10 Salisbury Square  
London EC4Y 8JD (GB)**

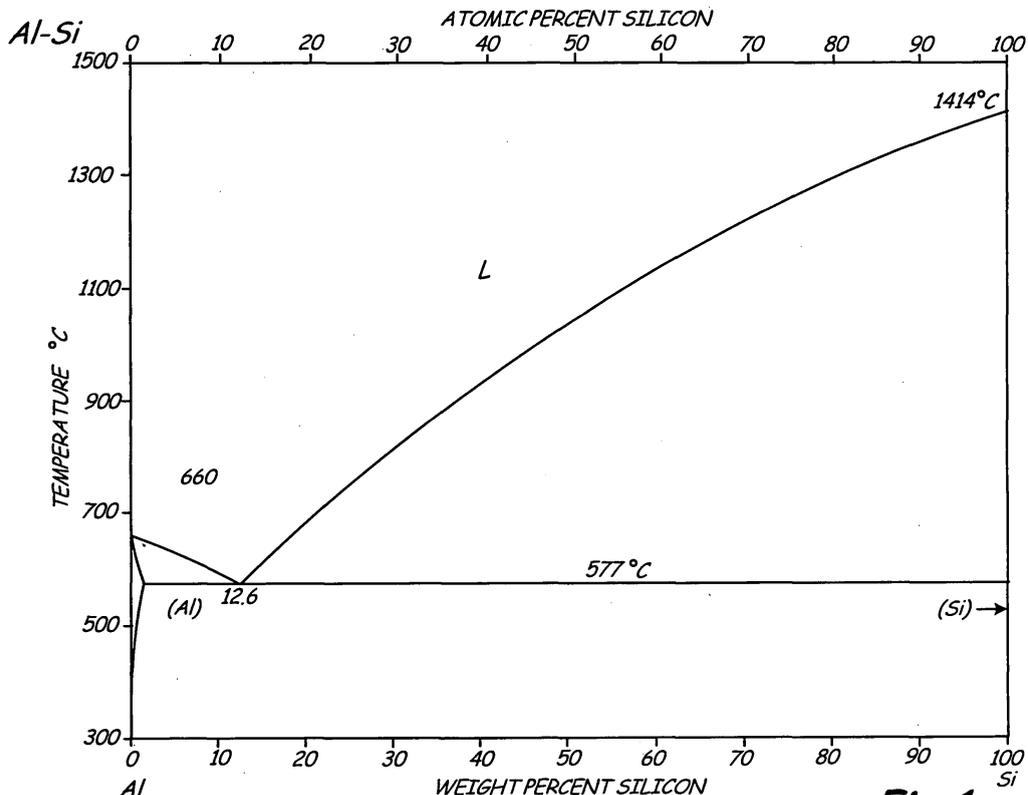
(30) Priority: **18.04.2008 US 148383**

(71) Applicant: **United Technologies Corporation  
Hartford, CT 06101 (US)**

(54) **Heat treatable L12 aluminium alloys**

(57) High temperature heat treatable aluminum alloys that can be used at temperatures from about -420°F (-251°C) up to about 650°F (343°C) are described. The alloys are strengthened by dispersion of particles based on the L<sub>12</sub> intermetallic compound Al<sub>3</sub>X. These alloys

comprise aluminum; silicon; at least one of scandium, erbium, thulium, ytterbium, and lutetium; and at least one of gadolinium, yttrium, zirconium, titanium, hafnium, and niobium. Magnesium and copper are optional alloying elements.



**EP 2 112 242 A1**

## Description

**[0001]** The present invention relates generally to aluminum alloys and more specifically to heat treatable aluminum alloys produced by melt processing and strengthened by L<sub>12</sub> phase dispersions.

**[0002]** The combination of high strength, ductility, and fracture toughness, as well as low density, make aluminum alloys natural candidates for aerospace and space applications. However, their use is typically limited to temperatures below about 300°F (149°C) since most aluminum alloys start to lose strength in that temperature range as a result of coarsening of strengthening precipitates.

**[0003]** The development of aluminum alloys with improved elevated temperature mechanical properties is a continuing process. Some attempts have included aluminum-iron and aluminum-chromium based alloys such as Al-Fe-Ce, Al-Fe-V-Si, Al-Fe-Ce-W, and Al-Cr-Zr-Mn that contain incoherent dispersoids. These alloys, however, also lose strength at elevated temperatures due to particle coarsening. In addition, these alloys exhibit ductility and fracture toughness values lower than other commercially available aluminum alloys.

**[0004]** Other attempts have included the development of mechanically alloyed Al-Mg and Al-Ti alloys containing ceramic dispersoids. These alloys exhibit improved high temperature strength due to the particle dispersion, but the ductility and fracture toughness are not improved.

**[0005]** US-A-6,248,453 discloses aluminum alloys strengthened by dispersed Al<sub>3</sub>X L<sub>12</sub> intermetallic phases where X is selected from the group consisting of Sc, Er, Lu, Yb, Tm, and U. The Al<sub>3</sub>X particles are coherent with the aluminum alloy matrix and are resistant to coarsening at elevated temperatures. The improved mechanical properties of the disclosed dispersion strengthened L<sub>12</sub> aluminum alloys are stable up to 572°F (300°C). In order to create aluminum alloys containing fine dispersions of Al<sub>3</sub>X L<sub>12</sub> particles, the alloys need to be manufactured by expensive rapid solidification processes with cooling rates in excess of 1.8x10<sup>3</sup> F/sec (10<sup>3</sup> C/sec). US-A-2006/0269437 discloses an aluminum alloy that contains scandium and other elements. While the alloy is effective at high temperatures, it is not capable of being heat treated using a conventional age hardening mechanism.

**[0006]** Heat treatable aluminum alloys strengthened by coherent L<sub>12</sub> intermetallic phases produced by standard, inexpensive melt processing techniques would be useful.

**[0007]** The present invention is heat treatable aluminum alloys that can be cast, wrought, or formed by rapid solidification, and thereafter heat treated. The alloys can achieve high temperature performance and can be used at temperatures up to about 650°F (343°C).

**[0008]** Viewed from a first aspect, the present invention provides a heat treatable aluminum alloy comprising:

about 4.0 to about 25.0 weight percent silicon;

at least one first element selected from the group comprising about 0.1 to about 0.5 weight percent scandium, about 0.1 to about 6.0 weight percent erbium, about 0.1 to about 10 weight percent thulium, about 0.1 to about 15.0 weight percent ytterbium, and about 0.1 to about 12 weight percent lutetium; at least one second element selected from the group comprising about 0.1 to about 4.0 weight percent gadolinium, about 0.1 to about 4.0 weight percent yttrium, about 0.05 to about 1.0 weight percent zirconium, about 0.05 to about 2.0 weight percent titanium, about 0.05 to about 2.0 weight percent hafnium, and about 0.05 to about 1.0 weight percent niobium; and

the balance substantially aluminum.

**[0009]** These alloys comprise silicon, and an Al<sub>3</sub>X L<sub>12</sub> dispersoid where X is at least one first element selected from scandium, erbium, thulium, ytterbium, and lutetium, and at least one second element selected from gadolinium, yttrium, zirconium, titanium, hafnium, and niobium. The balance is substantially aluminum.

**[0010]** The alloys may also contain magnesium and, optionally, copper, and have less than 1.0 weight percent total impurities.

**[0011]** Viewed from a second aspect, the present invention provides a heat treatable aluminum alloy comprising:

about 4.0 to about 25.0 weight percent silicon; and an aluminum solid solution matrix containing a plurality of dispersed Al<sub>3</sub>X second phases having L<sub>12</sub> structures where X comprises at least one of scandium, erbium, thulium, ytterbium, lutetium, and at least one of gadolinium, yttrium, zirconium, titanium, hafnium, niobium.. Preferably, the alloy comprises at least one of: about 0.2 to about 3.0 weight percent magnesium and about 0.5 to about 5.0 weight percent copper. Preferably the alloy comprises at least one of: about 0.1 to about 0.5 weight percent scandium, about 0.1 to about 6.0 weight percent erbium, about 0.1 to about 10 weight percent thulium, about 0.1 to about 15.0 weight percent ytterbium, about 0.1 to about 12 weight percent lutetium, and about 0.1 to about 4.0 weight percent gadolinium, about 0.1 to about 4.0 weight percent yttrium, about 0.05 to about 1.0 weight percent zirconium, about 0.05 to about 2.0 weight percent titanium, about 0.05 to about 2.0 weight percent hafnium, and about 0.05 to about 1.0 weight percent niobium.

**[0012]** The alloys may be formed by a process selected from casting, deformation processing and rapid solidification. The alloys may then be heat treated at a temperature of from about 800°F (426°C) to about 1100°F (593°C) for between about 30 minutes and four hours, followed by quenching in water, and thereafter aged at a temperature from about 200°F (93°C) to about 600°F

(315°C) for about two to forty eight hours.

**[0013]** Viewed from a third aspect, the present invention provides a method of forming a heat treatable aluminum alloy, the method comprising:

(a) forming a melt comprising:

about 4.0 to about 25.0 weight percent silicon; about 0.2 to about 3.0 weight percent magnesium; about 0.5 to about 5.0 weight percent copper; at least one first element selected from the group comprising about 0.1 to about 0.5 weight percent scandium, about 0.1 to about 6.0 weight percent erbium, about 0.1 to about 10 weight percent thulium, about 0.1 to about 15.0 weight percent ytterbium, and about 0.1 to about 12 weight percent lutetium; at least one second element selected from the group comprising about 0.1 to about 4.0 weight percent gadolinium, about 0.1 to about 4.0 weight percent yttrium, about 0.05 to about 1.0 weight percent zirconium, about 0.05 to about 2.0 weight percent titanium, about 0.05 to about 2.0 weight percent hafnium, and about 0.05 to about 1.0 weight percent niobium; and the balance substantially aluminum;

(b) solidifying the melt to form a solid body; and  
(c) heat treating the solid body.

**[0014]** Certain preferred embodiments of the present invention will now be described in greater detail by way of example only and with reference to the accompanying drawings, in which:

FIG. 1 is an aluminum silicon phase diagram;  
FIG. 2 is an aluminum scandium phase diagram;  
FIG. 3 is an aluminum erbium phase diagram;  
FIG. 4 is an aluminum thulium phase diagram;  
FIG. 5 is an aluminum ytterbium phase diagram; and  
FIG. 6 is an aluminum lutetium phase diagram.

**[0015]** The alloys of this invention are based on the aluminum silicon system. The aluminum silicon phase diagram is shown in FIG. 1. The binary system is a simple eutectic alloy system with a eutectic reaction at 12.5 weight percent silicon and 1077°F (577°C). There is little solubility of silicon in aluminum at temperatures up to 930°F (500°C) and none of aluminum in silicon. Hypoeutectic alloys with less than 12.6 weight percent silicon solidify with a microstructure consisting of primary aluminum grains in a finely divided aluminum/silicon eutectic matrix phase. Hypereutectic alloys with silicon contents greater than the eutectic composition solidify with a microstructure of primary silicon grains in a finely divided aluminum/silicon eutectic matrix phase. Alloys of this invention include alloys with the addition of about 4 to about

25 weight percent silicon, more preferably about 4 to about 18 weight percent silicon, and even more preferably about 5 to about 11 weight percent silicon.

**[0016]** Other alloys of this invention include aluminum silicon containing copper or magnesium, or both copper and magnesium. Copper and magnesium are completely soluble in aluminum in the compositions of the inventive alloys discussed herein. Aluminum copper and aluminum magnesium alloys are heat treatable with Al<sub>2</sub>Cu (0'), Al<sub>2</sub>CuMg (S') and Si crystals precipitating in aluminum-copper-silicon alloys; Mg<sub>2</sub>Si and Si crystals precipitating in aluminum-magnesium-silicon alloys following a solution heat treatment, quench, and age process. In aluminum-copper-magnesium-silicon alloys, strengthening phases are Al<sub>2</sub>Cu (θ'), Al<sub>2</sub>CuMg (S'), Mg<sub>2</sub>Si and Si crystals following a solution heat treatment, quench, and age process. Mg<sub>2</sub>Al<sub>3</sub> (β) phase precipitates as large intermetallic particle in high magnesium containing aluminum alloys which is not desired from strengthening point of view. The presence of L<sub>12</sub> phase prevents formation of β phase in material which improves ductility and toughness of material. The alloys of this invention contain phases consisting of aluminum copper solid solutions, aluminum magnesium solid solutions, and aluminum copper magnesium solid solutions. In the solid solutions are dispersions of Al<sub>3</sub>X having an L<sub>12</sub> structure where X is at least one first element selected from scandium, erbium, thulium, ytterbium, and lutetium. Also present is at least one second element selected from gadolinium, yttrium, zirconium, titanium, hafnium, and niobium.

**[0017]** Exemplary aluminum alloys of this invention include, but are not limited to (in weight percent):

about Al-(4-25)Si-(0.1-0.5)Sc-(0.1-4)Gd;  
about Al-(4-25)Si-(0.1-6)Er-(0.1-4)Gd;  
about Al-(4-25)Si-(0.1-10)Tm-(0.1-4)Gd;  
about Al-(4-25)Si-(0.1-15)Yb-(0.1-4)Gd;  
about Al-(4-25)Si-(0.1-12)Lu-(0.1-4)Gd;  
about Al-(4-25)Si-(0.1-0.5)Sc-(0.1-4)Y;  
about Al-(4-25)Si-(0.1-6)Er-(0.1-4)Y;  
about Al-(4-25)Si-(0.1-10)Tm-(0.1-4)Y;  
about Al-(4-25)Si-(0.1-15)Yb-(0.1-4)Y;  
about Al-(4-25)Si-(0.1-12)Lu-(0.1-4)Y;  
about Al-(4-25)Si-(0.1-0.5)Sc-(0.05-1)Zr;  
about Al-(4-25)Si-(0.1-6)Er-(0.05-1)Zr;  
about Al-(4-25)Si-(0.1-10)Tm-(0.05-1)Zr;  
about Al-(4-25)Si-(0.1-15)Yb-(0.05-1)Zr;  
about Al-(4-25)Si-(0.1-12)Lu-(0.05-1)Zr;  
about Al-(4-25)Si-(0.1-0.5)Sc-(0.05-2)Ti;  
about Al-(4-25)Si-(0.1-6)Er-(0.05-2)Ti;  
about Al-(4-25)Si-(0.1-10)Tm-(0.05-2)Ti;  
about Al-(4-25)Si-(0.1-15)Yb-(0.05-2)Ti;  
about Al-(4-25)Si-(0.1-12)Lu-(0.05-2)Ti;  
about Al-(4-25)Si-(0.1-0.5)Sc-(0.05-2)Hf;  
about Al-(4-25)Si-(0.1-6)Er-(0.05-2)Hf;  
about Al-(4-25)Si-(0.1-10)Tm-(0.05-2)Hf;  
about Al-(4-25)Si-(0.1-15)Yb-(0.05-2)Hf;  
about Al-(4-25)Si-(0.1-12)Lu-(0.05-2)Hf;

about Al-(4-25)Si-(0.1-0.5)Sc-(0.05-1)Nb;  
 about Al-(4-25)Si-(0.1-6)Er-(0.05-1)Nb;  
 about Al-(4-25)Si-(0.1-10)Tm-(0.05-1)Nb;  
 about Al-(4-25)Si-(0.1-15)Yb-(0.05-1)Nb; and  
 about Al-(4-25)Si-(0.1-12)Lu-(0.05-1)Nb.

**[0018]** Examples of similar alloys to these are alloys with the addition of about 0.2 to about 3 weight percent Mg, more preferably alloys with the addition of about 0.3 to about 1.5 weight percent Mg, and even more preferably alloys with the addition of about 0.5 to about 1.5 weight percent Mg; and alloys with the addition of about 0.5 to about 5 weight percent Cu, more preferably alloys with the addition of about 1 to about 4 weight percent Cu, and even more preferably alloys with the addition of about 2 to about 4 weight percent Cu. In one embodiment, the alloy comprises about 0.2 to about 3.0 weight percent magnesium and about 0.5 to about 5.0 weight percent copper, more particularly about 0.3 to about 1.5 weight percent magnesium and about 1.0 to about 4.0 weight percent copper.

**[0019]** In the inventive aluminum based alloys disclosed herein, scandium, erbium, thulium, ytterbium, and lutetium are potent strengtheners that have low diffusivity and low solubility in aluminum. All these elements form equilibrium  $Al_3X$  intermetallic dispersoids where X is at least one of scandium, erbium, ytterbium, lutetium, that have an  $L1_2$  structure that is an ordered face centered cubic structure with the X atoms located at the corners and aluminum atoms located on the cube faces of the unit cell.

**[0020]** Scandium forms  $Al_3Sc$  dispersoids that are fine and coherent with the aluminum matrix. Lattice parameters of aluminum and  $Al_3Sc$  are very close (0.405nm and 0.410nm respectively), indicating that there is minimal or no driving force for causing growth of the  $Al_3Sc$  dispersoids. This low interfacial energy makes the  $Al_3Sc$  dispersoids thermally stable and resistant to coarsening up to temperatures as high as about 842°F (450°C). Addition of magnesium in solid solution in aluminum increases the lattice parameter of the aluminum matrix, and decreases the lattice parameter mismatch further increasing the resistance of the  $Al_3Sc$  to coarsening. Addition of copper increases the strength of alloys through precipitation of  $Al_2Cu$  ( $\theta'$ ) and  $Al_2CuMg$  ( $S'$ ) phases. In the alloys of this invention these  $Al_3Sc$  dispersoids are made stronger and more resistant to coarsening at elevated temperatures by adding suitable alloying elements such as gadolinium, yttrium, zirconium, titanium, hafnium, niobium, or combinations thereof, that enter  $Al_3Sc$  in solution.

**[0021]** Erbium forms  $Al_3Er$  dispersoids in the aluminum matrix that are fine and coherent with the aluminum matrix. The lattice parameters of aluminum and  $Al_3Er$  are close (0.405 nm and 0.417 nm respectively), indicating there is minimal driving force for causing growth of the  $Al_3Er$  dispersoids. This low interfacial energy makes the  $Al_3Er$  dispersoids thermally stable and resistant to coars-

ening up to temperatures as high as about 842°F (450°C). Addition of magnesium in solid solution in aluminum increases the lattice parameter of the aluminum matrix, and decreases the lattice parameter mismatch further increasing the resistance of the  $Al_3Er$  to coarsening. Addition of copper increases the strength of alloys through precipitation of  $Al_2Cu$  ( $\theta'$ ) and  $Al_2CuMg$  ( $S'$ ) phases. In the alloys of this invention, these  $Al_3Er$  dispersoids are made stronger and more resistant to coarsening at elevated temperatures by adding suitable alloying elements such as gadolinium, yttrium, zirconium, titanium, hafnium, niobium, or combinations thereof that enter  $Al_3Er$  in solution.

**[0022]** Thulium forms metastable  $Al_3Tm$  dispersoids in the aluminum matrix that are fine and coherent with the aluminum matrix. The lattice parameters of aluminum and  $Al_3Tm$  are close (0.405 nm and 0.420 nm respectively), indicating there is minimal driving force for causing growth of the  $Al_3Tm$  dispersoids. This low interfacial energy makes the  $Al_3Tm$  dispersoids thermally stable and resistant to coarsening up to temperatures as high as about 842°F (450°C). Addition of magnesium in solid solution in aluminum increases the lattice parameter of the aluminum matrix and decreases the lattice parameter mismatch further increasing the resistance to coarsening of the dispersoid. Addition of copper increases the strength of alloys through precipitation of  $Al_2Cu$  ( $\theta'$ ) and  $Al_2CuMg$  ( $S'$ ) phases. In the alloys of this invention these  $Al_3Tm$  dispersoids are made stronger and more resistant to coarsening at elevated temperatures by adding suitable alloying elements such as gadolinium, yttrium, zirconium, titanium, hafnium, niobium, or combinations thereof that enter  $Al_3Tm$  in solution.

**[0023]** Ytterbium forms  $Al_3Yb$  dispersoids in the aluminum matrix that are fine and coherent with the aluminum matrix. The lattice parameters of Al and  $Al_3Yb$  are close (0.405 nm and 0.420 nm respectively), indicating there is minimal driving force for causing growth of the  $Al_3Yb$  dispersoids. This low interfacial energy makes the  $Al_3Yb$  dispersoids thermally stable and resistant to coarsening up to temperatures as high as about 842°F (450°C). Addition of magnesium in solid solution in aluminum increases the lattice parameter of the aluminum matrix and decreases the lattice parameter mismatch further increasing the resistance to coarsening of the  $Al_3Yb$ . Addition of copper increases the strength of alloys through precipitation of  $Al_2Cu$  ( $\theta'$ ) and  $Al_2CuMg$  ( $S'$ ) phases. In the alloys of this invention, these  $Al_3Yb$  dispersoids are made stronger and more resistant to coarsening at elevated temperatures by adding suitable alloying elements such as gadolinium, yttrium, zirconium, titanium, hafnium, niobium, or combinations thereof that enter  $Al_3Yb$  in solution.

**[0024]** Lutetium forms  $Al_3Lu$  dispersoids in the aluminum matrix that are fine and coherent with the aluminum matrix. The lattice parameters of Al and  $Al_3Lu$  are close (0.405 nm and 0.419 nm respectively), indicating there is minimal driving force for causing growth of the  $Al_3Lu$

dispersoids. This low interfacial energy makes the  $\text{Al}_3\text{Lu}$  dispersoids thermally stable and resistant to coarsening up to temperatures as high as about 842°F (450°C). Addition of magnesium in solid solution in aluminum increases the lattice parameter of the aluminum matrix and decreases the lattice parameter mismatch further increasing the resistance to coarsening of  $\text{Al}_3\text{Lu}$ . Addition of copper increases the strength of alloys through precipitation of  $\text{Al}_2\text{Cu}$  ( $\theta'$ ) and  $\text{Al}_2\text{CuMg}$  ( $S'$ ) phases. In the alloys of this invention, these  $\text{Al}_3\text{Lu}$  dispersoids are made stronger and more resistant to coarsening at elevated temperatures by adding suitable alloying elements such as gadolinium, yttrium, zirconium, titanium, hafnium, niobium, or mixtures thereof that enter  $\text{Al}_3\text{Lu}$  in solution.

**[0025]** Gadolinium forms metastable  $\text{Al}_3\text{Gd}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition. The  $\text{Al}_3\text{Gd}$  dispersoids are stable up to temperatures as high as about 842°F (450°C) due to their low diffusivity in aluminum. The  $\text{Al}_3\text{Gd}$  dispersoids have a  $D0_{19}$  structure in the equilibrium condition. Despite its large atomic size, gadolinium has fairly high solubility in the  $\text{Al}_3\text{X}$  intermetallic dispersoids (where X is scandium, erbium, thulium, ytterbium or lutetium). Gadolinium can substitute for the X atoms in  $\text{Al}_3\text{X}$  intermetallic, thereby forming an ordered  $L1_2$  phase which results in improved thermal and structural stability.

**[0026]** Yttrium forms metastable  $\text{Al}_3\text{Y}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition and a  $D0_{19}$  structure in the equilibrium condition. The metastable  $\text{Al}_3\text{Y}$  dispersoids have a low diffusion coefficient which makes them thermally stable and highly resistant to coarsening. Yttrium has a high solubility in the  $\text{Al}_3\text{X}$  intermetallic dispersoids allowing large amounts of yttrium to substitute for X in the  $\text{Al}_3\text{X}$   $L1_2$  dispersoids which results in improved thermal and structural stability.

**[0027]** Zirconium forms  $\text{Al}_3\text{Zr}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition and  $D0_{23}$  structure in the equilibrium condition. The metastable  $\text{Al}_3\text{Zr}$  dispersoids have a low diffusion coefficient which makes them thermally stable and highly resistant to coarsening. Zirconium has a high solubility in the  $\text{Al}_3\text{X}$  dispersoids allowing large amounts of zirconium to substitute for X in the  $\text{Al}_3\text{X}$  dispersoids, which results in improved thermal and structural stability.

**[0028]** Titanium forms  $\text{Al}_3\text{Ti}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition and  $D0_{22}$  structure in the equilibrium condition. The metastable  $\text{Al}_3\text{Ti}$  dispersoids have a low diffusion coefficient which makes them thermally stable and highly resistant to coarsening. Titanium has a high solubility in the  $\text{Al}_3\text{X}$  dispersoids allowing large amounts of titanium to substitute for X in the  $\text{Al}_3\text{X}$  dispersoids, which results in improved thermal and structural stability.

**[0029]** Hafnium forms metastable  $\text{Al}_3\text{Hf}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition and a  $D0_{23}$  structure in the equilibrium condition. The  $\text{Al}_3\text{Hf}$  dispersoids have a low diffusion

coefficient, which makes them thermally stable and highly resistant to coarsening. Hafnium has a high solubility in the  $\text{Al}_3\text{X}$  dispersoids allowing large amounts of hafnium to substitute for scandium, erbium, thulium, ytterbium, and lutetium in the above mentioned  $\text{Al}_3\text{X}$  dispersoids, which results in stronger and more thermally stable dispersoids.

**[0030]** Niobium forms metastable  $\text{Al}_3\text{Nb}$  dispersoids in the aluminum matrix that have an  $L1_2$  structure in the metastable condition and a  $D0_{22}$  structure in the equilibrium condition. Niobium has a lower solubility in the  $\text{Al}_3\text{X}$  dispersoids than hafnium or yttrium, allowing relatively lower amounts of niobium than hafnium or yttrium to substitute for X in the  $\text{Al}_3\text{X}$  dispersoids. Nonetheless, niobium can be very effective in slowing down the coarsening kinetics of the  $\text{Al}_3\text{X}$  dispersoids because the  $\text{Al}_3\text{Nb}$  dispersoids are thermally stable. The substitution of niobium for X in the above mentioned  $\text{Al}_3\text{X}$  dispersoids results in stronger and more thermally stable dispersoids.

**[0031]**  $\text{Al}_3\text{X}$   $L1_2$  precipitates improve elevated temperature mechanical properties in aluminum alloys for two reasons. First, the precipitates are ordered intermetallic compounds. As a result, when the particles are sheared by glide dislocations during deformation, the dislocations separate into two partial dislocations separated by an anti-phase boundary on the glide plane. The energy to create the anti-phase boundary is the origin of the strengthening. Second, the cubic  $L1_2$  crystal structure and lattice parameter of the precipitates are closely matched to the aluminum solid solution matrix. This results in a lattice coherency at the precipitate/matrix boundary that resists coarsening. The lack of an inter-phase boundary results in a low driving force for particle growth and resulting elevated temperature stability. Alloying elements in solid solution in the dispersed strengthening particles and in the aluminum matrix that tend to decrease the lattice mismatch between the matrix and particles will tend to increase the strengthening and elevated temperature stability of the alloy.

**[0032]** The amount of scandium present in the alloys of this invention, if any, may vary from about 0.1 to about 0.5 weight percent, more preferably from about 0.1 to about 0.35 weight percent, and even more preferably from about 0.1 to about 0.25 weight percent. The Al-Sc phase diagram shown in FIG. 2 indicates a eutectic reaction at about 0.5 weight percent scandium at about 1219°F (659°C) resulting in a solid solution of scandium and aluminum and  $\text{Al}_3\text{Sc}$  dispersoids. Aluminum alloys with less than 0.5 weight percent scandium can be quenched from the melt to retain scandium in solid solution that may precipitate as dispersed  $L1_2$  intermetallic  $\text{Al}_3\text{Sc}$  following an aging treatment. Alloys with scandium in excess of the eutectic composition (hypereutectic alloys) can only retain scandium in solid solution by rapid solidification processing (RSP) where cooling rates are in excess of about  $10^3$ °C/second.

**[0033]** The amount of erbium present in the alloys of this invention, if any, may vary from about 0.1 to about

6.0 weight percent, more preferably from about 0.1 to about 4 weight percent, and even more preferably from about 0.2 to 2 weight percent. The Al-Er phase diagram shown in FIG. 3 indicates a eutectic reaction at about 6 weight percent erbium at about 1211°F (655°C). Aluminum alloys with less than about 6 weight percent erbium can be quenched from the melt to retain erbium in solid solutions that may precipitate as dispersed L<sub>12</sub> intermetallic Al<sub>3</sub>Er following an aging treatment. Alloys with erbium in excess of the eutectic composition can only retain erbium in solid solution by rapid solidification processing (RSP) where cooling rates are in excess of about 10<sup>3</sup>C/second. Alloys with erbium in excess of the eutectic composition (hypereutectic alloys) cooled normally will have a microstructure consisting of relatively large Al<sub>3</sub>Er dispersoid in a finely divided aluminum-Al<sub>3</sub>Er eutectic phase matrix.

**[0034]** The amount of thulium present in the alloys of this invention, if any, may vary from about 0.1 to about 10 weight percent, more preferably from about 0.2 to about 6 weight percent, and even more preferably from about 0.2 to about 4 weight percent. The Al-Tm phase diagram shown in FIG. 4 indicates a eutectic reaction at about 10 weight percent thulium at about 1193°F (645°C). Thulium forms metastable Al<sub>3</sub>Tm dispersoids in the aluminum matrix that have an L<sub>12</sub> structure in the equilibrium condition. The Al<sub>3</sub>Tm dispersoids have a low diffusion coefficient which makes them thermally stable and highly resistant to coarsening. Aluminum alloys with less than 10 weight percent thulium can be quenched from the melt to retain thulium in solid solution that may precipitate as dispersed metastable L<sub>12</sub> intermetallic Al<sub>3</sub>Tm following an aging treatment. Alloys with thulium in excess of the eutectic composition can only retain Tm in solid solution by rapid solidification processing (RSP) where cooling rates are in excess of about 10<sup>3</sup>C/second.

**[0035]** The amount of ytterbium present in the alloys of this invention, if any, may vary from about 0.1 to about 15 weight percent more preferably from about 0.2 to about 8 weight percent, and even more preferably from about 0.2 to about 4 weight percent. The Al-Yb phase diagram shown in FIG. 5 indicates a eutectic reaction at about 21 weight percent ytterbium at about 1157°F (625°C). Aluminum alloys with less than about 21 weight percent ytterbium can be quenched from the melt to retain ytterbium in solid solution that may precipitate as dispersed L<sub>12</sub> intermetallic Al<sub>3</sub>Yb following an aging treatment. Alloys with ytterbium in excess of the eutectic composition can only retain ytterbium in solid solution by rapid solidification processing (RSP) where cooling rates are in excess of about 10<sup>3</sup>C/second.

**[0036]** The amount of lutetium present in the alloys of this invention, if any, may vary from about 0.1 to about 12 weight percent, more preferably from 0.2 to about 8 weight percent, and even more preferably from about 0.2 to about 4 weight percent. The Al-Lu phase diagram shown in FIG. 6 indicates a eutectic reaction at about 11.7 weight percent Lu at about 1202 °F (650°C). Alumi-

num alloys with less than about 11.7 weight percent lutetium can be quenched from the melt to retain Lu in solid solution that may precipitate as dispersed L<sub>12</sub> intermetallic Al<sub>3</sub>Lu following an aging treatment. Alloys with Lu in excess of the eutectic composition can only retain Lu in solid solution by rapid solidification processing (RSP) where cooling rates are in excess of about 10<sup>3</sup>C/second.

**[0037]** The amount of gadolinium present in the alloys of this invention, if any, may vary from about 0.1 to about 4 weight percent, more preferably from 0.2 to about 2 weight percent, and even more preferably from about 0.5 to about 2 weight percent.

**[0038]** The amount of yttrium present in the alloys of this invention, if any, may vary from about 0.1 to about 4 weight percent, more preferably from 0.2 to about 2 weight percent, and even more preferably from about 0.5 to about 2 weight percent.

**[0039]** The amount of zirconium present in the alloys of this invention, if any, may vary from about 0.05 to about 1 weight percent, more preferably from 0.1 to about 0.75 weight percent, and even more preferably from about 0.1 to about 0.5 weight percent.

**[0040]** The amount of titanium present in the alloys of this invention, if any, may vary from about 0.05 to 2 about weight percent, more preferably from 0.1 to about 1 weight percent, and even more preferably from about 0.1 to about 0.5 weight percent.

**[0041]** The amount of hafnium present in the alloys of this invention, if any, may vary from about 0.05 to about 2 weight percent, more preferably from 0.1 to about 1 weight percent, and even more preferably from about 0.1 to about 0.5 weight percent.

**[0042]** The amount of niobium present in the alloys of this invention, if any, may vary from about 0.05 to about 1 weight percent, more preferably from 0.1 to about 0.75 weight percent, and even more preferably from about 0.1 to about 0.5 weight percent.

**[0043]** In order to have the best properties for the alloys of this invention, it is desirable to limit the amount of other elements. Specific elements that should be reduced or eliminated include no more than about 0.1 weight percent iron, 0.1 weight percent chromium, 0.1 weight percent manganese, 0.1 weight percent vanadium, 0.1 weight percent cobalt, and 0.1 weight percent nickel. The total quantity of additional elements should not exceed about 1% by weight, including the above listed elements.

**[0044]** Other additions in the inventive alloys include at least one of about 0.001 weight percent to about 0.10 weight percent sodium, about 0.001 weight percent to about 0.10 weight percent calcium, about 0.001 to about 0.10 weight percent strontium, about 0.001 to about 0.10 weight percent antimony, 0.001 to 0.10 weight percent barium and about 0.001 to about 0.10 weight percent phosphorus. These are added to refine the microstructure of the eutectic phase and the primary silicon particle morphology and size.

**[0045]** These aluminum alloys may be made by any and all consolidation and fabrication processes known

to those in the art such as casting (without further deformation), deformation processing (wrought processing), rapid solidification processing, forging, extrusion, rolling, die forging, powder metallurgy and others. The rapid solidification process should have a cooling rate greater than about 10<sup>3</sup>°C/second including but not limited to powder processing, atomization, melt spinning, splat quenching, spray deposition, cold spray, plasma spray, laser melting and deposition, ball milling and cryomilling.

**[0046]** Preferred exemplary aluminum alloys of this invention include, but are not limited to (in weight percent):

about Al-(4-18)Si-(0.1-0.35)Sc-(0.2-2)Gd;  
 about Al-(4-18)Si-(0.1-4)Er-(0.2-2)Gd;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.2-2)Gd;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.2-2)Gd;  
 about Al-(4-18)Si-(0.2-8)Lu-(0.2-2)Gd;  
 about Al-(4-18)Si-(0.1-0.35)Sc-(0.2-2)Y;  
 about Al-(4-18)Si-(0.1-4)Er-(0.2-2)Y;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.2-2)Y;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.2-2)Y;  
 about Al-(4-18)Si-(0.2-8)Lu-(0.2-2)Y;  
 about Al-(4-18)Si-(0.1-0.35)Sc-(0.1-0.75)Zr;  
 about Al-(4-18)Si-(0.1-4)Er-(0.1-0.75)Zr;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.1-0.75)Zr;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.1-0.75)Zr;  
 about Al-(4-18)Si-(0.2-8)Lu-(0.1-0.75)Zr;  
 about Al-(4-18)Si-(0.1-0.35)Sc-(0.1-1)Ti;  
 about Al-(4-18)Si-(0.1-4)Er-(0.1-1)Ti;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.1-1)Ti;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.1-1)Ti;  
 about Al-(4-18)Si-(0.2-8)Lu-(0.1-1)Ti;  
 about Al-(4-18)Si-(0.1-0.35)Sc-(0.1-1)Hf;  
 about Al-(4-18)Si-(0.1-4)Er-(0.1-1)Hf;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.1-1)Hf;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.1-1)Hf;  
 about Al-(4-18)Si-(0.2-8)Lu-(0.1-1)Hf;  
 about Al-(4-18)Si-(0.1-0.35)Sc-(0.1-0.75)Nb;  
 about Al-(4-18)Si-(0.2-2)Er-(0.1-0.75)Nb;  
 about Al-(4-18)Si-(0.2-6)Tm-(0.1-0.75)Nb;  
 about Al-(4-18)Si-(0.2-8)Yb-(0.1-0.75)Nb; and  
 about Al-(4-18)Si-(0.2-8)Lu-(0.1-0.75)Nb.

**[0047]** Examples of similar alloys to these are alloys with the addition of about 0.2-3 weight percent Mg, more preferably alloys with the addition of about 0.3-1.5 weight percent Mg, and even more preferably alloys with the addition of about 0.5-1.5 weight percent Mg; and alloys with the addition of about 0.5-5 weight percent Cu, more preferably alloys with the addition of about 1-4 weight percent Cu, and even more preferably alloys with the addition of about 2-4 weight percent Cu.

**[0048]** Even more preferred exemplary aluminum alloys of this invention include, but are not limited to (in weight percent):

about Al-(5-11)Si-(0.1-0.25)Sc-(0.5-2)Gd;  
 about Al-(5-11)Si-(0.2-2)Er-(0.5-2)Gd;

about Al-(5-11)Si-(0.2-4)Tm-(0.5-2)Gd;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.5-2)Gd;  
 about Al-(5-11)Si-(0.2-4)Lu-(0.5-2)Gd;  
 about Al-(5-11)Si-(0.1-0.25)Sc-(0.5-2)Y;  
 about Al-(5-11)Si-(0.2-2)Er-(0.5-2)Y;  
 about Al-(5-11)Si-(0.2-4)Tm-(0.5-2)Y;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.5-2)Y;  
 about Al-(5-11)Si-(0.2-4)Lu-(0.5-2)Y;  
 about Al-(5-11)Si-(0.1-0.25)Sc-(0.1-0.5)Zr;  
 about Al-(5-11)Si-(0.2-2)Er-(0.1-0.5)Zr;  
 about Al-(5-11)Si-(0.2-4)Tm-(0.1-0.5)Zr;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.1-0.5)Zr;  
 about Al-(5-11)Si-(0.2-4)Lu-(0.1-0.5)Zr;  
 about Al-(5-11)Si-(0.1-0.25)Sc-(0.1-0.5)Ti;  
 about Al-(5-11)Si-(0.2-2)Er-(0.1-0.5)Ti;  
 about Al-(5-11)Si-(0.2-4)Tm-(0.1-0.5)Ti;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.1-0.5)Ti;  
 about Al-(5-11)Si-(0.2-4)Lu-(0.1-0.5)Ti;  
 about Al-(5-11)Si-(0.1-0.25)Sc-(0.1-0.5)Hf;  
 about Al-(5-11)Si-(0.2-2)Er-(0.1-0.5)Hf;  
 about Al-(5-11)Si-(0.2-4)Tm-(0.1-0.5)Hf;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.1-0.5)Hf;  
 about Al-(5-11)Si-(0.2-4)Lu-(0.1-0.5)Hf;  
 about Al-(5-11)Si-(0.1-0.25)Sc-(0.1-0.5)Nb;  
 about Al-(5-11)Si-(0.2-2)Er-(0.1-0.5)Nb;  
 about Al-(5-11)Si-(0.2-4)Tm-(0.1-0.5)Nb;  
 about Al-(5-11)Si-(0.2-4)Yb-(0.1-0.5)Nb; and  
 about Al-(5-11)Si-(0.2-4)Lu-(0.1-0.5)Nb.

**[0049]** Examples of similar alloys to these are alloys with the addition of about 0.2-3 weight percent Mg, more preferably alloys with the addition of about 0.3-1.5 weight percent Mg, and even more preferably alloys with the addition of about 0.5-1.5 weight percent Mg; and alloys with the addition of about 0.5-5 weight percent Cu, more preferably alloys with the addition of about 1-4 weight percent Cu, and even more preferably alloys with the addition of about 2-4 weight percent Cu.

**[0050]** Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the scope of the invention.

## Claims

1. A heat treatable aluminum alloy comprising:

about 4.0 to about 25.0 weight percent silicon;  
 at least one first element selected from the group comprising about 0.1 to about 0.5 weight percent scandium, about 0.1 to about 6.0 weight percent erbium, about 0.1 to about 10 weight percent thulium, about 0.1 to about 15.0 weight percent ytterbium, and about 0.1 to about 12 weight percent lutetium;  
 at least one second element selected from the

- group comprising about 0.1 to about 4.0 weight percent gadolinium, about 0.1 to about 4.0 weight percent yttrium, about 0.05 to about 1.0 weight percent zirconium, about 0.05 to about 2.0 weight percent titanium, about 0.05 to about 2.0 weight percent hafnium, and about 0.05 to about 1.0 weight percent niobium; and the balance substantially aluminum.
2. The alloy of claim 1, wherein the alloy comprises an aluminum solid solution matrix containing a plurality of dispersed  $Al_3X$  second phases having  $L1_2$  structures, wherein X includes at least one first element and at least one second element.
3. The alloy of claim 1 or 2 further comprising about 0.2 to about 3.0 weight percent magnesium.
4. The alloy of any preceding claim further comprising about 0.5 to about 5.0 weight percent copper.
5. The alloy of any preceding claim further comprising at least one of about 0.001 to about 0.1 weight percent sodium, about 0.001 to about 0.1 weight percent calcium, about 0.001 to about 0.1 weight percent strontium, about 0.001 to about 0.1 weight percent antimony, about 0.001 to about 0.1 weight percent barium, and about 0.001 to about 0.1 weight percent phosphorus.
6. The alloy of any preceding claim, comprising no more than about 1.0 weight percent total other elements including impurities.
7. The alloy of any preceding claim comprising no more than about 0.1 weight percent iron, about 0.1 weight percent chromium, about 0.1 weight percent manganese, about 0.1 weight percent vanadium, about 0.1 weight percent cobalt, and about 0.1 weight percent nickel.
8. The alloy of any preceding claim, wherein the amount of silicon ranges from about 4.0 to about 18.0 weight percent.
9. The alloy of claim 8, wherein the amount of silicon ranges from about 5.0 to about 11.0 weight percent.
10. The alloy of any preceding claim, which has been formed by a process selected from casting, deformation processing, and rapid solidification processing.
11. The alloy of claim 10, which has been heat treated after forming.
12. The alloy of claim 11, in which the alloy has been heat treated by a solution anneal at a temperature of about 800°F (426°C) to about 1100°F (593°C) for about 30 minutes to four hours, followed by quenching.
13. The heat treatable aluminum alloy of any preceding claim, wherein the alloy is capable of being used at temperatures from about -420°F (-251°C) up to about 650°F (343°C).
14. A method of forming a heat treatable aluminum alloy, the method comprising:
- (a) forming a melt comprising:
- about 4.0 to about 25.0 weight percent silicon;  
 about 0.2 to about 3.0 weight percent magnesium;  
 about 0.5 to about 5.0 weight percent copper;  
 at least one first element selected from the group comprising about 0.1 to about 0.5 weight percent scandium, about 0.1 to about 6.0 weight percent erbium, about 0.1 to about 10 weight percent thulium, about 0.1 to about 15.0 weight percent ytterbium, and about 0.1 to about 12 weight percent lutetium;  
 at least one second element selected from the group comprising about 0.1 to about 4.0 weight percent gadolinium, about 0.1 to about 4.0 weight percent yttrium, about 0.05 to about 1.0 weight percent zirconium, about 0.05 to about 2.0 weight percent titanium, about 0.05 to about 2.0 weight percent hafnium, and about 0.05 to about 1.0 weight percent niobium; and  
 the balance substantially aluminum;
- (b) solidifying the melt to form a solid body; and  
 (c) heat treating the solid body.
15. The method of claim 14, further comprising: wherein solidifying comprises a rapid solidification process in which the cooling rate is greater than about  $10^3$ °C/second including at least one of: powder processing, atomization, melt spinning, splat quenching, spray deposition, cold spray, plasma spray, laser melting and deposition, ball milling, and cryomilling, wherein the heat treating comprises:
- solution heat treatment at about 800°F (426°C) to about 1100°F (593°C) for about thirty minutes to four hours;  
 quenching; and  
 aging at a temperature of about 200°F (93°C) to about 600°F (315°C) for about two to forty eight

hours, and  
refining the structure of the solid body by deformation processing includes at least one of:

extrusion, forging and rolling.

5

10

15

20

25

30

35

40

45

50

55

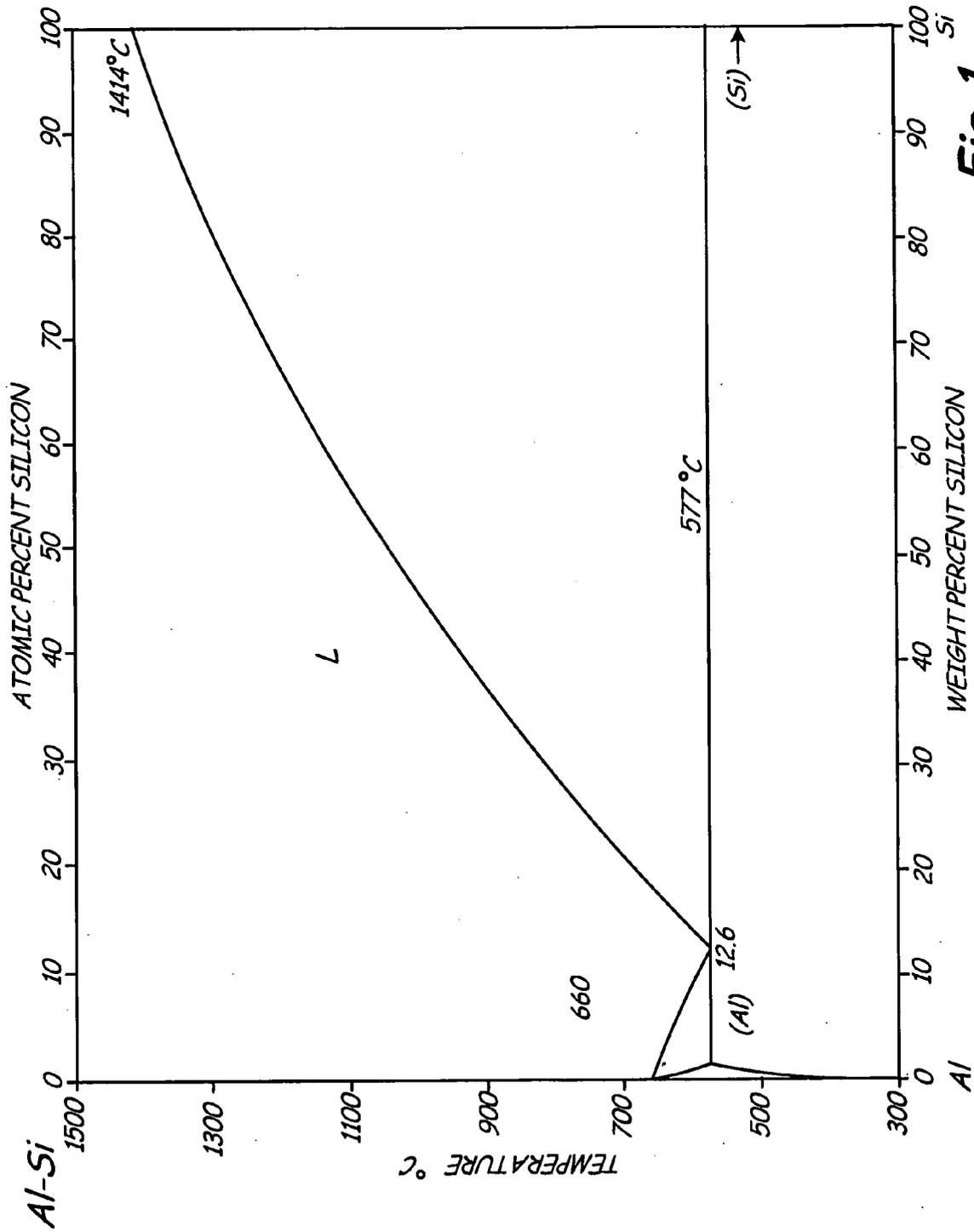


Fig. 1

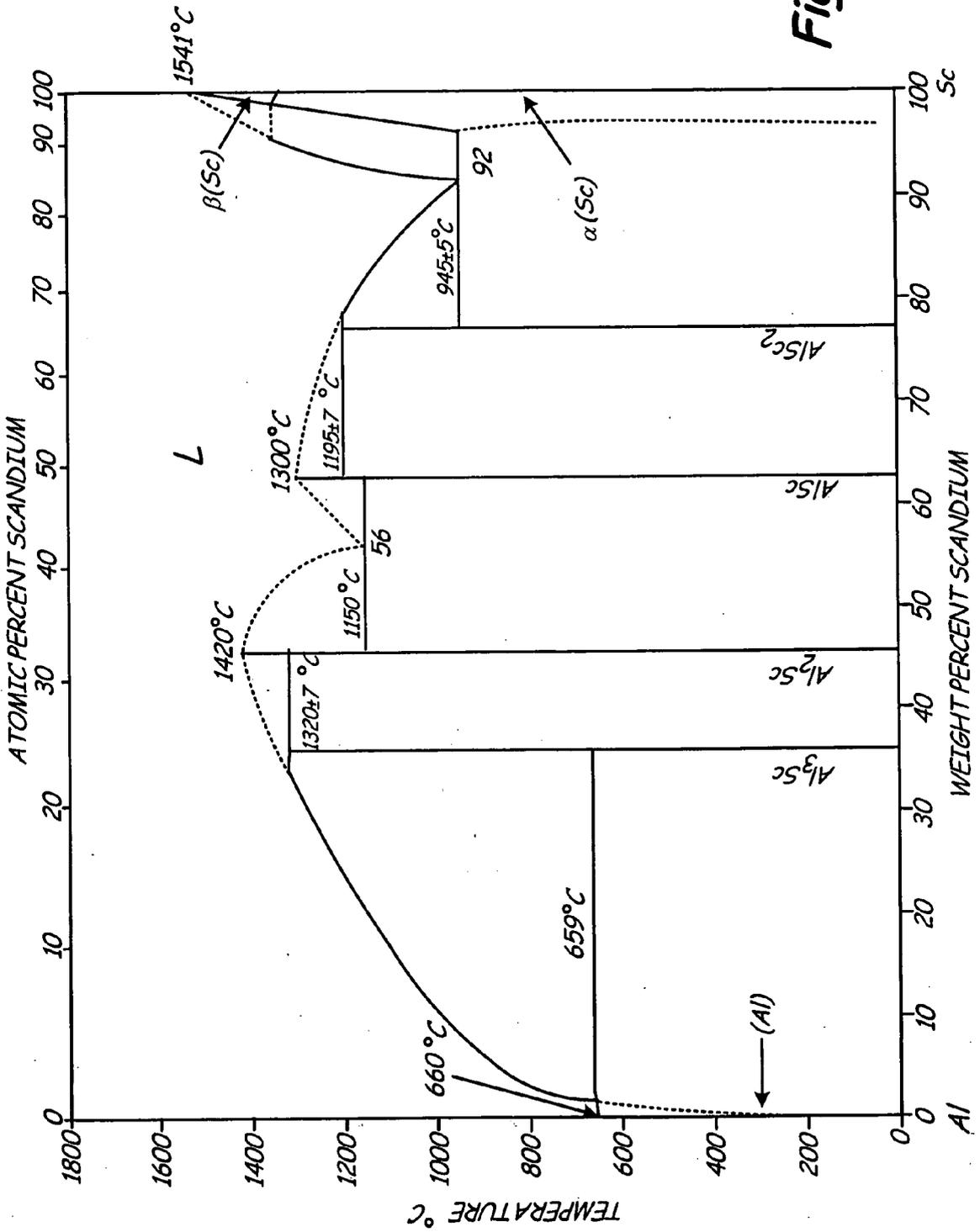


Fig. 2

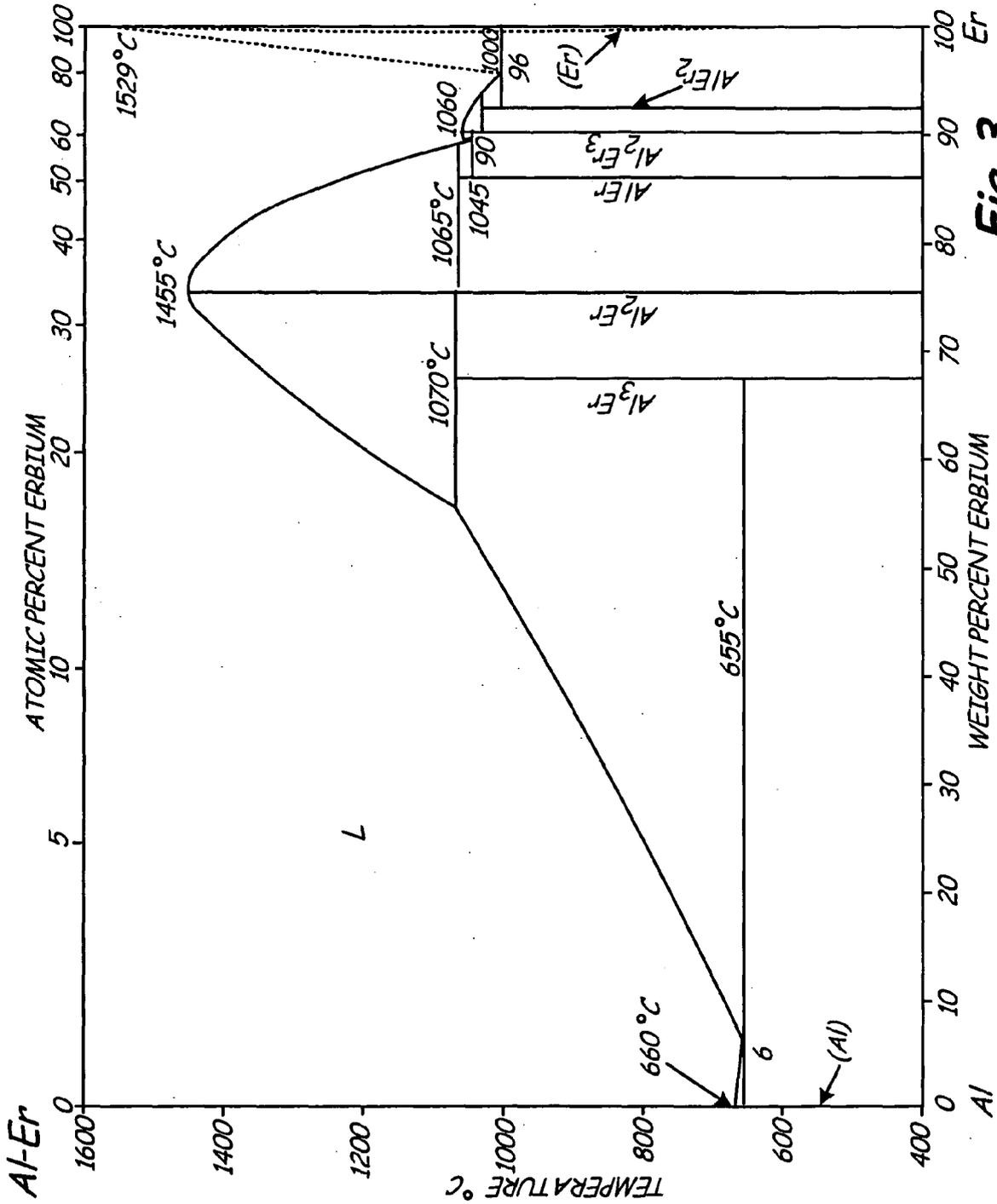


Fig. 3

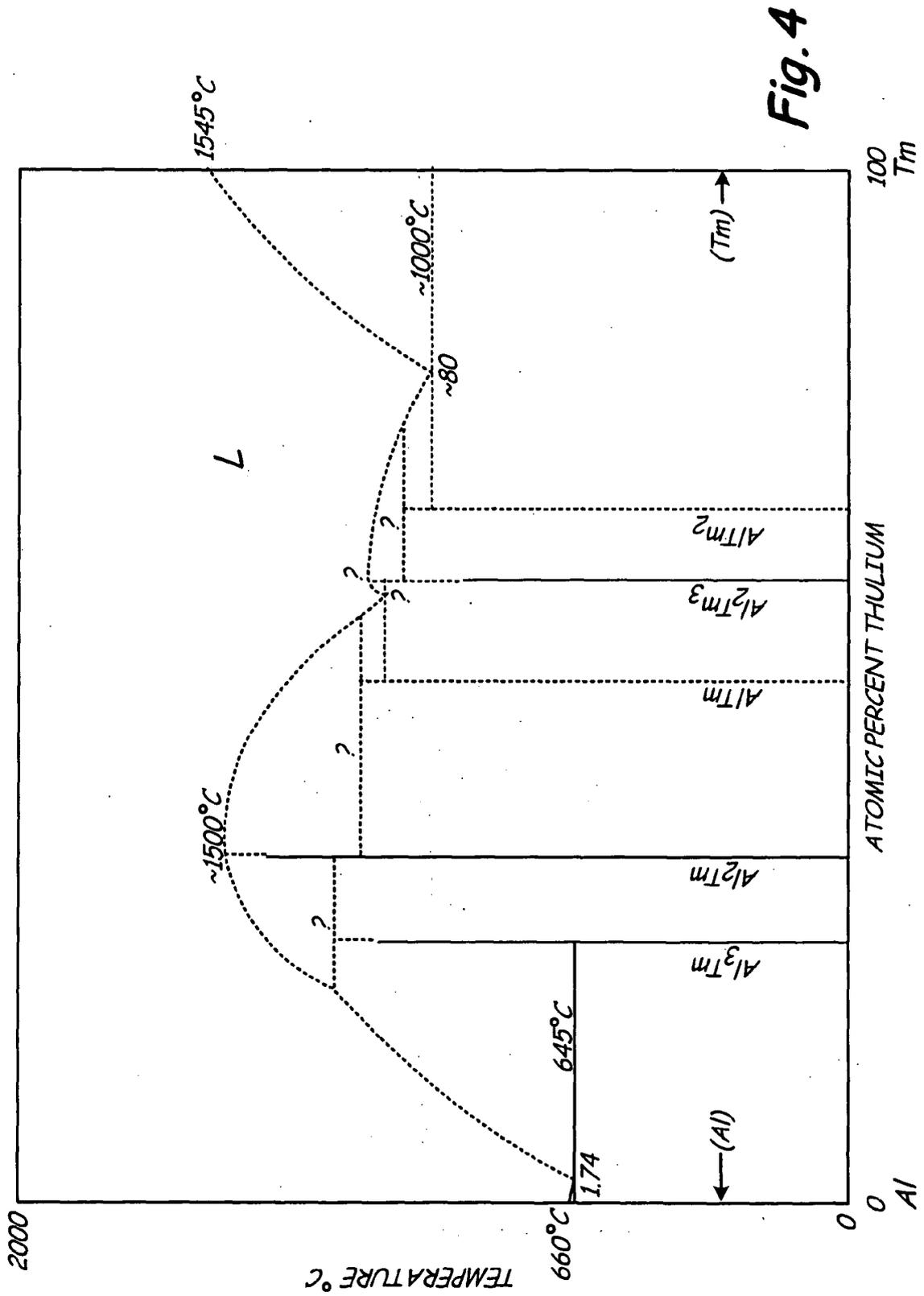


Fig. 4

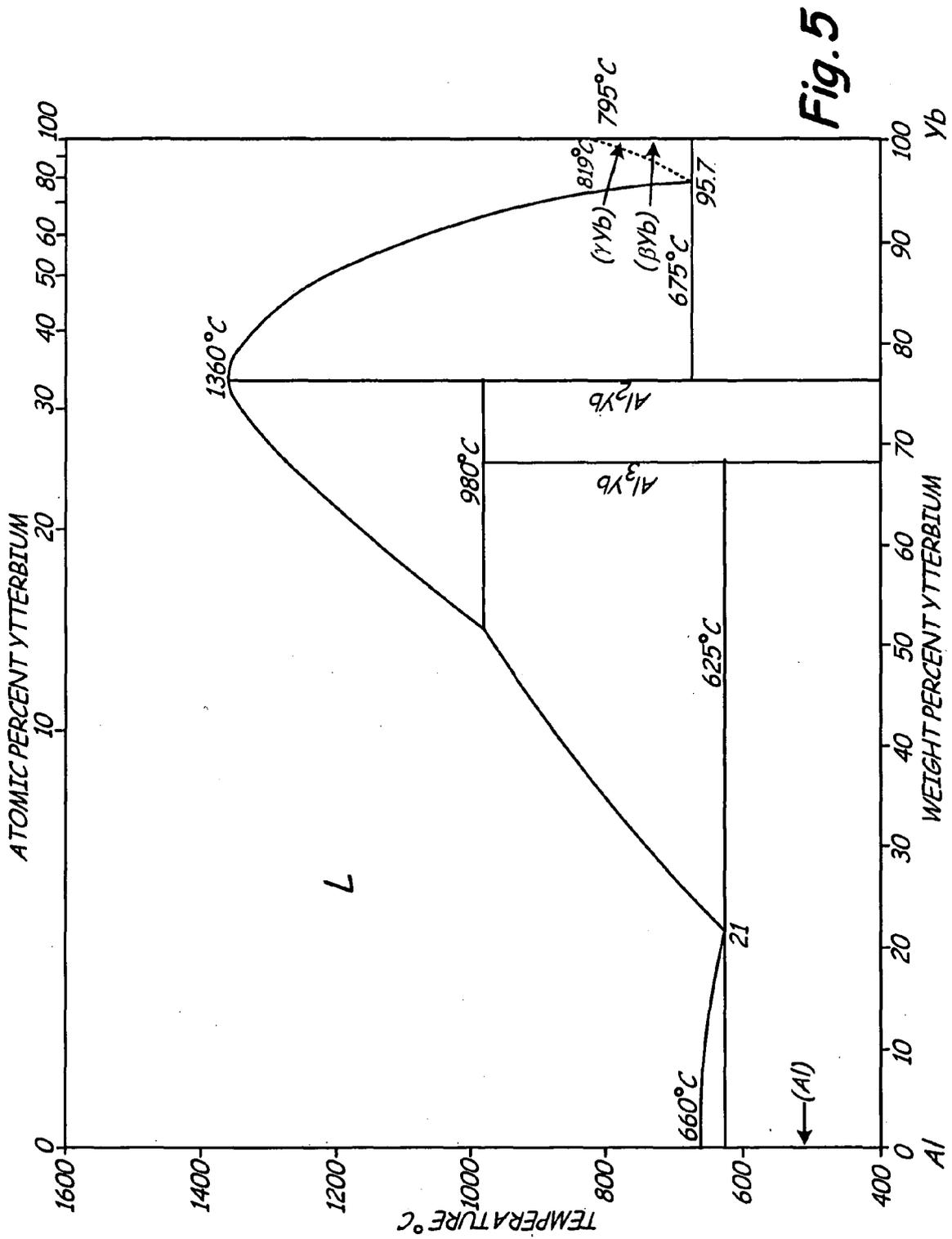


Fig. 5

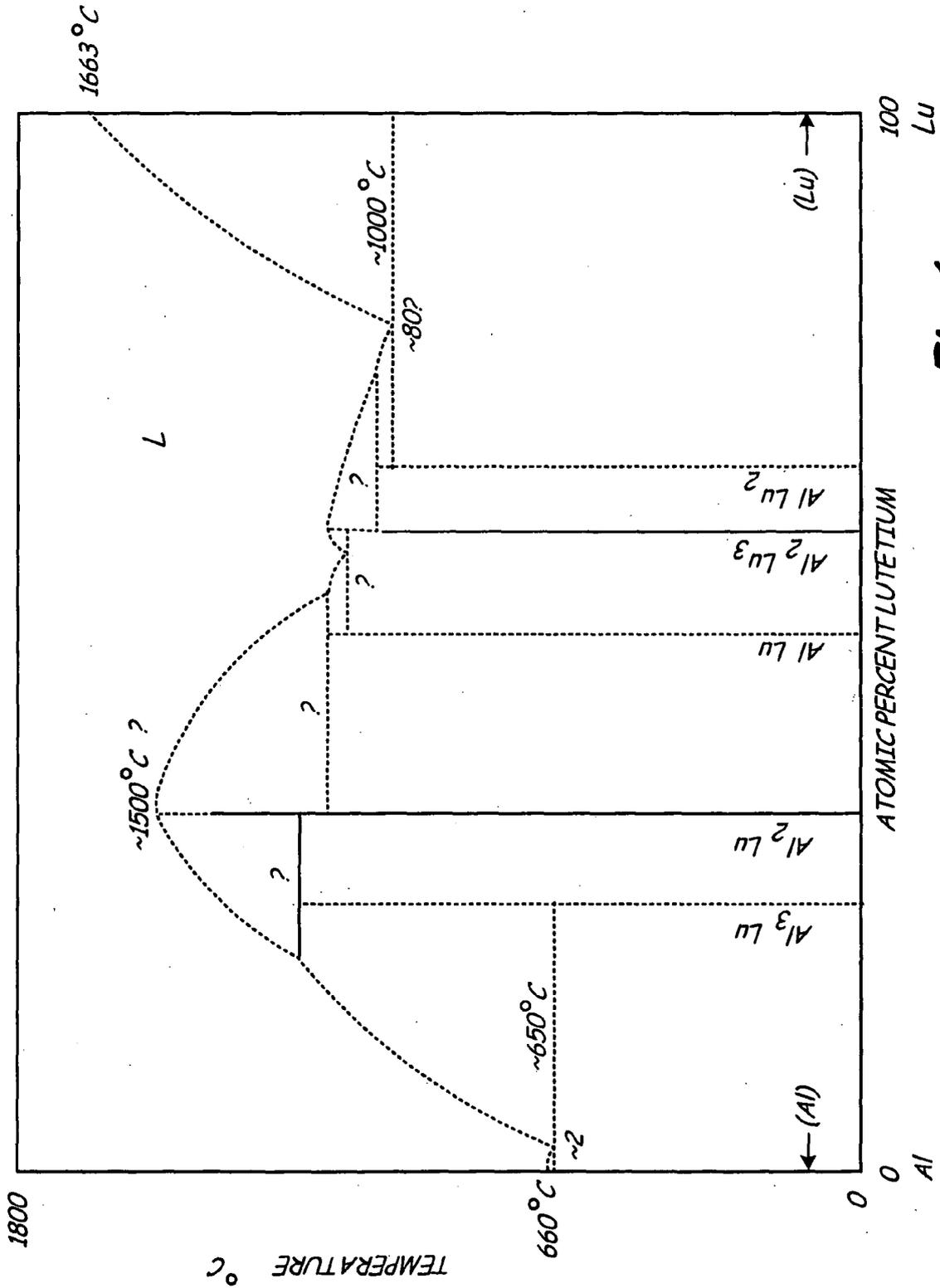


Fig. 6



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

EP 09 25 1012

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.

20-05-2009

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9532074	A	30-11-1995	AU 2651595	A 18-12-1995
			CA 2190951	A1 30-11-1995
			EP 0760727	A1 12-03-1997
			JP 10505282	T 26-05-1998
			NO 964958	A 14-01-1997
-----				
WO 9610099	A	04-04-1996	AU 3813795	A 19-04-1996
-----				
EP 1439239	A	21-07-2004	JP 3929978	B2 13-06-2007
			JP 2004218090	A 05-08-2004
			US 2006093512	A1 04-05-2006
-----				
WO 2005047554	A	26-05-2005	DE 10352932	A1 16-06-2005
			EP 1682688	A1 26-07-2006
			US 2007240796	A1 18-10-2007
-----				
JP 11156584	A	15-06-1999	JP 3592052	B2 24-11-2004
-----				
EP 0208631	A	14-01-1987	BR 8602980	A 17-02-1987
			CA 1274107	A1 18-09-1990
			DE 3664789	D1 07-09-1989
			ES 2000175	A6 01-01-1988
			FR 2584095	A1 02-01-1987
			JP 1667232	C 29-05-1992
			JP 3028500	B 19-04-1991
			JP 62007828	A 14-01-1987
			US 4804423	A 14-02-1989
-----				
US 4874440	A	17-10-1989	NONE	
-----				

**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 6248453 A [0005]
- US 20060269437 A [0005]