



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
30.09.2015 Bulletin 2015/40

(51) Int Cl.:
C22C 21/00 (2006.01) C22F 1/04 (2006.01)

(21) Application number: **14168188.2**

(22) Date of filing: **13.05.2014**

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

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(30) Priority: **26.03.2014 US 201461970586 P**

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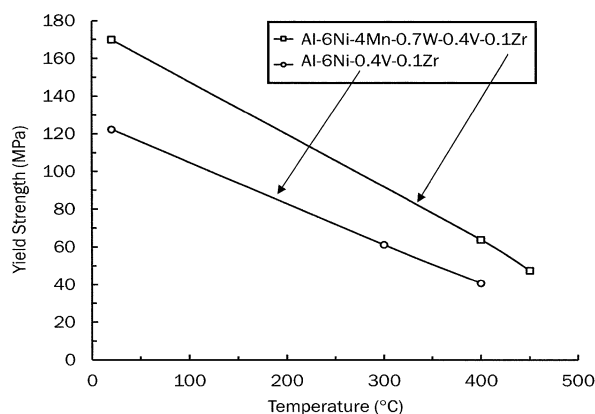
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(54) **Aluminium die casting alloys**

(57) An aluminum die-casting alloy comprising: 1 to 6 % by weight nickel, 1 to 5 % by weight manganese, 0.1 to 0.4 % by weight zirconium, 0.1 to 0.4 % by weight vanadium, 0.1 to 1 % by weight tungsten and/ or 0.1 to 1 % molybdenum, optionally up to 2 % by weight iron, optionally up to 1 % by weight titanium, optionally up to 2 % by weight magnesium, optionally up to 0.5 % by weight silicon, optionally up to 0.5 % by weight copper,

optionally up to 0,5 % by weight zinc, optionally total maximum 5 % by weight transition elements including strontium, scandium, lanthanum, yttrium, hafnium, niobium, tantalum, and/or chromium, and aluminum as the remainder with further elements present as impurities due to production such that the total maximum of impurity elements is 1 % by weight.

Fig. 1



Description

FIELD OF THE INVENTION

[0001] The present invention relates to aluminum alloys that are dispersion-strengthened, age-hardenable, and can be processed by die-casting into shaped objects that have useful mechanical properties at temperatures up to at least 350°C.

BACKGROUND OF THE INVENTION

[0002] Automotive engines made with aluminum alloys have a high power-to-weight ratio, and therefore they have better fuel efficiency and less negative impact on the environment than cast iron engines. However, with the demand for yet higher fuel efficiencies, 'supercharged' engines are being designed to operate at even higher temperatures than regular engines. Accordingly, cylinder heads and engine blocks in 'supercharged' engines are subjected to thermal cycling over a wider temperature range, and the alloy used in their construction has to withstand the resulting severe thermo-mechanical loading over long periods of time. Conventional casting aluminum alloys are not capable of withstanding these temperatures because their precipitation hardening effects disappear at about 200°C. Consequently, the dimensional stability, strength, and durability of cylinder heads and engine blocks made with these alloys become compromised at the elevated temperatures that are encountered during the operation of 'supercharged' engines. Supercharged engines and cylinder heads are not the only automotive components that could benefit from an aluminum alloy that is specifically designed for service at elevated temperatures. Connecting rods, impellers, brake calipers, and brake rotors could also benefit from such an alloy. Therefore, there is a need for a light, thermally stable alloy that is designed specifically for such applications.

PRIOR ART

[0003] Several attempts have been made in the past to provide aluminum casting alloys with enhanced thermal stability. Most notable among these attempts are alloys described in WO 2011/124590, which is therewith incorporated by reference.

[0004] When properly processed, the alloys represented in WO 2011/124590 have better mechanical properties at elevated temperatures than traditional aluminum casting alloys. However, and because the volume fraction of the fine zirconium-vanadium tri-aluminide ($\text{Al}_3\text{V}_{1-x}\text{Zr}_x$) particles in the prior art alloys do not exceed 1 % by volume; they have a limited strengthening effect. For this reason, an option of the prior art invention calls for adding up to 5 % by weight manganese to the alloy. Upon aging at a temperature between 350°C and 450°C, manganese, together with aluminum, forms metastable

manganese aluminide particles (Al_{12}Mn) that further increase the strength of the alloy. However, although these additional precipitate particles add strength to the alloy at room temperature, their strengthening effect disappears with increased service time at elevated temperatures.

DISCLOSURE OF THE INVENTION

[0005] The present invention relates to a class of aluminum alloys that (i) are dispersion-strengthened, (ii) can be processed by die-casting to produce useful shaped objects, and (iii) can be age-hardened for improved room temperature mechanical properties that are retained at temperatures up to at least 350°C.

[0006] It is an objective of the present invention to provide lightweight, wear-resistant, and corrosion-resistant materials that can be cast into useful objects by the conventional die-casting process and that are thermally stable up to at least 350°C.

[0007] Alloys of the present invention have the general chemical composition: aluminum-nickel-manganese-tungsten/molybdenum-zirconium-vanadium, and their chemical composition is optimized such that their liquidus temperature is less than 725°C. Such low liquidus temperature allows the alloys of the present invention to be processed into useful objects by traditional high-pressure die-casting.

[0008] Unlike traditional aluminum-silicon alloys, and similar to alloys of the prior art article, alloys of the present invention contain a eutectic structure that is stable at temperatures approaching 640°C, and it contains strengthening precipitate particles that are thermally stable at temperatures approaching 350°C. Also similar to alloys of the prior art article, the microstructure of the aluminum alloys of the present invention contains nickel trialuminide and aluminum as its eutectic structure, together with other transition metal tri-aluminide particles, namely $\text{Al}_3\text{V}_{1-x}\text{Zr}_x$. These transition metal trialuminide particles have the highly symmetric $\text{L}1_2$ crystal structure, which is analogous to the face centered cubic crystal structure of aluminum. It is this similarity in crystal structure between the aluminum matrix and these strengthening particles that allows for a coherent interface between the two phases; and by doing so, it maximizes the strengthening ability of the particles, impedes their coarsening, and enhances the thermal stability of the alloy.

[0009] A feature of the alloys of the present invention that distinguishes them from the prior art aluminum alloys that contain nickel, vanadium, and zirconium together with manganese, but without tungsten is that in the alloys of the present invention, the $\text{Al}_3\text{V}_{1-x}\text{Zr}_x$ particles are not the only thermally stable strengthening precipitates in the alloy. Alloys of the present invention rely on a relatively large amount of $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ precipitate particles for added strength at elevated temperature. Alloys of the present invention also rely on carefully designed tungsten containing manganese-aluminide ($\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$) precipitate

particles for strength at elevated temperature. $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ precipitate particles have the body centered cubic crystal structure, which is akin to the face centered cubic crystal structure of the α -aluminum matrix; and therefore they are semi-coherent with the α -aluminum matrix. Moreover, $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles do not readily coarsen when exposed to elevated temperatures and therefore - as shown in figure 1 - unlike the aluminum alloys of the prior art, alloys of the present invention retain a significant fraction of their room temperature mechanical properties at elevated temperatures.

[0010] The main feature of the alloys of the present invention that distinguishes them from those of the prior art is that alloys of the present invention contain tungsten and/ or molybdenum. For this reason, in alloys of the present invention, the $\text{Al}_3\text{V}_{1-x}\text{Zr}_x$ particles are not the only thermally stable strengthening precipitates. Because of their small quantity in the alloy ($\leq 1\%$ by volume), by themselves the $\text{Al}_3\text{V}_{1-x}\text{Zr}_x$ particles can contribute only limited high temperature strength. Alloys of the present invention rely on a relatively large amount of $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ precipitate particles for added strength at elevated temperature.

[0011] In general, when precipitation-strengthened aluminum alloys are subjected to high temperature during service, the metastable precipitates that were formed by thermal aging coarsen and begin to transform into the stable phase. When this happens, the alloy begins to lose its strength. Therefore, precipitates that have a low coarsening rate have enhanced thermal stability, and alloys that employ such precipitates for strengthening have good tensile properties at high temperature. Figure 1 shows that the measured yield strength at elevated temperatures of the $\text{Al-6Ni-4Mn-0.7W-0.4V-0.1Zr}$ alloy of the present invention is 90 MPa at 300°C, which is significantly higher than that of the Al-6Ni-0.4V-0.1Zr alloy of the prior art, which is only 60 MPa at 300°C. The reason for this distinguishing feature of the present invention alloy is described in detail in the following paragraphs.

[0012] The precipitation sequence during thermal aging of binary Al-Mn alloys starts with formation of metastable Al_{12}Mn particles. These particles are, to a large extent, responsible for the observed strength of thermally aged binary Al-Mn alloys. With extended time at an elevated temperature, these metastable Al_{12}Mn particles coarsen and eventually they transform to the stable Al_6Mn phase. The Al_6Mn particles have the rhombohedral crystal structure, and therefore they have incoherent interfaces with the surrounding α -aluminum matrix. Transformation of the metastable, semi-coherent Al_{12}Mn particles into stable, incoherent Al_6Mn particles signals the loss of their strengthening effect.

[0013] The present invention capitalizes on the fact that the lattice of the metastable Al_{12}Mn phase is similar to that of the Al_{12}W phase (both are body centered cubic), and also on the fact that the lattice parameter of the Al_{12}Mn phase (0.754 nm) is close to that of the Al_{12}W phase (0.758 nm). For these two reasons, during precip-

itation from the super saturated solid solution, tungsten can dissolve into the Al_{12}Mn phase to form $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ co-precipitates. Similar to the Al_{12}Mn particles, the $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles have body centered cubic lattice structure and semi-coherent interfaces with the α -aluminum matrix. However, thermodynamic calculations show that dissolution of tungsten into Al_{12}Mn lowers the Gibbs free energy of the thus-formed $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles relative to the Gibbs free energy of Al_{12}Mn . This makes the $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles more resistant to coarsening when exposed to elevated temperature, and therefore less prone to transforming into the incoherent Al_6Mn phase, than the Al_{12}Mn particles.

[0014] A comparable effect on the strength at elevated temperatures can be observed with an addition of molybdenum or a combined addition of tungsten and molybdenum.

[0015] The foregoing objective is achieved according to the present invention by an aluminum die-casting alloy comprising the following:

1 to 6 % by weight nickel,

1 to 5 % by weight manganese,

0.1 to 0.4 % by weight zirconium,

0.1 to 0.4 % by weight vanadium,

0.1 to 1 % by weight tungsten and/or 0.1 to 1 % by weight molybdenum,

optionally up to 2 % by weight iron,

optionally up to 1 % by weight titanium,

optionally up to 2 % by weight magnesium,

optionally up to 0.5 % by weight silicon,

optionally up to 0.5 % by weight copper,

optionally up to 0.5 % by weight zinc,

optionally total maximum 5 % by weight transition elements including strontium, scandium, lanthanum, yttrium, hafnium, niobium, tantalum, and/or chromium, and aluminum as the remainder with further elements present as impurities due to production such that the total maximum of impurity elements is 1 % by weight.

[0016] In a preferred embodiment the aluminum die-casting alloy comprises 4 to 6 % by weight nickel.

[0017] In a preferred embodiment the aluminum die-casting alloy further comprises 2 to 4% by weight manganese.

[0018] In a further preferred embodiment the aluminum

die-casting alloy comprises 0.2 to 0.8 % by weight tungsten.

[0019] In a further preferred embodiment the aluminum die-casting alloy comprises 0.2 to 0.8 % by weight molybdenum.

[0020] In a further preferred embodiment the aluminum die-casting alloy comprises 0.1 to 0.3 % by weight zirconium.

[0021] In a further preferred embodiment the aluminum die-casting alloy comprises 0.3 to 0.4 % by weight vanadium.

[0022] According to one embodiment the aluminum die-casting alloy includes substantially uniformly dispersed particles of $Al_3V_xZr_{1-x}$, where x is a fraction of unity that depends on the ratio of Zr : V in the alloy. The particles having an equivalent diameter of less than about 50 nm, preferably less than about 30 nm, more preferably less than about 10 nm, particularly less than about 5 nm.

[0023] In a further embodiment the aluminum die-casting alloy includes particles of Al_3Ni having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than about 100 nm.

[0024] In a further embodiment the aluminum die-casting alloy includes substantially uniformly dispersed particles of $Al_{12}Mn_{1-x}W_x$, where x is a fraction of unity that depends on the ratio of W : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. The $Al_{12}Mn_{1-x}W_x$ particles have a body centered cubic crystal structure. The $Al_{12}Mn_{1-x}W_x$ particles are semi-coherent with the α -aluminum matrix.

[0025] In a further embodiment the aluminum die-casting alloy includes substantially uniformly dispersed particles of $Al_{12}Mn_{1-x}Mo_x$, where x is a fraction of unity that depends on the ratio of Mo : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. The $Al_{12}Mn_{1-x}Mo_x$ particles have a body centered cubic crystal structure. The $Al_{12}Mn_{1-x}Mo_x$ particles are semi-coherent with the α -aluminum matrix.

[0026] In a further embodiment the die casting alloy includes substantially uniformly dispersed particles of $Al_{12}Mn_{1-x-y}W_xMo_y$, where x and y are fractions of unity that depend on the ratio of W : Mo : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. The $Al_{12}Mn_{1-x-y}W_xMo_y$ particles have a body centered cubic crystal structure. The $Al_{12}Mn_{1-x-y}W_xMo_y$ particles are semi-coherent with the α -aluminum matrix.

[0027] In a further embodiment of the invention a high pressure die-cast component is made is made of the alloy according to the invention.

[0028] In a further embodiment of the invention the aluminum die-casting alloy is solidified in a metal water-cooled mold.

[0029] In a method according to the invention a cast component is made from an aluminum die-casting alloy

according to the invention, wherein the alloy is age-hardened by holding the solidified cast component at a temperature of 350°C to 450°C for 2 to 12 hours.

[0030] According to one embodiment the aluminum alloy comprises 5.5 to 6.0 % by weight nickel, 1.75 to 2.0 % by weight manganese, 0.1 to 0.3 % by weight of zirconium, 0.3 to 0.4 % by weight of vanadium and 0.3 to 0.4 % by weight tungsten.

[0031] According to a further embodiment the aluminum alloy comprises 5.75 to 6.00 % by weight nickel, 3.75 to 4.25 % by weight manganese, 0.3 to 0.4 % by weight of vanadium, 0.1 to 0.2 % by weight zirconium, 0.25 to 0.30 % by weight tungsten, 0.25 to 0.30 by weight molybdenum and Al as remainder.

EXAMPLE

[0032] The following example is intended to illustrate the present invention and it is by no means restrictive thereof.

[0033] Measured amounts of aluminum-nickel, aluminum-manganese, aluminum-zirconium, and aluminum-vanadium master alloys, together with pure tungsten powder were added to commercially pure aluminum in order to constitute an alloy of the present invention with the nominal chemical composition: Al-6Ni-4Mn-0.8W-0.4V-0.1Zr. This alloy was melted in an induction furnace at 850°C for sufficient time to allow dissolution of the master alloys and tungsten powder into the commercially pure aluminum, and homogenization of the resulting melt. The melt temperature was then lowered to 750°C, and the melt was degassed for 30 minutes with argon utilizing a rotating impeller degasser. After degassing, the melt was poured into a water-cooled copper mold to produce disk-shaped castings that were then machined into ASTM standard sub-size tensile test specimens. The tensile test specimens were aged in an electric box furnace at 450°C for 10 hours and then divided into four groups each group containing six identical specimens. The elevated temperature yield strength of each group of specimens was measured by means of an Instron Universal Testing machine. Prior to performing the measurements, the tensile specimens were soaked in an electric box furnace at the following test temperatures for 100 hours; and during the test, each tensile specimen was soaked in the furnace of the Instron Universal Testing machine at the test temperature for an additional 30 minutes in order to allow the specimen to equilibrate at the test temperature.

Group No.	Temperature (°C)
1	25
2	300
3	350
4	400

[0034] Figure 3 shows the change in the measured yield strength of the Al-6Ni-4Mn-0.8W-0.4V-0.1 Zr alloy of the present invention compared to that of 380-F and 356-T6 commercial aluminum-silicon alloys. Clearly, the alloy of the present invention outperforms both commercial alloys at all temperatures above 150°C.

DESCRIPTION OF THE DRAWINGS

[0035]

Figure 1 is a chart that shows the change in measured yield strength with temperature for the Al-6Ni-0.7W-0.4V-0.1Zr alloy of the present invention and the Al-6Ni-0.4V-0.1Zr alloy of the prior art: At all temperatures, the measured yield strength of the alloy of the present invention is higher than that of the alloy of the prior art.

Figure 2 is a chart that shows the change with soak time in measured yield strength for the binary Al-2Mn and ternary Al-2Mn-0.75W alloys. The samples were soaked at 450°C for the various times and their yield strength was measured at room temperature: While the measured yield strength of the binary Al-2Mn alloy decreases rapidly when the alloy is held at 450°C, the measured yield strength of the ternary Al-2Mn-0.75W alloy does not degrade with time up to 250 hours, beyond which time the experiment was terminated.

Figure 3 is a chart that shows the change with temperature in measured yield strength of some commercial alloys compared to that of the alloy of the present invention. The tensile test specimens were soaked at the test temperature for 100 hours and tested at the soak temperature. Chart legend: 380-F ≡ standard aluminum-silicon alloy with nominal chemical composition Al-8.5Si-3.5Cu in the as-cast condition, 356-T6 ≡ standard aluminum-silicon-magnesium alloy with nominal chemical composition Al-7Si-0.35Mg-0.2Cu heat-treated according to the T6 schedule, HPDC ≡ high-pressure die-casting, and PM ≡ permanent mold casting. The data source for the 380-F and 356-T alloys is Kaufman, J.G. and Rooy, E.L., Aluminum Alloy Castings: Properties, Processes, and Applications, AFS, Schaumburg, IL(2004).

Claims

1. An aluminum die-casting alloy comprising:

1 to 6 % by weight nickel,
1 to 5 % by weight manganese,
0.1 to 0.4 % by weight zirconium,
0.1 to 0.4 % by weight vanadium,
0.1 to 1 % by weight tungsten and/ or 0.1 to 1 % molybdenum,
optionally up to 2 % by weight iron,
optionally up to 1 % by weight titanium,
optionally up to 2 % by weight magnesium,
optionally up to 0.5 % by weight silicon,
optionally up to 0.5 % by weight copper,
optionally up to 0.5 % by weight zinc,
optionally total maximum 5 % by weight transition elements including strontium, scandium, lanthanum, yttrium, hafnium, niobium, tantalum, and/or chromium, and aluminum as the remainder with further elements present as impurities due to production such that the total maximum of impurity elements is 1 % by weight.

2. An aluminum die-casting alloy according to claim 1, comprising 4 to 6 % by weight nickel.
3. An aluminum die-casting alloy according to any one of the claims 1 to 2, comprising 2 to 4 % by weight manganese.
4. An aluminum die-casting alloy according to any one of the claims 1 to 3, comprising 0.2 to 0.8 % by weight tungsten.
5. An aluminum die-casting alloy to any one of the claims 1 to 4, comprising 0.2 to 0.8 % by weight molybdenum.
6. An aluminum die-casting alloy according to any one of the claims 1 to 5, comprising 0.1 to 0.3 % by weight zirconium.
7. An aluminum die-casting alloy according to any one of the claims 1 to 6, comprising 0.3 to 0.4 % by weight vanadium.
8. An aluminum die-casting alloy according to any one of claims 1 to 7, including substantially uniformly dispersed particles of $Al_3V_xZr_{1-x}$, where x is a fraction of unity that depends on the ratio of Zr : V in the alloy, the particles having an equivalent diameter of less than about 50 nm, preferably less than about 30 nm, more preferably less than about 10 nm, particularly less than about 5 nm.
9. An aluminum die-casting alloy according to any one of claims 1 to 7, including particles of Al_3Ni having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than about 100 nm.

10. An aluminum die casting alloy according to any one of claims 1 to 7, including sub-stancially uniformly dispersed particles of $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$, where x is a fraction of unity that depends on the ratio of W : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. 5
11. The alloy of claim 10 wherein the $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles have a body centered cubic crystal structure. 10
12. The alloy of claim 10 wherein the $\text{Al}_{12}\text{Mn}_{1-x}\text{W}_x$ particles are semi-coherent with the aluminum matrix.
13. An aluminum die casting alloy according to any one of claims 1 to 7, including substantially uniformly dispersed particles of $\text{Al}_{12}\text{Mn}_{1-x}\text{Mo}_x$, where x is a fraction of unity that depends on the ratio of Mo : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. 15 20
14. The alloy of claim 13 wherein the $\text{Al}_{12}\text{Mn}_{1-x}\text{Mo}_x$ particles have a body centered cubic crystal structure. 25
15. The alloy of claim 13 wherein the $\text{Al}_{12}\text{Mn}_{1-x}\text{Mo}_x$ particles are semi-coherent with the aluminum matrix.
16. An aluminum die casting alloy according to any one of claims 1 to 7, including substantially uniformly dispersed particles of $\text{Al}_{12}\text{Mn}_{1-x-y}\text{W}_x\text{Mo}_y$, where x and y are fractions of unity that depend on the ratio of W : Mo : Mn in the alloy, the particles having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than 100 nm. 30 35
17. The alloy of claim 16 wherein the $\text{Al}_{12}\text{Mn}_{1-x-y}\text{W}_x\text{Mo}_y$ particles have a body centered cubic crystal structure. 40
18. The alloy of claim 16 wherein the $\text{Al}_{12}\text{Mn}_{1-x-y}\text{W}_x\text{Mo}_y$ particles are semi-coherent with the -aluminum matrix. 45
19. A high pressure die-cast component made from an aluminum alloy according to any one of claims 1 to 18.
20. A cast component made from an aluminum alloy according to any one of claims 1 to 18 where in the alloy is solidified in a metal water-cooled mold. 50
21. A method of producing a cast component made from an aluminum alloy according to any one of claims 1 to 18, wherein the alloy is age-hardened by holding the solidified cast component at a temperature of 350°C to 450°C for 2 to 12 hours. 55

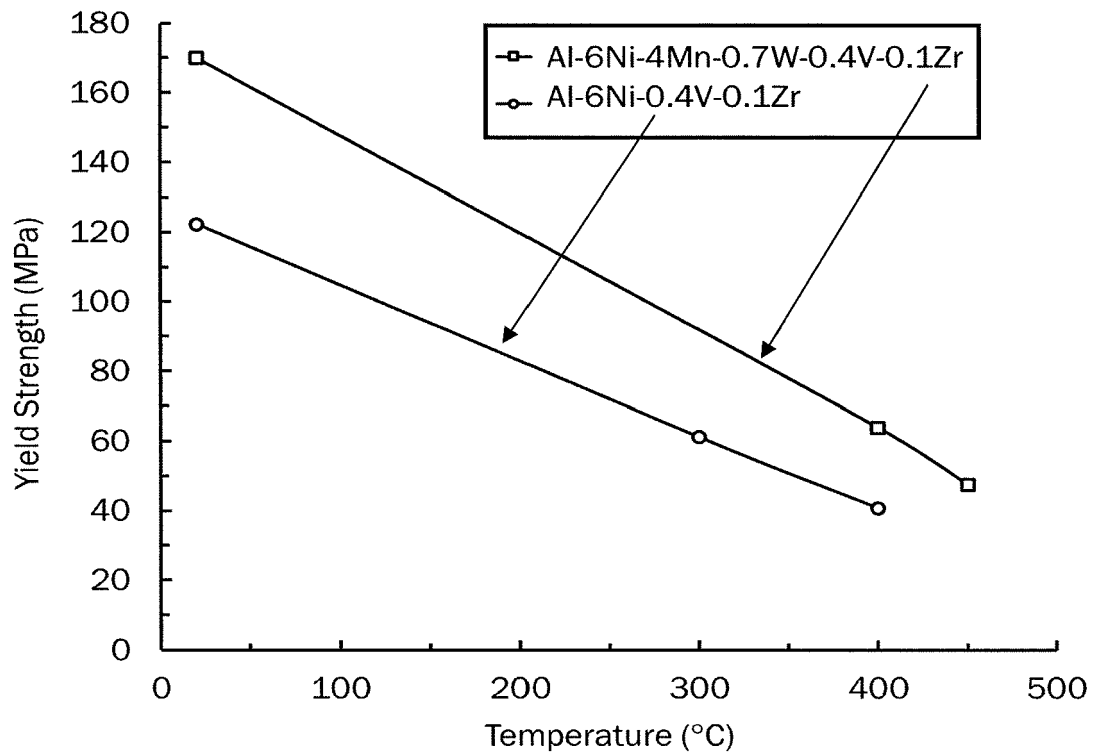
Fig. 1

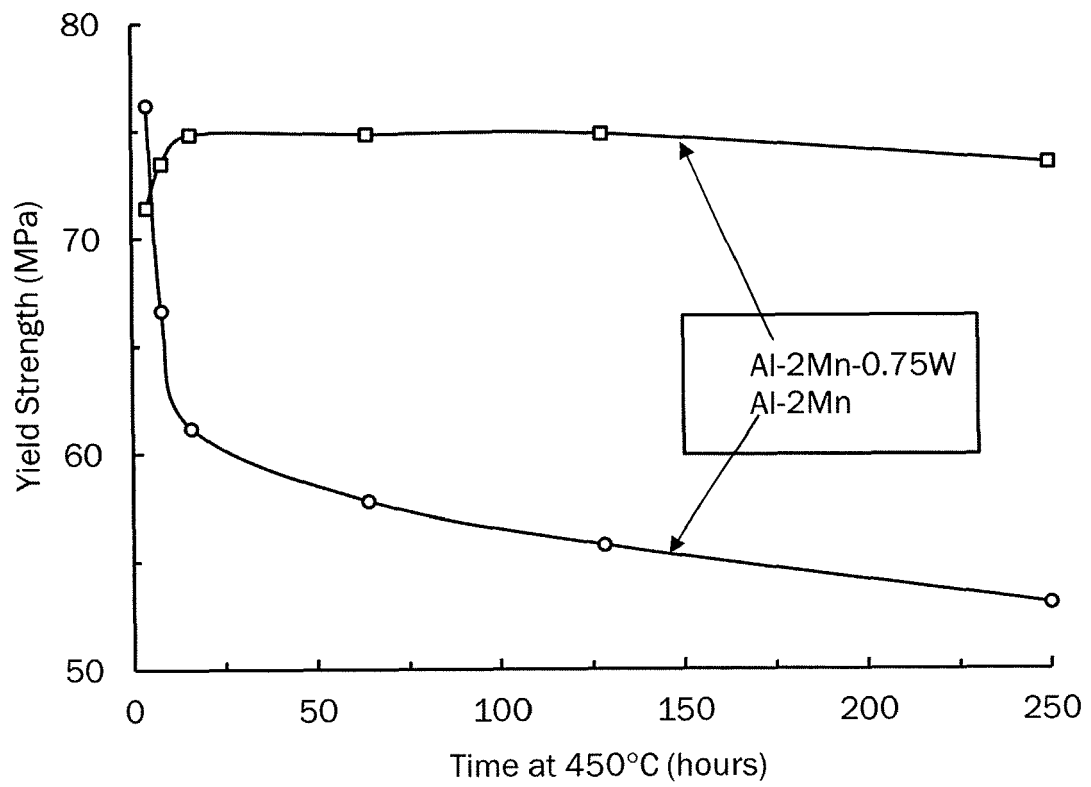
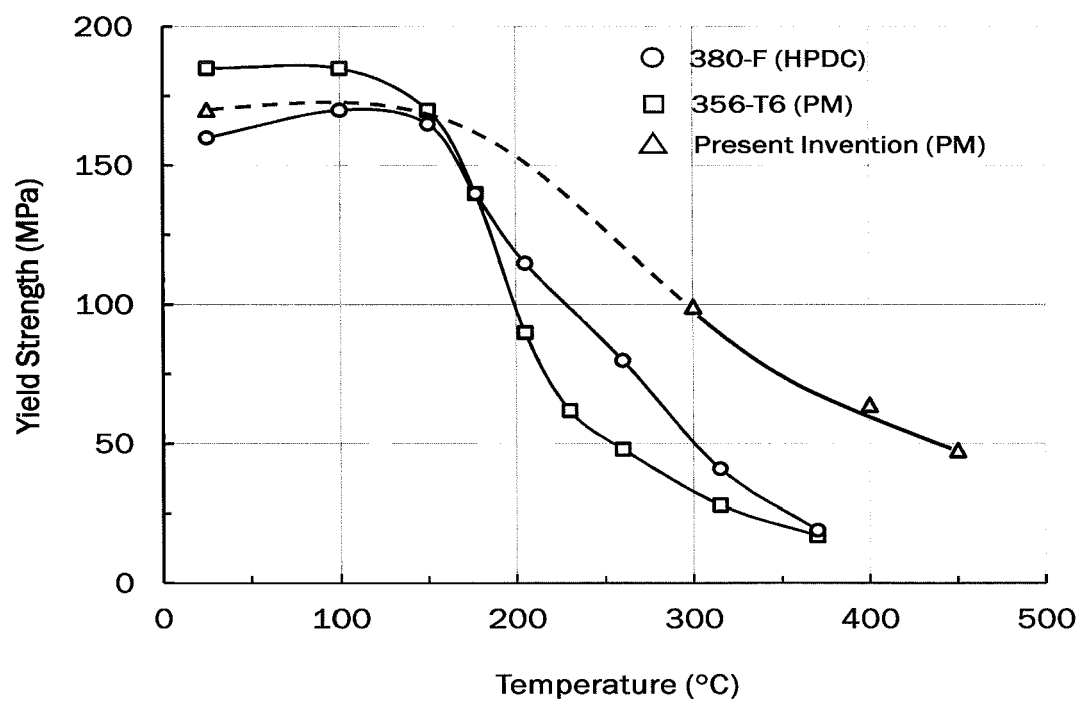
Fig. 2

Fig. 3



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Application Number
EP 14 16 8188

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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