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(54) HIGH STRENGTH THERMALLY RESISTANT DUCTILE CAST ALUMINUM ALLOYS

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(57) **ABSTRACT**

The invention relates to a high-strength, thermally-resistant, ductile, cast aluminium alloy (Al Si 7 Mg 0.25 Zr wa, or Al Si 7 Mg 0.25 Hf wa) and (Al Si 6 Mg 0.25 Zr wa or Al Si 6 Mg 0.25 Hf wa), comprising Si: 6.5 to 7.5 wt. % and 5.5 to 6.5 wt.-%, Mg: 0.20 to 0.32 wt. %, Zr: 0.03 to 0.50 wt. % and/or Hf: 0.03 to 1.50 wt. %, Ti: 0 to 0.20 wt. %, Fe: <0.20 wt. %, Mn: <0.50 wt. %, Cu: <0.05 wt. %, Zn: <0.07 wt. % and made up to 100 wt. % with Al. The invention relates to the use thereof for workpieces or parts thereof with elevated thermal loading, such as a cylinder head.

HIGH STRENGTH THERMALLY RESISTANT DUCTILE CAST ALUMINUM ALLOYS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a national stage of PCT/EP2004/004654 filed May 3, 2004 and based upon DE 103 23 741.0 filed May 24, 2003 under the International Convention.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to a high strength, thermally resistant, tough, ductile cast aluminum alloys containing Zr and/or Hf and their use in the fabrication of work pieces or parts thereof.

[0004] 2. Related Art of the Invention

[0005] In order to reduce emissions and fuel consumption and to increase the power output of engines, the combustion pressures and temperatures of internal combustion engines, especially for diesel engines, have increased over the past few years. These increases lead to more demanding requirements in terms of the thermo-mechanical load on the work pieces.

[0006] According to the state of the art cast aluminum (Al) alloys are known, particularly for the manufacturing of internal combustion engines. Cast Al parts from cast Al alloys are utilized widely because of their low specific weight, the simple shaping and the ease of manufacturing. In addition, it is possible through various casting processes to fabricate complicated work pieces or parts thereof such as pistons for internal combustion engines, cylinder heads, crank cases or engine blocs. Such work pieces and particularly certain regions of these work pieces are exposed to high thermo-mechanical loads during operating conditions.

[0007] The known high strength and tough cast Al alloy Al Si 7 Mg 0.3 T6, for instance, reaches its performance limits under these operational conditions. Because of its Cu content the known cylinder head alloy GK-Al Si 7 Mg 0.3 Cu 0.5 T6 is brittle and susceptible to notch effects. Also of disadvantage is that during tests such cylinder head alloys have proven to be susceptible to fissuring in the combustion chamber plate (inter cylinder spacing, valve seat, valve channels, glow plug bores) and in the water channels. In addition such Cu containing cast Al alloys form corrosion slurries as a result of their reaction with the cooling fluid used in the cylinder head. In each of the above mentioned cast Al alloys strength enhancing Mg_2Si and Al_2Cu precipitations are formed with a heat treatment, but they are not stable above a temperature of 150° C. and thus are no match for the thermo-mechanical loads of modern engines. Losses in strength of at least 30% occur under long term thermal load above 150° C. In addition the precipitation of further Mg_2Si and Al_2Cu phases comes along with an irreversible thermal expansion of the thermally highly stressed regions of the part which reduces the thermal cycling durability of the alloy in operation.

SUMMARY OF THE INVENTION

[0008] The objective of the invention is to create a high strength, thermally resistant and at the same time tough cast Al alloy which at temperatures equal to or above 150° C. retains its strength values, and which features a lower thermal expansion through a reduction of phase formation and thus enhanced thermo-mechanical stability at temperatures up to 240° C.

[0009] For cast Al alloys, usually a grain refining is done with titanium (Ti) which forms Al_3Ti-nuclei within the melt. Since as a consequence of the higher thermal loads the cast structure of today's alloys for work pieces, in particular in cylinder heads, is susceptible to creeping, the grain boundaries of the structure need to be stabilized with high temperature resistant precipitations.

[0010] Besides Ti those chemical elements come into consideration which on the one hand promote the growth of a fine grain and on the other hand thermally stabilize the fine structure up to temperatures of 250-300° C. through a high temperature stabile grain boundary precipitation and/or solid solution hardening. It must be pointed out that the fine structure at temperatures above 250° C. is stabilized through high temperature stable grain boundary precipitations and/or or solid solution hardening. This improves the resistance against creeping and prevents grain boundary sliding and grain growth. Additionally, the desired increased high temperature strength is achieved through solid solution and precipitation hardening without embrittling the alloy. For a high ultimate strain and heat resistance a high content of solid solution hardening is advantageous.

[0011] In order to fulfill the desired requirements according to the invention intermetallic high temperature phases need to be identified which particularly during casting do not form an acicular structure which embrittles the material.

[0012] Starting with the high strength, tough cast Al alloy Al Si 7 Mg T6 this alloy is, according to the invention, modified through the elements Zr and/or Hf. In a surprising manner Zr and/or Hf fulfill the above mentioned requirements respectively, resulting in connection with Al in temperature stable intermetallic Al_3Zr and Al_3Hf as well as in Zr and Hf containing aluminum silicides like Al_x Zr_y Si_z, Al_xHf_y Si_z respectively in Alx $(Zr, Hf)_y$ Si_z high temperature phases with a melting point of 1582° C. (for Al_3Zr) and 1590° C. (for Al_3Hf). Because of their higher temperature stability and very low solubility in Al, Zr and/or Hf, in form of Al_3Zr or, as the case may be, Al_3Hf containing Al pre-alloys, are highly efficient as a grain refining additive and critically determine the thermo-mechanical strength of the cast Al alloy according to the invention. In a later thermal treatment additional high temperature resistant Zr and/or Hf containing aluminum suicides are formed which thermally stabilize the structure or, as the case may be, result in a lower irreversible thermal expansion at 240° C. In order to avoid acicular or, as the case may be, brittle precipitations, Zr or Hf in form of fine Al_3Zr or Al_3Hf phases through Al pre-alloys with max. 10 wt % Zr and/or Hf needs to be brought into the Al melt in the form of powder or wire. For grain refining, the smallest amounts or, as the case may be, a minimum content of 0.03 wt % of Zr and/or Hf is necessary.

[0013] Compared to the known Ti grain refining, especially the Zr and/or Hf grain refining according to the invention are preferred since the Al_3Zr and/or Al_3Hf phases are more temperature stable than Al_3Ti, and in addition Zr or Hf feature a significantly lower solubility in Al.

[0014] With GK-Al Si 7 Mg T6 cylinder heads the effect of grain refining has been demonstrated. Using conventional Ti containing grain refining additives like Al Ti 10, Al Ti 5 or Al Ti 3 B 1, a structure with an Al dendrite arm spacing of 20 to 70 μm in the combustion chamber plate has been achieved. Through a Zr or Hf additive of 0.10 to 0.20 wt % in the form of Al_3Zr or Al_3Hf containing Al pre-alloys like Al Zr 5, Al Zr 10, Al Hf 5 or Al Hf 10 in GK-Al Si 7 Mg the Al dendrite arm spacing could be economically reduced to 10 to 50 μm. An additional Ti grain refining leads to a similar small dendrite arm spacing. During the alloying with Zr or Hf above 690° C. according to the invention only a fraction of the Al_3Zr or, as the case may be, Al_3Hf phases are dissolved from the Zr or, as the case may be, Hf containing Al pre-alloys such that sufficient Al_3Zr or, as the case may be, Al_3Hf nuclei are left for an Al grain refining. Depending on the setting rate during the pressure or gravity die casting the already dissolved Zr and Hf in contrast remains dissolved in the aluminum. During a later heat treatment consisting of solution annealing between 470° C. and 560° C., water quenching and age hardening above 160° C., according to the invention, besides the composition of the alloy, also the ratio of solid solution hardening to precipitation hardening is established. Long solution annealing at high temperatures with subsequent water quenching results in a high content of solid solution hardening, whereas long solution annealing at temperatures between 200° C. and 250° C. results in a high precipitation hardening under formation of Zr or Hf containing aluminum silicides like Al_x Zr_y Si_z, Al_xHf_y Si_z respectively Alx (Zr, $Hf)_y$ Si_z and reduction of the solid solution hardening. During solution annealing between 470° C. and 560° C. not more than 0.15 wt % Zr or, as the case may be, 1.00 wt % Hf can be dissolved. Thus, with respect to an increase in strength without embrittling the alloy, Hf is preferred compared to Zr. At engine temperatures (operation temperatures) between 150° C. and 250° C. the solid solution hardening remains mostly preserved. In contrast, under thermal load the precipitation hardening decreases through Al_3Zr and/or Al_3Hf. However the reduction in material strength is only small respectively smaller compared to the Mg_2Si precipitation hardening because of the high temperature stability of Al_3Zr or Al_3Hf from un-dissolved Al grain refining additives and from later on formed Zr and Hf containing aluminum silicides like Al_x Zr_y Si_z, Al_xHf_y Si_z or, as the case may be, Alx (Zr, $Hf)_y$ Si_z. With additional Ti grain refining, besides Al_3Zr/Al_3Hf dispersoids Al_3 (Zr, Ti) or Al_3 (Hf, Ti), mixed dispersoids or, in reaction with the silicon, Zr, Hf or Ti containing aluminum silicides like Al_x Zr_y Si_z, Al_xHf_y Si_z or, as the case may be, Alx (Zr, $Hf)_y$ Si_z are formed. These precipitations are very temperature stable so that according to the invention they result in a lower irreversible thermal expansion in Zr respectively Hf containing Al Si 7 Mg T6. For instance after 100 h at 240° C. the irreversible thermal expansion of T7-heat treated cylinder heads made of Zr/Hf-free GK-Al Si 7 Mg is between 0.05 and 0.06%. Addition of only 0.10 wt % Zr reduces the irreversible thermal expansion to approximately 0.04% and with a Zr addition of 0.20 wt % even lower to about 0.025%. According to the invention the irreversible thermal expansion of T7-heat treated cylinder heads made from GK-Al Si 6 Mg 0.26 Zr/Hf could be reduced an additional 10% through a reduced Si content of 4.5 to 6.5 wt %, which is outside the range of Al Si 7 Mg (Al Si 7 Mg: 6.5 to 7.5 wt % Si). Furthermore the ultimate strain of the cylinder head was improved about 1% in comparison to Al Si 7 Mg, so that overall a higher temperature cycling durability is achieved. The Si content is preferably in a range between 5.5 and 7.5 wt %, particularly preferred between 6.5 and 7.5 wt %.

[0015] In order to guarantee the desired high toughness or, as the case may be, resistance against notch effect of the alloy according to the invention, the content of Fe and Mg in the Al Si 7 Mg alloy needs to be restricted according to the invention. According to the invention the following chemical composition is proposed.

[0016] Chemical composition of the cast Al alloy according to the invention (short: Al Si 7 Mg 0.25 Zr T6 or Al Si 7 Mg 0.25 Hf T6 or Al Si 6 Mg 0.25 Zr T6 or Al Si 6 Mg 0.25 Hf T6):

[0017] Si: 4.5 to 7.5 wt %, in particular 6.5 to 7.5 wt %

[0018] Mg: 0.20 to 0.32 wt %

[0019] Zr: 0.03 to 0.50 wt % and/or Hf: 0.03 to 1.50 wt %

[0020] Ti: 0 to 0.20 wt %

[0021] Fe: <0.20 wt %

[0022] Mn: <0.50 wt %

[0023] Cu: <0.05 wt %

[0024] Zn: <0.07 wt %

and in each case brought up to 100 wt % with Al.

[0025] As the case may be, residual contaminants (Nb, V, B, Ni, Co) from the fabrication process as known to those working in this art may be included.

[0026] Additionally Zr, Ti and Hf may also exist as a mixture (e.g. Zr "contaminated" with Hf) in the mentioned areas.

[0027] With GK-Al Si 7 Mg 0.25 Zr T6 cylinder heads it has been found that through an addition of Zr of 0.10 to 0.20 wt % the tensile strength as well as the yield point could be improved by at least 10% without embrittling the alloy. That means, the ultimate strain remains unchanged because of the Zr grain refining effect. The irreversible thermal expansion at 240° C. could be reduced by approximately 50%.

[0028] The high strength values according to the objective, concurrent with high toughness, are furthermore achievable via a fine cast structure. Thus, during casting, high setting rates are desirable. Also, at comparable cast thicknesses, the structure in gravity die casting and pressure die casting is finer compared to sand casting.

[0029] The invention also relates to the use of the above mentioned cast Al alloy for the fabrication of a work piece or a part thereof. Here "part thereof" means an inherent part of the work piece, such as a constituent, a casing, a coating or such.

[0030] Work pieces are particularly but not exclusively pieces such as pistons for internal combustion engines, cylinder heads, crank cases, or engine blocks.

[0031] For the fabrication of cast Al alloys as well as work pieces according to the invention, customary processes as they are known to the person working in this industry can be utilized unless defined otherwise herein.

1-5. (canceled)

6. A cast aluminum alloy comprising

Si: 5.5 to 7.5 wt %

Mg: 0.20 to 0.32 wt %

Zr: 0.03 to 0.50 wt % and

Hf: 0.03 to 1.50 wt %

Ti: 0 to 0.20 wt %

Fe: <0.20 wt %

Mn: <0.50 wt %

Cu: <0.05 wt %

Zn: <0.07 wt %

and Al to make 100 wt %, said alloy containing intermetallic Al_3Zr and/or Al_3Hf high temperature phases.

7. A cast aluminum alloy according to claim 6, wherein Zr and Hf exist in a mixture in the mentioned regions.

8. A cast aluminum alloy according to claim 6, wherein the alloy contains $Al_3(Zr, Ti)$ and/or $Al_3(Hf, Ti)$ phases.

9. An internal combustion engine including a component made of a cast aluminum alloy.

10. An internal combustion engine according to claim 9, wherein said component is selected from the group consisting of pistons, cylinder heads, crank cases and engine blocs, and parts thereof.

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