PCT/FR04/01759

A cast component with high hot-process mechanical strength and high creep strength in the 230-380°C temperature range, made of aluminum alloy containing, in wt %: Mg < 0.1, and preferably < 0.03; Si: 4.5-10; Cu: 2.0-5.0 and preferably 3.0-4.0; Ni: < 0.4 and preferably < 0.1; Ti: 0.05-0.25 and preferably 0.08-0.20; Zr: 0.05-0.25 and preferably 0.12-0.20; Fe: < 0.9 and preferably < 0.3; Zn < 0.3 and preferably < 0.1; optionally V: 0.02-0.30 preferably 0.04-0.20; Mn: 0.1-0.5 preferably 0.15-0.40; Hf, Nb, Ta, Cr, Mo and/or W: 0.03-0.30; other elements < 0.10 each and < 0.30 in total, the rest being aluminum. The alloy is used for the manufacture of internal combustion engine cylinder heads.
MOULDED AL-SI-CU ALUMINIUM ALLOY COMPONENT WITH HIGH HOT-PROCESS RESISTANCE

TECHNICAL DOMAIN

This invention relates to cast parts made from aluminium alloy subject to high thermal and mechanical stresses, particularly cylinder heads for internal combustion engines, and more particularly turbo-charged engines running on gasoline or diesel fuel.

STATE OF THE ART

Two families of aluminium alloys are usually used for the manufacture of engine cylinder heads:

1) Alloys containing from 5% to 9% of silicon, from 3% to 4% of copper and magnesium. These are usually secondary alloys, with iron contents of between 0.5% and 1%, and fairly high contents of impurities, particularly manganese, zinc, lead, tin or nickel. These alloys are usually used without heat treatment (temper F) or are simply stabilized (temper T5). They are used more particularly for the manufacture of cylinder heads for gasoline engines with fairly low thermal stresses. First melt alloys with an iron content of less than 0.3% are used for parts with greater stresses intended for diesel or turbo-diesel engines, heat treated to temper T6 (annealing to peak mechanical strength) or T7 (over-aged).

2) Primary alloys containing from 7% to 10% of silicon and magnesium treated to temper T6 or T7 for more highly stressed parts such as those intended for turbo-diesel engines.

These two major alloy families lead to different compromises between different usage properties: mechanical strength, ductility, resistance to creep and fatigue. This problem was described for example in the article by R. Chatmire and M. Garat: "Choice of aluminium casting alloys for highly stressed cylinder head", published in the SIA Review, March 1990. This article summarizes the properties of three different studied alloys as follows:

**AlSi5Cu3MgFe0.15** T7: high strength—high ductility

**AlSi5Cu3MgFe0.7** F: high strength—low ductility

**AlSi7Mg0.3Fe0.15** T6: low strength—extreme ductility

The first and third alloy-temper combinations may be used for highly stressed cylinder heads. However, work continued to search for an improved compromise between strength and ductility. Patent FR 2690927 issued by the applicant, filed in 1992, describes aluminium alloys resistant to creep containing from 4% to 23% of silicon, at least one of the elements magnesium (0.1%-1%), copper (0.3%-4.5%) and nickel (0.2%-3%), and from 0.1% to 2% of titanium, from 0.1% to 0.2% of zirconium, and from 0.2% to 0.4% of vanadium. Improved resistance to creep is observed at 300°C with no significant loss of elongation measured at 250°C.

**DESCRIPTION OF THE INVENTION**

This invention is based on the applicant’s observation that it is possible to obtain significantly better strength properties at high temperatures, and particularly between 230°C and 380°C, than is possible with existing alloys, with no loss of ductility, by associating structural...
hardening in an Al—Si type cast alloy based on the addition of 2% to 5% of copper with no magnesium, and the addition of 0.05% to 0.25% of zirconium.

[0035] The inventors believe that the good mechanical properties of heat treated parts at high temperatures are the result of a microstructure simultaneously comprising zirconium dispersion phases formed during the solution heat treatment and metastable 0-0° copper phases derived from the Al_xCu precipitation system. These phases are more stable at high temperatures than the β'β° binary phases based on Mg_xSi and AlCuMgSi 3Al quaternary phases that form during annealing in the presence of magnesium.

[0036] Due to the choice of the copper content, different compromises between mechanical properties at high temperatures and ductility are possible. It is thus possible to obtain a good ductility with alloys according to the invention that is just as good with very ductile alloys such as A-S7G, by limiting the copper content to the lower part of the 2% -5% interval.

[0037] As in most alloys intended for the manufacture of cylinder heads for engines, iron is kept to below 0.9%, which means that primary or secondary alloys may be used; this limit may be lowered to below 0.3% (primary alloys) and preferably below 0.2% when a high elongation at rupture is required.

[0038] The alloy must contain zirconium with a content of between 0.05% and 0.25%, and preferably between 0.12% and 0.20%, to obtain an optimum dispersoid content after heat treatment.

[0039] The titanium content is kept at between 0.03% and 0.25%, which is fairly normal for this type of alloy. Titanium contributes to refining of the primary grain during solidification, but in the case of alloys according to the invention it works in liaison with zirconium and also leads to the formation of very fine AlSiZrTi dispersoids (<1 μm) during solution heat treatment of the cast part, located at the heart of the α-Al solid solution and that are stable above 300°C, unlike copper structural hardening phases for which coalescence becomes important at this temperature, although less than in magnesium phases.

[0040] The alloy may also include vanadium with a content of between 0.02 and 0.30%, and preferably between 0.04% and 0.20%, and other peritectic elements such as hafnium, niobium, tantalum, chromium, molybdenum or tungsten, at contents of between 0.03% and 0.30%. Due to their solubility curve and their low coefficient of diffusion in aluminum, these elements also form dispersoid stables at high temperatures during the solution heat treatment.

[0041] At a content of more than 0.1%, manganese has a positive effect on the mechanical strength between 250°C and 380°C, but this effect does not increase further for contents higher than 0.5%.

[0042] Unlike alloys for cylinder heads in which the presence of magnesium is usually required or accepted, alloys for parts according to the invention have a solidus temperature and a burning temperature of more than 507°C. Consequently, they can be heat treated to a 16 or 17 temper with a solution heat treatment temperature of between 515°C and 525°C, depending on the copper content, without any special precautions, in other words without the need for a slow temperature rise or an intermediate constant temperature, while alloys of the same type with more than 0.2% of magnesium form a quaternary eutectic that does not vary with the risk of a burn at 507°C.

[0043] The possibility of a heat treatment at more than 515°C has several advantages: it is possible to obtain greater homogenisation of copper phases, with better globulisation of silicon phases and more complete precipitation of zirconium phases and other peritectic elements.

[0044] Finally, another advantage of this type of composition is its lower sensitivity to the quenching rate after solution heat treatment than Al—Si—Mg and Al—Si—Cu—Mg type alloys. Although they can be quenched with water using standard techniques, these alloys have greater possibilities of soft quenching (sprayed water, quenching in fluidised bed, quenching by blown air) with relative losses of mechanical properties much lower than for traditional alloys with magnesium.

[0045] Parts are made using usual casting methods, particularly permanent mold gravity casting and low pressure die casting for cylinder heads, and also sand casting, squeeze casting (particularly for insertion of composites) and lost foam casting.

[0046] These parts may also be used as inserts for hot parts of a traditional alloy part or for hot parts of dual casting parts made from two different alloys.

[0047] The heat treatment includes a solution heat treatment typically lasting from 1 h to 10 h at a temperature of between 515°C and 525°C, quenching preferably in cold water or soft quenching, and 0.5 h to 10 h annealing at a temperature of between 150°C and 250°C. The annealing temperature and duration are adjusted so as to obtain either annealing to the peak mechanical strength (T6) or over-ageing (T7) frequently used for engine cylinder heads.

[0048] Parts according to the invention, and particularly cylinder heads for automobile engines or aircraft engines, engine casings sumps, scrools and other aeronautical equipment subject to high temperatures, have excellent mechanical strength when hot, better creep strength than parts according to prior art in the temperature range 230°C-380°C and if there is a limitation in the copper content, they have an excellent ductility. On the other hand, mechanical performances at ambient or moderate temperature are slightly lower than equivalent performances for Al—Si—Cu—Mg alloys.

**EXAMPLE**

[0049] Ten alloys with the composition (% by weight) indicated in Table 1 were produced in a silicon carbide crucible in a 100 kg electric furnace. These compositions were measured by spark emission spectrometry, except for copper and zirconium that were measured by induced plasma emission spectrometry.

**TABLE 1**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Zr</th>
<th>V</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0.15</td>
<td>3.1</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.15</td>
<td>3.1</td>
<td>0.30</td>
<td>0.14</td>
<td>0.25</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.15</td>
<td></td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
</tbody>
</table>
AFNOR permanent mold tensile test pieces were cast for each alloy. These test pieces were subjected to a heat treatment including solution heat treatment under conditions defined in Table 2, quenching in cold water, maturing at ambient temperature for 24 h and annealing for 5 h at 160°C or 200°C.

These test pieces were used to machine tensile test pieces and creep test pieces so as to measure mechanical characteristics (resistance to failure Rm in MPa, yield strength Rpo,2 in MPa and elongation at rupture A in %) at ambient temperature, at 250°C and at 300°C. Table 2 indicates the results:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Rm</th>
<th>Rpo,2</th>
<th>A</th>
<th>Rm</th>
<th>Rpo,2</th>
<th>A</th>
<th>Rm</th>
<th>Rpo,2</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>358</td>
<td>311</td>
<td>2.5</td>
<td>111</td>
<td>92</td>
<td>16</td>
<td>62</td>
<td>47</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>299</td>
<td>257</td>
<td>9.9</td>
<td>61</td>
<td>55</td>
<td>35</td>
<td>43</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>294</td>
<td>255</td>
<td>9.7</td>
<td>62</td>
<td>56</td>
<td>35</td>
<td>43</td>
<td>41</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>327</td>
<td>275</td>
<td>9.8</td>
<td>73</td>
<td>66</td>
<td>35</td>
<td>44</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>324</td>
<td>270</td>
<td>9.8</td>
<td>68</td>
<td>63</td>
<td>35</td>
<td>45</td>
<td>42</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>367</td>
<td>287</td>
<td>1.9</td>
<td>126</td>
<td>103</td>
<td>16</td>
<td>72</td>
<td>63</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>313</td>
<td>165</td>
<td>12.3</td>
<td>100</td>
<td>80</td>
<td>33</td>
<td>64</td>
<td>54</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>281</td>
<td>140</td>
<td>13.3</td>
<td>94</td>
<td>75</td>
<td>37</td>
<td>60</td>
<td>51</td>
<td>44</td>
</tr>
</tbody>
</table>

Solutions heat treatment 10 h 495°C, cold water quenching, annealing 4 h

1, 2 210°C.

3, 4 Solution heat treatment 10 h 540°C, cold water quenching, 24 h wait, annealing 4 h 210°C.

Solution heat treatment 4 h 500°C + 40 h 540°C, cold water quenching, 24 h wait—annealing 4 h

5-6 210°C.

7, 8, 9 Solution heat treatment 10 h 515°C, cold water quenching, annealing 4 h 210°C.

7 bis Solution heat treatment 10 h 495°C, cold water quenching, annealing 4 h 210°C.

Unlike conventional alloys 1 and 2 with copper and magnesium for which the heat treatment can only be carried out at temperatures of the order of 495°C, due to risks of burning at 507°C, alloys 7, 8 and 9 according to the invention with copper without magnesium and containing zirconium were solution heat treated at 515°C.

For these alloys 7 to 9, the results show that yield strength and ultimate strength levels at failure at 250°C and 300°C are very much higher than the equivalent values for alloys 1 and 2 according to prior art. Thus, the yield strength of test pieces made of alloys 7 to 9 exceeds 50 MPa, while the yield strength of test pieces made of alloys 1 to 6 is very much lower than this level.

The same effects are demonstrated in creep test results at 250°C and 300°C, using the coefficient of \( g^{5.175} \) representing the stress (in MPa) leading to a 0.1% deformation after 100 h exposure to these temperatures. The results are given in Table 3.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( \sigma ) at 250°C</th>
<th>( \sigma ) at 300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>61</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>39</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>41</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>53</td>
<td>32</td>
</tr>
<tr>
<td>7 bis</td>
<td></td>
<td>29</td>
</tr>
</tbody>
</table>

The creep test on test piece 7 at 300°C gave a creep resistance of 32 MPa, significantly higher than the creep resistance measured on test pieces made of alloys 1 to 6 containing magnesium.

It is observed that for an identical heat treatment at 495°C, test piece 7 bis has a creep strength of 29 MPa, which is slightly higher than the creep strength of alloys 1 and 2 with magnesium containing or not containing zirconium. The heat treatment at 515°C on test piece 7 enables an additional increase of 3 MPa.

Finally, apart from excellent values of resistance at high temperatures, the results of test piece 8 indicate that with a copper content of the order of 3%, high elongation at rupture values are obtained with the same level and sometimes even better than values obtained with the most ductile magnesium alloys 3 to 6. For equal ductility, the yield strength above of test pieces according to the invention is about 20% higher at 250°C and 30% higher at 300°C.

1. Cast part with high creep resistance, made from an alloy consisting essentially of (% by weight):
   Mg<0.1
   Si: 4.5-10
   Cu: 2.0-5.0
   Ni<0.4
   Ti: 0.03-0.25
   Zr: 0.05-0.25
   Fe<0.9
   Zn<0.3
   Possibly V: 0.02-0.30
   Mn: 0.1-0.5
   Hf, Nb, Ta, Cr, Mo and/or W: 0.03-0.30
   other elements <0.10 each and <0.30 total, the remainder being aluminum.

2. Cast part according to claim 1, characterised in that the magnesium content is less than 0.03%.
3. Cast part according to claim 1, characterised in that the copper content is between 3% and 4%.
4. Cast part according to claim 1, characterised in that the nickel content is less than 0.1%.
5. Cast part according to claim 1, characterised in that the iron content is less than 0.3%.
6. Cast part according to claim 1, characterised in that the zinc content is less than 0.1%.
7. Cast part according to claim 1, characterised in that the zirconium content is between 0.12% and 0.20%.
8. Cast part according to claim 1, characterised in that the titanium content is between 0.08% and 0.20%.

9. Cast part according to claim 1, characterised in that the vanadium content is between 0.04% and 0.20%.
10. Cast part according to claim 1, characterised in that the manganese content is between 0.15% and 0.40%.
11. Cast part according to claim 1, characterised in that it is an insert for a hot part of a traditionally alloyed part.
12. Cast part according to claim 1, characterised in that it is a cylinder head for an internal combustion engine.