CASTING ALLOY OF THE AlMgSI TYPE

Field of the invention: The invention relates to non-ferrous metallurgy, particularly aluminium casting alloys and can be employed for high temperature application. Objective of the invention: the prior art use of the known components in combination with new ones. The alloy comprises the following elements, by weight percent (wt. %): 2.0 to 16.0 for magnesium, 2.0 to 9.0 for silicon, 0.05 to 1.5 for manganese, 0.01 to 0.6 for scandium, 0.05 to 0.5 for zirconium, at least one or more elements selected from the group comprising (wt. %): 0.05 to 0.5 for chromium, 0.1 to 2.0 for copper, 0.05 to 1.0 for nickel, 0.01 to 0.6 for hafnium as well as one or more elements selected from the group comprising (wt. %): 0.05 to 0.6 titanium, 0.005 to 0.05 for boron, 0.01 to 0.85 for yttrium, 0.001 to 0.2 for germanium, wherein 0.001% < (Ti + B + Y + Ge) < 1.5%, aluminium as the balance. Technical result: said casting alloy of the AlMgSi type having high strength and wear resistance at temperatures of more than 250°C in combination with high fluidity.
CASTING ALLOY OF THE AIMgSi TYPE

FIELD OF THE INVENTION
This invention relates to non-ferrous metallurgy, particularly aluminium casting alloys and can be employed to produce component parts for high temperature application.

BACKGROUND OF THE INVENTION
Presently, the industry sees a wide application of aluminium alloys based on the eutectic of the binary Al-Si system additionally alloyed with Mg, Cu, Zn, Fe, Ni, Mn, Ti and other elements. Improvements of prior art alloys include: improving their chemical and phase compositions, updating and inventing casting technologies, using of special additions for refining melts, modifying structure, etc. One of the worst drawbacks of the existing aluminium casting alloys is the decrease of melting temperature when increasing the number of alloying elements. It sets a limit on using them in the state-of-the-art high temperature internal combustion engines.

According to the concentration of silicon, complexly alloyed alloys based on the Al-Si system may be divided into 3 groups: hypoeutectic comprising <12 wt. % for silicon (356.0, 360.0, AK7, AK9), eutectic comprising 12-13 wt. % for silicon (AK12, AK12M2MrH, Mahle 124) and hypereutectic comprising 14-26 wt. % for silicon (390.0, Mahle 138, Mahle 244).

A large number of primary silicon crystals in said alloys leads to the lowering of ductility and technological properties thereof and make it necessary to employ expensive casting techniques.

For example, aluminium alloy (UA 22435A) containing, by weight percent (wt. %): 14.0-16.5 for silicon, 1.2-2.5 for copper, 0.8-1.5 for magnesium, 0.5-1.3 for manganese, 0.05-0.20 for titanium, 0.01-0.6 for nickel, 0.01-0.5 for zinc, 0.7-1.6 for iron, 0.01-0.2 for chromium, 0.01-0.4 for zirconium, 0.03-0.1 for phosphorus, and aluminium as the balance.

The disadvantages of said alloy are conventionally instable mechanical properties thereof, which is caused by primary silicon crystals and fusible ternary silicon containing eutectics as well as the environment polluted by the production of the alloy and the casting of ingots because of phosphorus present therein.

The hypoeutectic and eutectic alloys which are widely used in industry have good castability, are technologically simpler and easy treatable. However, temperature of using thereof does not exceed 200-230°C.
Another aluminium casting alloy (RU 2237096) containing, by weight percent (wt. %): 5.0-10.0 for silicon, 2.0-5.0 for copper, 0.3-0.7 for magnesium, 0.05-0.4 for titanium, 0.01-0.3 for zirconium, 0.2-0.4 for stibium, 0.05-0.6 for scandium, 0.1-0.3 wt. % for neodymium, 0.3-2.0 for calcium, and aluminium as the-balance.

The disadvantages of said alloy tend to be low high temperature strength and poor wear resistance.

There are some more methods of improving the mechanical properties of materials used in high-temperature environment. For example, reinforcing of eutectic alloys matrix by fibers or whiskers of $\text{Al}_2\text{O}_3$, SiC, C, etc. (so-called Metal Matrix Composites - MMCs) or using of the CMC-technique (Ceramic Matrix Composites). However, the use of said techniques is more expensive than casting. Therefore, they did not gain popularity in production.

There is another solution to these problems. It includes the use of the ternary eutectic Al-Mg-Si system instead of the binary Al-Si one. The Al-Mg-Si system comprises a quasi-binary eutectic used to create new aluminium casting alloys with improved properties. This eutectic is formed by the phase a-Al and the intermetallic phase $\text{Mg}_2\text{Si}$ which is higher-melting and thermodynamically more stable in contrast to silicon. This will ensure a higher melting temperature of the alloys developed and its conservation on a high level on the introduction of alloying elements and will lead to a damping of the diffusion-dependent processes on high temperatures of the operation.

For example, the ALMGSI casting alloy (US 6,623,570 B2) containing, by weight percent (wt. %) 3.0 to 7.0 for magnesium, 1.7 to 3.0 for silicon, 0.2 to 0.48 for manganese, 0.15 to 0.35 for iron, titanium as desired max. 0.2 %, 0.1 to 0.4 for nickel, aluminium as the-rest.

The disadvantages of said alloy tend to be low high temperature strength and poor wear resistance.

The AL/MG/SI cast aluminium alloy containing scandium (WO 2005/047554 Al) comprising at least 1.0-8.0 wt. % magnesium (Mg), >1.0-4.0 wt. % silicon (Si), 0.01-0.5 wt. % scandium (Sc), 0.005-0.2 wt. % titanium (Ti), 0-0.5 wt. % of an element or group of elements, selected from the group comprising zirconium (Zr), hafnium (Hf), molybdenum (Mo), terbium (Tb), niobium (Nb), gadolinium (Gd), erbium (Er) and vanadium (V), 0-0.88 wt. % manganese (Mn), 0-0.3 wt. % chromium (Cr), 0-1.0 wt. % copper (Cu), 0-0.1 wt. % zinc (Zn), 0-0.6 wt. % iron (Fe), 0-0.004 wt. % beryllium (B) and the remainder
aluminium with further impurities to an individual max. of 0.1 wt. % and total max. of 0.5 wt. %.

The low content of transition metals and copper in said alloy doesn't ensure strength and wear resistance at high temperature thereof, while alloying elements such as terbium, gadolinium, and erbium make it more expensive.

The technically most comparable to what is claimed is the aluminium casting alloy (UA 83776) containing, by weight percent (wt. %): 3.0-22.0 for magnesium, 2.8-10.0 for silicon, 0.05-1.0 for zirconium, 0.5-2.5 for copper, 0.05-1.0 for manganese, 0.05-1.5 for nickel, 0.05-1.5 for cobalt, 0.05-1.0 for titanium, 0.05-1.0 % for iron, 0.05-1.0 for boron, 0.05-0.5 for carbon, 0.05-1.0 for chromium, 0.05-0.3 % for molybdenum, 0.05-0.5 for tungsten, 0.01-0.6 for scandium, and aluminium as the balance.

The high content of alloying refractory elements in said alloy and the necessity of considerable overheating and holding the melt at temperatures of ~ 800 °C may increase evaporation of magnesium and scandium and lead to instable mechanical properties.

SUMMARY OF THE INVENTION

The general purpose of the present invention is to provide an improved aluminium casting alloy for high temperature application (at temperature > 250°C) and combines good mechanical and technological properties.

An object of the invention is to use a combination of known and new components that ensures high mechanical properties said alloy at temperatures of more than 250°C, more wear resistance and improving some casting properties thereof, e.g. fluidity.

A further object of the invention is to provide an improved composition of said aluminium casting alloy, modifying the qualitative and quantitative content of basic and alloying elements and adding germanium, hafnium and yttrium, which improves mechanical properties without deteriorating the casting ones.

The aforesaid object is accomplished by providing an aluminium casting alloy containing, by weight percent (wt. %):

- Magnesium (Mg) 4.0-16.0
- Silicon (Si) 2.0-9.0
- Manganese (Mn) 0.05-1.5
- Scandium (Sc) 0.01-0.6
- Zirconium (Zr) 0.05-0.5

at least one or more elements selected from the group comprising:
Chromium (Cr) 0.05-0.5
Copper (Cu) 0.1-2.0
Nickel (Ni) 0.05-1.0
Hafnium (Hf) 0.01-0.6

as well as one or more elements selected from the group comprising:

Titanium (Ti) 0.05-0.6
Boron (B) 0.005-0.05
Yttrium (Y) 0.01-0.85
Germanium (Ge) 0.001-0.2

wherein 0.001% < (Ti+B+Y+Ge) < 1.5%

Aluminium (Al) the balance.

The essential feature of said alloy is the presence, by weight percent (wt. %): of magnesium (4.0-16.0), silicon (2.0-9.0), manganese (0.05-1.5), scandium (0.01-0.6) and zirconium (0.05-0.5). Distinctive feature of the invention is the presence therein of at least one or more elements selected from the group comprising, by weight percent (wt. %): chromium (0.05-0.5), copper (0.1-2.0), nickel (0.05-1.0), hafnium (0.01-0.6) as well as one or more elements selected from the group comprising: titanium (0.05-0.6), boron (0.005-0.05 %), yttrium (0.01-0.85) and germanium (0.001-0.2) wherein 0.001% < (Ti + Br + Y + Ge) < 1.5%.

The reason for the percentages above mentioned is explained by the following factors.

A combination of magnesium and silicon used in aluminium alloy forms a eutectic structure, which provides high-temperature strength, good wear resistance and fluidity. The superior and inferior limits of the percentage are stipulated by the phase equilibria in the ternary Al-Mg-Si system. In combination with other components these elements determine the area of existence of composite binary eutectic alloys which contain Mg₂Si phase. Said alloy is features a well-differentiated structure provided by the phase Mg₂Si located in the metallic matrix a-Al in the form of fibers and plates. The above mentioned percentage of magnesium and silicon in said alloy provides the required properties. When the content of magnesium and silicon in an alloy is lower, respectively 4.0 % of its mass and 2.0 % of its mass, the volume part of the Mg₂Si in eutectic is not sufficient to provide the required mechanical, tribotechnical and casting properties. When the content of magnesium and silicon in an alloy is higher, respectively 16.0 % of its mass and 9.0 % of its mass, large
primary crystals Mg$_2$Si are formed and the amount of the eutectic is reduced, which causes the embrittlement of the alloy and deteriorates the castability thereof.

Manganese has a low diffusion rate in aluminium, hence a positive influence on the high temperature strength of alloys. Furthermore, manganese slows down the diffusion of copper in aluminium, which also improves properties of alloys. When the manganese content in an alloy is lower than 0.05 % of its mass, its effect on the high temperature strength and wear resistance of the alloy is insignificant, while its content of higher than 1.5 % of its mass causes coarse intermetallic compounds crumbling the alloy.

The simultaneous introduction of Sc and Zr in the above mentioned proportions leads to the formation of nanoparticles of the phase L1$_2$ and improves the strength of the alloy. Said particles are formed as a result of high temperature heat treatment. They are coherent with the eutectic alloy matrix, do not react with the eutectic colonies of the alloy and provide uniform structures of an ingot, which makes it possible to use the alloy at high temperatures.

Scandium also provides a better heat stability of the structure, improves the weldability thereof, and minimizes the tendency thereof toward the formation of shrinkage cracks. In order to provide necessary high temperature strength the scandium content must be at 0.01 to 0.6 wt. %. When the content is less than 0.01 wt. %, the amount of dispersoids of the strengthening phase is not enough and as a result thereof dispersion strengthening is not reached. When the scandium content is more than 0.6 wt. %, large primary crystals of the aluminide thereof is formed, which lowers the mechanical properties of the alloy.

Zirconium together with scandium forms nanoparticles of the phase Al$_3$(Sc$_i$Zr$_r$). Zirconium present in the alloy minimizes the tendency of the particles toward coagulation, which provides good thermal stability of structure and properties. When the zirconium content is less than 0.05 wt. %, its effect on the high temperature strength and wear resistance is insignificant. When the content is more than 1.0 wt. %, large crystals of the Al$_2$Zr intermetallic are formed, which lowers the alloy ductility.

The use of at least one or more elements of the group comprising chromium, copper, nickel, hafnium in the above mentioned proportions improves the strength of the alloy at temperatures of more than 250°C. When the chromium content is less than 0.05 wt. %, its effect on the mechanical properties of the alloy is insignificant, while the chromium content of more than 0.5 wt. % causes the formation of fusible multiphase eutectics on the edges boundary of grains, which lowers the high temperature strength of the alloy.
Copper and nickel increasing a degree of alloying of the aluminium solid solution and make it possible to achieve high-temperature strength of the alloy with moderate ductility preserved. The strengthening effect is achieved by the aluminium solid solution alloyed as well as by metastable and stable phases present in the structure, which are formed as a result of the partial decomposition of supersaturated solid solution caused by crystallization or high-temperature heating. These elements influence on mutual diffusive mobility of atoms and high temperature strength of the alloy. Concentrations of copper and nickel are changed in relation to the concentration and temperature limits of the two-phase eutectic equilibrium in the multicomponent system when additional elements are used.

When the copper content is less than 0.1 wt. %, its effect on the high temperature strength is insignificant. The copper content is necessary to limit 2.0 wt. %, as at its excess the multiphase fusible eutectics and additional phases are formed, which causes the embrittlement of the alloy and lowers the high temperature strength thereof.

When the nickel content is less than 0.05 wt. %, its effect on the high temperature strength of the alloy is insignificant, while the nickel content of more than 1.0 wt. % causes the formation of fusible multiphase eutectics, which lowers the high temperature strength of the alloy.

Hafnium decreases the misfit between the lattice of the aluminium matrix and the L12 particles, improving the thermal stability thereof. When the hafnium content is less than 0.01 wt. %, its effect on the high temperature strength and wear resistance of the alloy is insignificant. The hafnium content of more than 0.6 wt. % results in formation of large intermetallic crystals, which lowers the alloy ductility.

The addition of one or more elements selected from the group comprising, by weight percent (wt. %): titanium (0.05-0.6), boron (0.005-0.05), yttrium (0.01-0.85) and germanium (0.001-0.2) wherein 0.001% < (Ti+Br+Y+Ge) < 1.5%, modifies the structure, provides the increase of uniformity of distribution of strengthening phases and the optimum correlation of strength and plasticity caused by it. The elements lose their modifying effect if the lower concentration limit is reduced. Excess of the upper concentration limit can result in formation of coarse intermetallic crystals, which lowers alloy castability and ductility. Moreover, titanium along with boron improves wear resistance.

Test ingots were melted in the electric resistor furnace or the induction furnace in the AlB2O3 crucibles in air using protective fluxes (LiCl and LiF) in a ratio of correspondingly 3:1, or in protective environment (Ar). The ingots were made from pure
charge materials and master alloys produced in the induction or the resistor furnace or using other methods. The crucibles components must be charged so that intermetallic crystals are not formed. Before using each of the components the melt was stirred and held till the previous components were completely dissolved. The melting and pouring temperatures were respectively (700-750)°C and (680-720)°C. After the dissolution of the components the melt was well stirred, refined by inert gas or special agents, cleaned from the slag, and moulded.

To achieve dispersion strengthening by the L12 nanoparticles heat treatment of the ingots in the resistance furnace at (200-400)°C for (2-50) h was carried out. After performing this type of heat treatment test pieces were prepared to determine tensile and tribotechnical properties.

**BRIEF DESCRIPTION OF THE DRAWING**

Fig. 1 shows wear resistance of the casting alloy of the AlMgSi type as compared with commercially available alloys 356.0 and 390.0. Wear resistance was determined in the quasi-stationary (Iq) and the dynamic (Id) under-load operations at 180°C and 300°C.

**EXAMPLES**

**Example 1**

To demonstrate tensile strength at elevated temperatures the casting alloy of the AlMgSi type was melted, by weight percent (wt. %):

- Magnesium 5.5-7.5
- Silicon 2.0-3.5
- Manganese 0.1-0.8
- Scandium 0.15-0.3
- Zirconium 0.08-0.15
- Chromium 0.05-0.2
- Titanium 0.05-0.2
- Boron 0.01-0.04
- Yttrium 0.03-0.4
- Aluminium the balance.
Ingots of 200 g were made using electric resistor furnaces with the A1203 crucibles in air and using protective fluxes. Thereafter, the ingots were subjected to heat treatment at temperatures of (250-340) °C for 2-10 h.

Mechanical tensile properties were tested using INSTRON. The specimen was held at no-load for 0.5h (stabilization time) at test temperature and carried to failure by subsequent loading. The rate of loading amounted to 10⁻³ c⁻¹, the diameter of the effective part of the specimen was 3 mm, the length - 18 mm.

The alloy has the following properties at 300°C:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate strength (σ_b)</td>
<td>50-200</td>
</tr>
<tr>
<td>Yield strength (σ_0.2)</td>
<td>30-155</td>
</tr>
<tr>
<td>Elongation (δ)</td>
<td>3.0-6.0</td>
</tr>
</tbody>
</table>

Example 2, by weight percent (wt. %):

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>7.0-10.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.0-5.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.15-0.3</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Copper</td>
<td>0.3-0.7</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>Hafnium</td>
<td>0.01-0.6</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Boron</td>
<td>0.01-0.04</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.01-0.05</td>
</tr>
<tr>
<td>Aluminium</td>
<td>the balance.</td>
</tr>
</tbody>
</table>

The alloy that was made as in Example 1 has the following properties at a temperature of 400 °C:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate strength (σ_b)</td>
<td>110-120</td>
</tr>
<tr>
<td>Yield strength (σ_0.2)</td>
<td>105-111</td>
</tr>
<tr>
<td>Elongation (δ)</td>
<td>1.2-2.0</td>
</tr>
</tbody>
</table>

The properties described are superior to those of the alloys filed in Patents UA 83776 and US 6,399,020 Bl.
Example 3
To demonstrate wear resistance the casting alloy of the AlMgSi type was made as in Example 1, by weight percent (wt. %):

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>8.4-10.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.0-5.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.15-0.3</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Boron</td>
<td>0.01-0.04</td>
</tr>
<tr>
<td>Aluminium</td>
<td>balance</td>
</tr>
</tbody>
</table>

Tribotechnical tests were carried out in the sphere-area contact circuit using the original ATCD unit [N.A. Zenkin, K.E. Grinkevych. Control. Diagnostics 6 (2002) 49]. For these purposes special conditions were created under which the sphere penetrator reciprocated sliding on the flat specimen at definite temperatures. The tests were carried out in both the permanent quasi-stationary and the alternating dynamic (Id) under-load operations [K.E. Grinkevych. Friction and Wear, Vol.24, № 3 (2003) 344].

The dynamic modulated component of the normal pressure force $\Delta P$ was assigned in the form of an oscillation train that is added simultaneously to the static force $P_0$; the value of the dynamic load component amounts to 10% taken from the static one and is determined from the formula:

$$\Delta P = \frac{A}{2} \left( 1 - \sin \frac{2\pi t}{T} \right),$$

where $A$ - load amplitude, $T$ - period, $t$ - time.

The modulated load was applied so that the total load was $P' = P_0 - AP$. $\Delta P$ alternates from 0 to $A$.

Moreover, one half of the friction track is conventionally loaded by the quasi-stationary force, the other one by the dynamic impact. Wear resistance is valued by the depth of friction tracks in the area of the quasi-stationary and the dynamic impacts (Is, Id).

Test conditions are as follows: 180°C and 300°C, $P_0=22H$, $AP_{\text{Max}}=A=5H$, 25 Hz, 10 minutes, sphere penetrator R=8 mm with Si$_3$N$_4$, silicon lubricant. Outcomes of the trial are shown in Fig. 1.
Example 4
To demonstrate the fluidity the casting alloy of the AlMgSi type was prepared as in Example, by weight percent (wt. %):

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>7.0-10.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.0-5.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.15-0.3</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Boron</td>
<td>0.01-0.04</td>
</tr>
<tr>
<td>Aluminium</td>
<td>the balance</td>
</tr>
</tbody>
</table>

Fluidity was determined using of a complex U-shaped sample of Nekhendzi-Kuptsov. A portion of melted metal of 350 g was poured at temperatures of 40 °C above liquidus.

The alloy made as in Example 1 and the commercially available alloy 356.0 have the fluidity of respectively 385 mm and 283 mm.

The above Examples show that said casting alloy of the AlMgSi type has high strength and wear resistance at temperatures of more than 250 °C in combination with high fluidity, and tends to be a better alternative to the prior art aluminium casting alloys. Said alloy can be produced under both laboratory and manufacturing conditions.
CLAIMS

1. Casting alloy of the AlMgSi type containing, by weight percent (wt. %):
   - Magnesium 0 to 16.0
   - Silicon 0 to 9.0
   - Manganese 0.5 to 1.5
   - Scandium 0.1 to 0.6
   - Zirconium 0.5 to 0.5

   at least one or more elements selected from the group comprising:
   - Chromium 0 to 0.5
   - Copper 1 to 2.0
   - Nickel 0.5 to 1.0
   - Hafnium 0.1 to 0.6

   as well as one or more elements selected from the group comprising:
   - Titanium 0.5 to 0.6
   - Boron 0.5 to 0.05
   - Yttrium 0.1 to 0.85
   - Germanium 0.01 to 0.2

   wherein \(0.001\% < (\text{Ti} + \text{B} + \text{Y} + \text{Ge}) < 1.5\%\)

   Aluminium the balance.

2. Alloy according to Claim 1 comprising 5.0 - 13.0 wt. % for magnesium and 2.4 - 7.0 wt. % for silicon, mostly ranging from 6.0 to 12.0 wt. % for magnesium and from 2.2 to 6.0 wt. % for silicon.

3. Alloy according to Claims 1-2 comprising 0.08 - 1.2 wt. % for manganese, mostly ranging from 0.1 to 1.0 wt. %.

4. Alloy according to Claims 1-3 comprising 0.05 - 0.5 wt. % for scandium, mostly ranging from 0.1 to 0.4 wt. %.

5. Alloy according to Claims 1-4 comprising 0.06 - 0.3 wt. % for zirconium, mostly ranging from 0.08 to 0.2 % wt. %.

6. Alloy according to Claims 1-5 comprising at least one or more elements selected from the group comprising chromium, copper, nickel and hafnium.

7. Alloy according to Claims 1-6 comprising 0.05 - 0.2 wt. % for chromium.

8. Alloy according to Claims 1-6 comprising 0.3 - 1.0 wt. % for copper.

9. Alloy according to Claims 1-6 comprising 0.1 - 0.4 wt. % for nickel.
10. Alloy according to Claims 1-6 comprising 0.3 - 0.6 wt. % for hafnium.

11. Alloy according to Claims 1-10, wherein 0.001 wt. % ≤ (Ti + Br + Y + Ge) < 1.5 wt. %.

12. According to items 1-11, the means of the production of ingots of the casting alloy of the AlMgSi type includes the following stages:
   a) heating components of the casting alloy of the AlMgSi type, which is claimed at item 1, to the melt temperature at such a charging sequence of components of the charge that prevents the formation of coarse crystals of intermetallic phases;
   b) using fluxes or a protecting medium to prevent the oxidation of components;
   c) refining the melt from nonmetallic and gases;
   d) cooling the melt at a rate sufficient for the preservation of doping elements ensuring the formation of disperse particles of the strengthening L₁₂ phase in the solid solution by the subsequent thermal treatment.

13. Alloy according to Claims 1-12, in the cast state is mainly two-phase and contains the eutectic (cc-Al+Mg₂Si), primary crystals of Mg₂Si, and/or primary dendrites of a-Al.

14. Alloy according to Claims 1-13, preserves the two-phase eutectic (a-Al+Mg₂Si) structure that is formed by the coupled growth mechanism in a wide interval of crystallization rates.

15. Alloy according to Claims 1-14, whose two-phase eutectic consists of lamellar and/or fibers of Mg₂Si placed in the a-Al matrix.

16. The method of thermal treatment of ingots of the alloy according to Claims 1-15, at which the alloy is annealed in air at the temperatures of 200-400 °C for 2-50 hs mainly between 250-350 °C for 2-10 hs for the formation of disperse nanoparticles of a phase with the L₁₂ structure in the solid solution of a-Al which are coherent to its lattice.

17. Alloy according to Claims 1-16, whose solid solution a-Al contains strengthening particles of the phase which have the L₁₂ structure, are coherent to its lattice, and their chemical composition differs from those of phases forming the eutectic.

18. Alloy according to Claims 1-17, in which the strengthening particles do not interact with phases forming the eutectic in the process of long-term high-temperature annealing at the temperatures of 200-400 °C.
19. Alloy according to Claims 1-18, in which all the main mechanisms of strengthening such as the solid-solution, composite and dispersion ones are applied.

20. Application of the casting alloy of the AlMgSi type according to Claims 1-19 for the fabrication of thermally highly stressed cast parts undergoing a thermal treatment after casting.

21. Aluminium alloy according to Claims 1-20 applied for the fabrication of parts with enhanced wear resistance contains 8.4 - 13.0 wt. % Mg and 2.4 - 6.0 wt. % Si.

22. Application of the alloy according to Claims 1-21 in the fabrication of automotive engine parts.

23. Casting alloy of the AlMgSi type according to Claims 1-22 is characterized by a complex of high mechanical properties at temperatures more than 250 °C as well as high tribotechnical and casting properties and can be used in the fabrication of parts with variable cross-sections under both laboratory and industrial conditions.
AMENDED CLAIMS
received by the International Bureau on 20 June 2011 (20.06.2011)

1. Casting alloy of the AlMgSi type containing, by weight percent (wt. %):
   - Magnesium  4.0 to 16.0
   - Silicon  2.0 to 9.0
   - Manganese  0.05 to 1.5
   - Scandium  0.01 to 0.6
   - Zirconium  0.05 to 0.5

   at least one or more elements selected from the group comprising:
   - Chromium  0.05 to 0.5
   - Copper  0.1 to 2.0
   - Nickel  0.05 to 1.0
   - Hafnium  0.01 to 0.6

   as well as one or more elements selected from the group comprising:
   - Titanium  0.05 to 0.6
   - Boron  0.005 to 0.05
   - Yttrium  0.01 to 0.85
   - Germanium  0.001 to 0.2

   wherein 0.001% < (Ti + B + Y + Ge) < 1.5%

   Aluminium  the balance.

2. Alloy according to Claim 1 comprising 5.0 - 13.0 wt. % for magnesium and 2.1 - 7.0 wt. % for silicon, mostly ranging from 6.0 to 12.0 wt. % for magnesium and from 2.2 to 6.0 wt. % for silicon.

3. Alloy according to Claims 1-2 comprising 0.08 - 1.2 wt. % for manganese, mostly ranging from 0.1 to 1.0 wt. %.

4. Alloy according to Claims 1-3 comprising 0.05 - 0.5 wt. % for scandium, mostly ranging from 0.1 to 0.4 wt. %.

5. Alloy according to Claims 1-4 comprising 0.06 - 0.3 wt. % for zirconium, mostly ranging from 0.08 to 0.2 % wt. %.

6. Alloy according to Claims 1-5 comprising at least one or more elements selected from the group comprising chromium, copper, nickel and hafnium.

7. Alloy according to Claims 1-6 comprising 0.05 - 0.2 wt. % for chromium.

8. Alloy according to Claims 1-6 comprising 0.3 - 1.0 wt. % for copper.

9. Alloy according to Claims 1-6 comprising 0.1 - 0.4 wt. % for nickel.

10. Alloy according to Claims 1-6 comprising 0.3 - 0.6 wt. % for hafnium.

AMENDED SHEET (ARTICLE 19)
11. Alloy according to Claims 1-10, wherein 0.001 wt. % < (Ti + Br + Y + Ge) < 1.5 wt. %.

12. The means of the ingots production of the casting alloy according to items 1-11 includes the following stages:

   a) heating components of the casting alloy of the AlMgSi type, which is claimed at item 1, to the melt temperature at such a charging sequence of components of the charge that prevents the formation of coarse crystals of intermetallic phases;

   b) using fluxes or a protecting medium to prevent the oxidation of components;

   c) refining the melt from nonmetallic and gases;

   d) cooling the melt at a rate sufficient for the preservation of doping elements ensuring the formation of disperse particles of the strengthening L1₂ phase in the solid solution by the subsequent thermal treatment.

13. Alloy according to Claims 1-12, in the cast state is mainly two-phase and contains the eutectic (α-Al+Mg₂Si), primary crystals of Mg₂Si, and/or primary dendrites of α-Al.

14. Alloy according to Claims 1-13, preserves the two-phase eutectic (α-Al+Mg₂Si) structure that is formed by the coupled growth mechanism in a wide interval of crystallization rates.

15. Alloy according to Claims 1-14, whose two-phase eutectic consists of lamellar and/or fibers of Mg₂Si placed in the α-Al matrix.

16. The method of thermal treatment of ingots of the alloy according to Claims 1-15, at which the alloy is annealed in air at the temperatures of 200-400 °C for 2-50 h, mainly between 250-350 °C for 2-10 h for the formation of disperse nanoparticles of a phase with the L1₂ structure in the solid solution of α-Al which are coherent to its lattice.

17. Alloy according to Claims 1-16, whose solid solution α-Al contains strengthening particles of the phase which have the L1₂ structure, are coherent to its lattice, and their chemical composition differs from those of phases forming the eutectic.

18. Alloy according to Claims 1-17, in which the strengthening particles do not interact with phases forming the eutectic in the process of long-term high-temperature annealing at the temperatures of 200-400 °C.

19. Application of the casting alloy of the AlMgSi type according to Claims 1-11, 13-15 and 17-18 for the fabrication of thermally highly stressed cast parts undergoing...
a thermal treatment after casting like the ingots by the method according to Claim 16.

20. Aluminium alloy according to Claims 1-19 applied for the fabrication of parts with enhanced wear resistance contains 8.4 - 13.0 wt. % Mg and 2.4 - 6.0 wt. % Si.

21. Application of the alloy of the AlMgSi type according to Claims 1-20 which characterized by the excellent casting properties in aggregate with advanced mechanical and tribotechnical properties at the temperatures interval of 250 - 400 °C in the fabrication of parts with variable cross-sections (like automotive engine parts).
Fig. 1
## A. CLASSIFICATION OF SUBJECT MATTER

**INV.** C22C21/08  C22F1/05

According to International Patent Classification (IPC) or to both national classification and IPC

**ADD.**

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C  C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>A</td>
<td>WO 2005/047554 AI (EADS DEUTSCHLAND GMBH [DE]; RHEINFELDEN ALUMINIUM GMBH [DE]; KOCH HUBE) 26 May 2005 (2005-05-26) cited in the application claims 1,9, 10, 14, 16; table 1</td>
<td>2-23</td>
</tr>
<tr>
<td>A</td>
<td>JP 9 279280 A (FURUKAWA ELECTRIC CO LTD) 28 October 1997 (1997-10-28) * abstract; tables 2-10</td>
<td>2-23</td>
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<tr>
<td>A</td>
<td>WO 2006/122341 A2 (ALUMINIUM LEYND GMBH &amp; CO KG [AT]; TREND GUENTHER [AT]; KRALY ANDREAS) 23 November 2006 (2006-11-23) claims 1-8; table 1</td>
<td>2-23</td>
</tr>
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</table>

Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search: 15 October 2010

Date of mailing of the international search report: 21/10/2010

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
N.L.- 2280 HV Rijswijk
Tel.: (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Gonzalez Junquera, J
INTERNATIONAL SEARCH REPORT

Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
- [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- [ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- [ ] No protest accompanied the payment of additional search fees.
Continuation of Box 11.2

Claims Nos.: 1

See item III of the Written Opinion

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.
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<tr>
<td>WO 2005047554 A1</td>
<td>26-05-2005</td>
<td>AT 454480 T</td>
<td>15-01-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 10352932 A1</td>
<td>16-06-2005</td>
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<tr>
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<td></td>
<td>ES 2339356 T3</td>
<td>19-05-2010</td>
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<td></td>
<td>US 2007240796 A1</td>
<td>18-10-2007</td>
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<td></td>
<td>AU 2006246965 A1</td>
<td>23-11-2006</td>
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<td>BR PI0611421 A2</td>
<td>08-09-2010</td>
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<td>CA 2645677 A1</td>
<td>23-11-2006</td>
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<td></td>
<td></td>
<td>EP 1896621 A2</td>
<td>12-03-2008</td>
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<td>JP 2008540843 T</td>
<td>20-11-2008</td>
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<td>KR 20080017374 A</td>
<td>26-02-2008</td>
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<td>US 2009214381 A1</td>
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