(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 298 947 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
**28.01.2015 Bulletin 2015/05**

(21) Application number: **09793824.5**

(22) Date of filing: **02.07.2009**

(51) Int Cl.:
***C22C 21/12*** *(2006.01)* ***C22F 1/057*** *(2006.01)*

(86) International application number:
**PCT/CN2009/072603**

(87) International publication number:
**WO 2010/003349 (14.01.2010 Gazette 2010/02)**

# (54) HIGH STRENGTH CASTING ALUMINIUM ALLOY MATERIAL

HOCHFEST GEGOSSENES ALUMINIUMLEGIERUNGSMATERIAL

MATIÈRE D'ALLIAGE D'ALUMINIUM DE FONDERIE À HAUTE RÉSISTANCE

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

(30) Priority: **09.07.2008 CN 200810302668**
**09.07.2008 CN 200810302669**
**09.07.2008 CN 200810302670**
**09.07.2008 CN 200810302671**

(43) Date of publication of application:
**23.03.2011 Bulletin 2011/12**

(73) Proprietors:
- **Guizhou Aluminums Factory**
  **Guizhou 550014 (CN)**
- **Guizhou University**
  **Guizhou 550014 (CN)**
- **Guizhou Academy Of Sciences**
  **Guizhou 550001 (CN)**

(72) Inventors:
- **CHE, Yun**
  **Guiyang city**
  **Guizhou 550014 (CN)**
- **LU, Jinde**
  **Guiyang city**
  **Guizhou 550014 (CN)**
- **ZHANG, Zhongke**
  **Guiyang city**
  **Guizhou 550001 (CN)**
- **ZHANG, De'en**
  **Guiyang city**
  **Guizhou 550014 (CN)**
- **ZHANG, Xiaoyan**
  **Guiyang city**
  **Guizhou 550014 (CN)**
- **YAN, Guangpu**
  **Guiyang city**
  **Guizhou 550014 (CN)**

(74) Representative: **Kling, Simone**
**Lavoix Munich**
**Bayerstrasse 83**
**80335 München (DE)**

(56) References cited:
**WO-A1-2004/018721**
**CN-A- 86 107 139**
**CN-A- 101 191 167**
**CN-A- 101 319 287**
**CN-A- 101 363 092**
**CN-A- 101 363 093**
**CN-A- 101 363 094**
**CN-C- 100 410 406**
**GB-A- 681 906**
**JP-A- 54 028 216**

- **ZENG MING ET AL.: 'Disquisition of New Type High Strength Casting Aluminium Alloy' APPLICABLE TECHNOLOGY MARKET no. 5, 1997, page 3, XP009138888**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 298 947 B1

## Description

### Technical Field

**[0001]** The invention relates to an aluminum alloy material, in particular to a high strength casting aluminum alloy material.

### Background

**[0002]** The aluminum alloy as a younger metal material was not put into industrial use until early in the twentieth century. During the World War II, the aluminum material was mainly used to manufacture military aircraft. In the post-war years, the sharp drop in the demand for the aluminum material in the military industry led the aluminum industry to turn to the development of the aluminum alloy for civil use, so as to extend the applicable range thereof from aviation industry to various fields of national economy such as construction industry, container packaging industry, transportation industry, power industry, electronic industry, mechanical manufacturing industry, petrochemical industry and so on and apply the aluminum alloy to daily life. Nowadays, owing to high consumption and wide range, the aluminum material ranks second next to steel in metal materials. The aluminum alloy can be dated back to 1906 when Alfred Wilm Duralumin discovered the age hardening by chance in Berlin and then the Duralumin was developed and applied to the structural parts of aircraft. Various Al-Cu alloys were developed based on the Duralumin. Early in the twentieth century, aluminum alloy A-U5GT ((W)Si<0.05%, (W)Fe<0.10% and tensile strength (T4) $\geq$ 275MPa according to SAE J452-1989), which has been listed in France's national standards and aerospace standards, was developed and put into use and production; aluminum alloys 201.0 (1968) and 206.0 (1967) according to the Aluminum Association were based on the A-U5GT, and aluminum alloy 204.0 (1974) was equivalent to A-U5GT; aluminum alloy 201.0 (AlCu4AgMgMn) containing Ag (0.4% to 1.0%) and having high cost is commercially named KO-1 (with the tensile strength (T7) thereof being 415MPa and the coefficient of elongation thereof being 3% according to ASTM B26/B26(M)-1999) and protected by US patent; BAJI10 is equivalent to ZL204 for domestic use in the aspect of major element components but its trace elements is under secret and it is only used in the military field or other fields having high requirements.

**[0003]** ZL204A, ZL205A and other grades of casting aluminum alloy are developed in China, wherein the tensile strength of the ZL204A ($\delta_5$>4%) under the T5 state is 440Mpa, however, the ZL204A has the poorest fluidity and hot-cracking resistance among the Al-Cu based casting alloys; the tensile strengths of ZL205A under the T5 state and T6 state are 435MPa and 465MPa respectively according to the technical standard (GB 1173-86), and the tensile strength of ZL205A (T6) is 470MPa according to the standard (GB/F1173-1995), so the ZL205A is one of casting aluminum alloy materials having highest strength worldwide at present.

**[0004]** The plasticity of ZL205A (T5) is good, and the coefficient of elongation thereof reaches 7%, so ZL205A has been widely applied in the field of aerospace, however, ZL205A contains precious metal V as an element and is high in cost; meanwhile, ZL205A is based on refined aluminum or high-purity aluminum as a base metal, thus increasing the cost and limiting the material supply. Additionally, ZL209, which is made by adding RE to ZL205A, is still subject to the limitation of high cost due to the addition of the element V. The aluminum alloy developed by LV Jie, BIAM (Beijing Institute of Aeronautical Materials) is similar to ZL205A in the aspect of main components, however, the aluminum alloy contains 0.1% to 0.25% of V in the trace elements, has a tensile strength of 385MPa to 405MPa and the coefficient of elongation reaching 19% to 23%, and it is disclosed only in document study, the tensile strength of the aluminum alloy is lower, and the raw materials include high-cost element V.

**[0005]** In conclusion, the existing research on the field of high-strength casting aluminum alloy at home and aboard has the following problems: the strength of the aluminum alloy is not high enough, more particularly, few of casting aluminum alloys has the tensile strength higher than 450MPa; precious metals and rare elements (Ag, V and Be) are added in an amount higher than 1‰, and high-impurity aluminum is used as the base metals, thus increasing the cost, limiting the material source and making the aluminum alloy difficult to be popularized and put into civil use; the problem of the ratio between strength and plasticity is yet to be solved, and the contradiction between the strength and castability of the alloy is serious; and the fatigue life is short, and the resistance to stress corrosion is poor.

### Summary of the Present Invention

**[0006]** The invention intends to solve the technical problems that the existing high-strength casting aluminum alloy has the disadvantages of high formula cost, low strength, poor castability, short fatigue life and poor resistance to stress corrosion and to develop a high-strength, high-toughness and high-corrosion-resistance casting aluminum alloy material for both military and civil uses by optimizing the common formula and the processes of casting and purifying.

**[0007]** In order to solve the problems, the invention provides a high-strength casting aluminum alloy material consisting of the following components by weight percentage: 2.0% to 6.0% of Cu, 0.05% to 1.0% of Mn, 0.01% to 0.5% of Ti,

0.01% to 0.2% of Cr, 0.01% to 0.4% of Cd, 0.01% to 0.25% of Zr, 0.005% to 0.04% of B, 0.05% to 0.3% of rare earth element and the balancing amount of Al and trace impurities.

**[0008]** The rare earth element may be Pr, Ce, La or mixed rare earth elements RE.

**[0009]** The total content of various rare earth elements in the mixed rare earth elements RE is not lower than 98% (based on the total weight of the mixed rare earth elements RE).

**[0010]** The mixed rare earth elements RE may contain 40wt% to 50wt% of Ce (based on the total weight of the mixed rare earth elements RE).

**[0011]** The method for preparing the high-strength casting aluminum alloy material comprises the following steps:

(1) adding a proper amount of aluminum ingots or molten aluminum liquid to a melting furnace, heating until the aluminum ingots or molten aluminum liquid is melted down, and holding at 660 to 850 DEG C;
(2) adding the alloying elements of Cu and Mn by formula ratio and evenly stirring, and then adding trace elements Ti, Cr, Cd, Zr, B, rare earth element Pr, Ce, La or rare earth RE and evenly stirring;
(3) then, refining the alloy melt in the melting furnace, adding a refining agent (chlorine gas, hexachloroethane, manganese chloride and the like may be selected as the refining agent according to different working conditions) to the alloy melt and evenly stirring, wherein the melt should be refined in a closed environment as possible, in order to prevent the melt from water absorption and melting loss;
(4) pouring the alloy liquid out of the melting furnace, and carrying out the online treatment of filtering, degassing and deslagging;
(5) permanent mold casting; and
(6) finally, carrying out solid-solution precipitation strengthening thermal treatment at lower than 620 DEG C within 72 hours.

**[0012]** Compared with the prior art, the invention has the following advantages:

(1) Advanced designs of alloying and micro-alloying. By determining the reasonable design of micro-alloying elements (Ti, Cr, B, Zr, Pr, Ce, La and mixed rare earth elements) and composition range thereof based on the main components of Al-Cu-Mn, the invention can achieve the effect of substituting for precious metals, such as Ag and V and reduce the formula cost by 5% to 10%.
(2) Advanced techniques for melting and impurity removal. The invention can effectively break through the technical bottleneck in impurity removal and ensure that the tensile strength of the material is higher than 450MPa and the coefficient of elongation is higher than 5% at the same time.
(3) The invention can maintain the high strength of the material and obviously increase the plasticity thereof at the same time.

**[0013]** According to the novelty research concluded by the novelty research center of the Southwest Information Center, MOST (Ministry of Science and Technology), the development and industrialization of the novel high-strength casting aluminum alloy 1, in which the parameters of the element components can be achieved by using the project, are not disclosed in documents or reports at home and abroad. Therefore, the disputes and conflicts can be avoided in the intellectual property and research achievement of the project.

**[0014]** The characterization of the composition and performance parameters of the novel materials: the comparison of mechanical properties between some Al-Cu alloys and the high-strength casting aluminum alloy material based on national standards is listed in the following table.

*Comparison of mechanical properties between Al-Cu alloys and high-strength casting aluminum alloy material 1 based on national standards*

**[0015]**

| Alloy Grade | Alloy Code | Thermal Treatment Conditions | Tensile Strength $\sigma_b$/MPa | Elongation after Fracture $\delta_\xi$(%) |
|---|---|---|---|---|
| | | | ≥ | |
| ZAlCu5Mn | ZL201 | T5 | 335 | 4 |
| ZAlCu5MnA | ZL201A | T5 | 390 | 8 |

(continued)

| Alloy Grade | Alloy Code | Thermal Treatment Conditions | Tensile Strength $\sigma_b$/MPa | Elongation after Fracture $\delta_\xi$(%) |
|---|---|---|---|---|
| | | | ≥ | |
| ZAlCu10 | ZL202 | T6 | 163 | - |
| ZAlCu4 | ZL203 | T5 | 225 | 3 |
| ZAlCu5MnCdA | ZL204A | T5 | 440 | 4 |
| ZAlCu5MnCdVA | ZL205A | T5 | 440 | 7 |
| | | T6 | 470 | 3 |
| | | T7 | 460 | 2 |
| ZAlRE5Cu3Si2 | ZL207 | T1 | 175 | - |
| AlCu4AgMgMn | (US) 201.0 | T7 | 415 | 3 |
| AlCu4MgTi | (US) 206.0 | T4 | 275 | 8 |
| Unknown components except Al and Cu | (RUS) BAJI10 | T4-T7 | Maximum 500, minimum 320 | Worst 4 (corr. MIN$\sigma_b$), Optimum 12 (corr. MAX$\sigma_b$ ) |
| AlCuMnTiCrCdZrBRE | Novel high-toughness 1 | ≤ 620 DEG C ≤ 72h | 450 | 5 |

**Detailed Description**

**[0016]** Example: the high-strength casting aluminum alloy material comprises the following components by weight percentage: 2.0% to 6.0% of Cu, 0.05% to 1.0% of Mn, 0.01% to 0.5% of Ti, 0.01% to 0.2% of Cr, 0.01% to 0.4% of Cd, 0.01% to 0.25% of Zr, 0.005% to 0.04% of B, 0.05% to 0.3% of Pr, Ce, La or mixed rare earth elements RE and the balancing amount of Al and trace impurities.

**[0017]** The total content of various rare earth elements in the mixed rare earth elements RE is not lower than 98%, and the content of Ce in the mixed rare earth elements is 45% by weight percentage.

**[0018]** (Because the ionic radius and oxidation state of the rare earth elements are similar to those of other elements, the rare earth elements generally coexist with other elements in minerals.)

(1) adding a proper amount of aluminum ingots or molten aluminum liquid to a melting furnace, heating until the aluminum ingots or molten aluminum liquid is melted down, and holding at 660 to 850 DEG C.
(2) adding the alloying elements of Cu and Mn by formula ratio and evenly stirring, and then adding trace elements Ti, Cr, Cd, Zr, B, rare earth elements Pr, Ce, La or RE and evenly stirring.
(3) then, refining the alloy melt in the melting furnace, adding a refining agent (chlorine gas, hexachloroethane, manganese chloride and the like may be selected as the refining agent according to different working conditions) to the alloy melt and evenly stirring, wherein the melt should be refined in a closed environment as possible, in order to prevent the melt from water absorption and melting loss.
(4) pouring the alloy liquid out of the melting furnace, and carrying out the online treatment of filtering, degassing and deslagging.
(5) permanent mold casting.
(6) finally, carrying out solid-solution precipitation strengthening thermal treatment at lower than 620 DEG C within 72 hours.

**Claims**

1. A high-strength casting aluminum alloy material, consisting of the following components by weight percentage: 2.0% to 6.0% of Cu, 0.05% to 1.0% of Mn, 0.01% to 0.5% of Ti, 0.01% to 0.2% of Cr, 0.01% to 0.4% of Cd, 0.01% to 0.25% of Zr, 0.005% to 0.04% of B, 0.05% to 0.3% of rare earth element and the balancing amount of Al and trace

impurities.

2. The high-strength casting aluminum alloy material according to Claim 1, wherein the rare earth element is Pr, Ce, La or mixed rare earth elements RE.

3. The high-strength casting aluminum alloy material according to Claim 2, wherein the total content of various rare earth elements in the mixed rare earth elements RE is not lower than 98wt%.

4. The high-strength casting aluminum alloy material according to Claim 2 or Claim 3, wherein the content of Ce in the mixed rare earth elements RE is 40wt% to 50wt%.

**Patentansprüche**

1. Hochfestes Gussaluminiumlegierungsmaterial, das gewichtsprozentual aus den folgenden Komponenten besteht: 2,0 % bis 6,0 % Cu, 0,05 % bis 1,0 % Mn, 0,01 % bis 0,5 % Ti, 0,01 % bis 0,2 % Cr, 0,01 % bis 0,4 % Cd, 0,01 % bis 0,25 % Zr, 0,005 % bis 0,04 % B, 0,05 % bis 0,3 % Seltene-Erde-Element und die restliche Menge aus Al und Spurenverunreinigungen.

2. Hochfestes Gussaluminiumlegierungsmaterial nach Anspruch 1, wobei das Seltene-Erde-Elemente Pr, Ce, La oder gemischte Seltene-Erde-Elemente RE ist.

3. Hochfestes Gussaluminiumlegierungsmaterial nach Anspruch 2, wobei der Gesamtgehalt an diversen Seltene-Erde-Elementen in den gemischten Seltene-Erde-Elementen RE nicht weniger als 98 Gew.-% beträgt.

4. Hochfestes Gussaluminiumlegierungsmaterial nach Anspruch 2 oder 3, wobei der Ce-Gehalt in den gemischten Seltene-Erde-Elementen RE 40 Gew.-% bis 50 Gew.-% beträgt.

**Revendications**

1. Matière d'alliage d'aluminium de fonderie à haute résistance, constituée des composants suivants en pourcentage en poids : 2,0 % à 6,0 % de Cu, 0,05 % à 1,0 % de Mn, 0,01 % à 0,5 % de Ti, 0,01 % à 0,2 % de Cr, 0,01 % à 0,4 % de Cd, 0,01 % à 0,25 % de Zr, 0,005 % à 0,04 % de B, 0,05 % à 0,3 % de terre rare et la quantité restante étant constituée d'Al et d'impuretés en traces.

2. Matière d'alliage d'aluminium de fonderie à haute résistance selon la Revendication 1, dans laquelle la terre rare est Pr, Ce, La ou des terres rares mixtes RE.

3. Matière d'alliage d'aluminium de fonderie à haute résistance selon la Revendication 2, dans laquelle la teneur totale des diverses terres rares dans les terres rares mixtes RE n'est pas inférieure à 98 % en poids.

4. Matière d'alliage d'aluminium de fonderie à haute résistance selon la Revendication 2 ou la Revendication 3, dans laquelle la teneur du Ce dans les terres rares mixtes RE est de 40 % en poids à 50 % en poids.