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(54) ALUMINIUM CASTING ALLOY

ALUMINIUMGUSSLEGIERUNG

ALLIAGE DE FONDERIE D'ALUMINIUM

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(56) References cited:
EP-A1- 2 653 579 **EP-A1- 2 865 772**

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Description

FIELD OF THE INVENTION

[0001] The field of the invention is related to aluminium casting alloys. Specifically, the present invention relates to a hypoeutectic secondary aluminium-silicon alloy, useful to produce, by high pressure die casting, components which have to fulfill premium abrasion resistance requirements in as-cast condition at room temperature.

BACKGROUND ART

[0002] Aluminium casting alloys have not been traditionally well suited for abrasion applications in which, among others, high hardness properties must be present.

[0003] Regarding the automotive sector, in which most of the aluminium castings are consumed, some well-known parts that must fulfill abrasion requirements are, among others, piston cylinders, brake discs or steering boxes. Brake discs and piston cylinders must support not only abrasion but also thermal fatigue resistance, and if aluminium is employed instead of steel, hypereutectic alloys have been traditionally applied to produce automotive components by gravity die casting (GC). Hypereutectic alloys present primary silicon grains that are normally refined with phosphorous and T5 thermal treatments to resist abrasion. Nickel is the most important alloying element, with also Copper and dissoluted Zinc, to keep mechanical properties at high temperatures.

[0004] For room temperature applications (i.e. steering boxes) hypereutectic alloys are not so well suited. They do not fulfill the required hardness (above 80HB for EN-AC 43000 Aluminium alloys), Nickel is superfluous and Phosphorous is so volatile that requires skilled technicians to melt the alloy, which must be hold at temperatures above 750°C. Only high hardness and high strength are the objective properties, which opens the door to components produced by high pressure die casting (HPDC) with hypoeutectic aluminum.

[0005] HPDC process has been widely employed to new applications in the last twenty years, due to its low cost for big series, a high component reproducibility and reliability, and it is hence mostly preferred when compared with GC.

[0006] Unfortunately, typical hardness of EN-AC 43000 hypoeutectic alloys lie on values around 65-70 HB in the as cast state, what is still below the required 80 HB. Therefore, when producing steering boxes for example, a steel sleeve is placed in the internal surface of the box to accommodate the steering shaft. Both shaft and box are typically AlSi9Cu3 as cast components produced by HPDC, and even the addition of a new step (sleeve placement) is worth when compared with expensive GC production with hypereutectic alloy and a T5 thermal treatment.

[0007] Some other new alloys have been later developed to eliminate the thermal treatments, as those belonging to the AlZn families, which after 1 week of natural aging reach hardness values close to 120 HB. Unfortunately, the main disadvantage of these alloys is that quality requirements are only achievable by primary alloys. Alloys of primary quality with a Fe/Mn ratio of ½ has been disclosed in the prior art, decreasing die soldering and reducing as much as possible the negative effect of Al5FeSi intermetallics on the elongation values. Primary alloys mean mainly iron content below 0.15% by weight, copper content below 0.03% by weight and zinc content below 0.1% by weight, being those contents only achievable if aluminium is produced by electrolysis smelting from raw alumina. All refined aluminum alloys produced from scraps, drosses and swarfs coming from post-processing operations and end of life products is hence limited to low mechanical secondary alloy applications, what is a large limitation for industry sustainability and for the aluminum recycling sector.

[0008] Unfortunately, heat treatment, which is mainly useful for the AlSiMg and AlCuTi aluminium alloys families implies costs increase and a new heat treatment facility, in addition to the already existing holding furnace and injection machine. Thin walls distortion and stresses appearance is more than probable for complex castings hindering the manufacturing. Blistering can take place as well on casts surface if no adequate mold filling and vacuum technique is performed, what requires skilled technicians.

[0009] Some other alloys of the AlMg family have been later developed to eliminate the thermal treatments, but always with a common characteristic, i.e. keeping very low percentages of impurity elements as iron, copper and zinc among others, only achievable by primary alloys.

[0010] Document WO 2006/0066314 discloses an aluminum alloy containing Si, Cu, Mg, Mn, Fe, Zn, Ni, Pb, Sn and Ti. WO 2006/0066314 mentions the obtained mechanical properties of the alloys, but there is not any comment about the hardness of the alloys.

[0011] Document DE 19524564 discloses an aluminium-silicon alloy for casting cylinder heads. Minor variations in the composition of the alloys produce a change over the different proprieties of the alloys. By a minor addition of alloying elements or by varying the concentration of an alloying element, non-expected properties can be obtained. This document is silent about the obtained mechanical properties of the alloy and it doesn't mention the high pressure die casting (HPDC) process. This document discloses an alloy with a 5-11 wt % and 8-11 wt % of Si and 0.8-2 wt % of Cu.

[0012] Depending on the process employed to produce some part, the mechanical properties that can be achieved change completely, as shown in the DIN 1706 Standard, where mechanical properties change for sand, permanent mould casting, pressure die casting (HPDC) and investment casting.

[0013] Annex A of standard EN AC 43000 series discloses mechanical properties of pressure die cast alloys (Table A.1 - Mechanical properties of pressure die cast alloys).

[0014] Document EP 1978120A1 discloses an aluminium-silicon alloy for engine components. In this document there are no references to the HPDC process. This documents discloses very low elongation values of the obtained samples at room temperature in the as cast state (<0.7%). All the samples disclosed in this document have Si values with an eutectic or hypereutectic composition. This document also discloses an alloy with a 5-25% by weight of Si and 0.0007-0.1 % by weight of C.

[0015] Secondary aluminium alloys disclosed in the prior art have limited elongation properties due to the presence of detrimental β-iron Al5FeSi needles. The prior art discloses different ways of suppressing the formation of β-Al5FeSi phase: addition of sufficient manganese and, in alloys without manganese, high cooling rates. Another way to avoid this problem is based on the development of primary aluminium alloys with small percentages of iron, as the Aural™ alloys with iron approximately less than 0.22% and 0.03% by weight of copper. It has also been disclosed alloys with high elongation with less than 0.2% by weight of iron content and others. It has also been disclosed limiting the silicon content to a maximum of 0.15% in weight in order to obtain high elongation alloys.

[0016] Document US 5573606 discloses addition of Mg and limiting the iron content to less than 0.6% by weight.

[0017] Document EP 2771493A2 discloses an AlSiMgCu casting alloy. This document discloses 0.5-2% by weight of copper and discloses the use of thermal treatments. This document discloses that an increasing Cu content can increase the strength due to higher amount of θ '-Al2Cu and Q' precipitates, but reducing the ductility. This document aims to optimize the alloy composition, the solution and aging heat treatments to minimize/eliminate un-dissolved Q-phase (AlSiMgSi) and maximize solid solution/precipitation strengthening.

[0018] Document JPH093610 (A) proposes a die-casting alloy having 5 to 13 wt % Si, up to 0.5 wt % Mg, 0.1 to 1.0 wt % Mn, 0.1 to 2.0 wt % Fe. In this document, Cu and Zn contaminants are not taken into consideration, as these usually occur in significant amounts in the case of secondary aluminium. The document discloses that thermal treatments are necessary to improve ductility because eutectic Si becomes roundish by heat treatment.

[0019] Document EP2657360 discloses a die casting alloy consisting of 6-12% by weight of Si, at least 0.3% by weight of iron, 0.25% by weight of Mn, 0.1% by weight of Cu, 0.24 to 0.8% by weight of Mg and 0.4 to 1.5% by weight of Zn. This document discloses the use of eutectic modificators, as Sr, Na and Sb, alone or in combination, and grain refiners as Ti, Zr, V.

[0020] Document EP 1612286 discloses an aluminium die casting alloy having 8 to 11.5% by weight of Si, 0.3 to 0.8% by weight of Mn, 0.08 to 0.4% by weight of Mg, max. 0.4% by weight of Fe, max. 0.1% by weight of Cu, max. 0.1% by weight of Zn, max. 0.15% by weight of Ti and 0.05 to 0.5% by weight of Mo. Cu and Zn content have been limited and the content of secondary aluminium is very restricted, which leads the production of the alloy by electrolysis. The European patent application EP 2 653 579 A1 discloses an Al-Si casting alloy having enhanced tensile and yield strength whilst also having a high level of elongation. The disclosed alloy is intended for use in the manufacture of structural parts for the automotive industry.

[0021] The problem to be solved is the provision of a novel alloy of secondary quality produced for HPDC which can be used in as-cast condition and that presents the following values of elongation and mechanical properties: elongation (A) equal to or more than 2%, yield strength (Rp0.2) equal to or more than 160 MPa, ultimate tensile strength (Rm) equal to or more than 250 MPa and Brinell Hardness (HB) equal to or more than >80 HB. Said values of elongation and mechanical properties are required for components designed to support simultaneously high abrasion and high static bending/torsion loads, maintaining a minimal ductility and other processing properties as alloy fluidity, low die soldering, easy welding or high machinability, among others.

SUMMARY OF INVENTION

[0022] The present invention provides an aluminium casting alloy, wherein said alloy is consisting of:

11.5-12% by weight of silicon,
0.3-1% by weight of iron,
0.05-0.4% by weight of copper,
less than 0.75% by weight of manganese,
less than 0.35% by weight of zinc,
0.45-0.8% by weight of magnesium,
less than 0.3% by weight of titanium,
0.05-0.2% by weight of chrome,
less than 0.3% by weight of nickel,

less than 0.05% by weight of strontium,
less than 0.05% by weight of lead,
less than 0.05% by weight of tin,
and aluminium as the remainder.

[0023] In the invention, silicon content is restricted to the range 11.5-12% by weight to reduce as much as possible the eutectic fraction, what helps to maximize the elongation but maintaining the fluidity at minimal values that allow an adequate mold filling.

[0024] In the invention, copper content is restricted to 0.05-0.4% by weight to guarantee a minimum elastic yield and ultimate tensile strength, and alloying the use of secondary aluminum, and also to obtain the required hardness above 80 HB and high strength.

[0025] In the invention, iron content is restricted to the range 0.3-1% by weight to guarantee both low mold soldering and small volume fraction of Al_5FeSi intermetallics, which at the same time are minimized by the manganese content, implying an elongation above 2%.

[0026] In the invention, manganese content is restricted to less than 0.75% by weight to transform the Al_5FeSi intermetallics into alpha-$Al_{12}(Mn,Fe)Si_2$ and to reduce as much as possible the negative effect of those intermetallics, and to avoid the sludge problem that occurs with high percentages of Mn in combination with Fe and other alloying elements. Values of manganese above 0.75% by weight were not found to be useful in terms of Al_5FeSi intermetallics transformation.

[0027] In the invention, magnesium content is also a key element to maximize the hardness and mechanical properties, whose content must be coupled with the copper content, showing best performance when are set to 0.45-0.8% by weight of Mg and 0.05-0.4% by weight of Cu. Magnesium content helps to increase the yield strength, but always with a minimum percentage of copper and iron to avoid elongation to be affected. For small increases of magnesium percentages if enough silicon is available Mg_2Si intermetallics can be produced.

[0028] The desired properties are obtained due to the formation of a very fine eutectic phase, the semi-globular shape of the dendrites, the absence of fragile β-iron needles, and the presence of labyrinthine $Al_{11.7\text{-}16.5}(Fe,Mn,Cr)_{2.3\text{-}3.3}Si_2$ and Mg_2Si in the HPDC samples due to the combination of the different elements with the iron in the new developed alloy and the good distribution of Mg_2Si. There is also very few micro-porosity in studied HPDC, probably related with the near eutectic composition of obtained parts.

[0029] It can be observed in Figure 1 an example of the described micro-structures at x25 augmentations.

[0030] It can be observed in Figure 2 with x400 augmentation the absence of large β-iron needles and the presence of well distributed $Al_{11.7\text{-}16.5}(Fe,Mn,Cr)_{2.3\text{-}3.3}Si_2$ and Mg_2Si precipitates.

[0031] The alloy according to the invention differs from WO 2006/0066314 in that it contains 0.05-0.4% by weight of Cu, where in the nine alloys disclosed in WO 2006/0066314 Cu % by weight is above 3.1%. % by weight and Ni is less than 0.3% in the alloy according to the invention. The values of the Ni content in WO 2006/0066314 are over the values of the range of the present application.

[0032] The present application increases the alloy hardness in the as cast state to values higher than 80 HB, in order to obtain HPDC casted parts with high resistance to wearing and high strength. In the present alloy, the objective of defining an alloy into a determinate range of composition is in relation with the obtained hardness and mechanical properties, which clearly vary with small changes in the composition, as can be seen in the present application, which discloses changes in the properties with minor composition variations in test alloys 1 to 3.

[0033] The present solution solves the problem of obtaining secondary aluminium alloys with high hardness in the as cast state for the high pressure die casting manufacturing process.

[0034] Nickel is commonly used with copper to enhance elevated temperature properties. It also reduces the thermal expansion coefficient. Nickel is characterized by low solubility in (Al) (maximum ~0.01-0.03%) and do not form supersaturated solid solutions even after relatively rapid solidification. Their introduction into aluminum alloys always causes the formation of excessive phases (constituent particles) that often reduce formability and corrosion resistance.

[0035] For this reason, in many cases this element is undesirable as an alloying element. However, the refractory Alloying Elements and aluminides of nickel are very beneficial for improving the alloy thermal stability, so when this property is the most important, Ni can be used as alloying element. Using high-temperature heat treatments it is possible to spheroidize these eutectic particles (similar to silicon), in which case their negative influence upon formability and elongation is practically neutralized. In WO 2006/0066314 alloys, the high percentage of Ni can be related with the development of a new thermal treatment for the alloys.

[0036] The alloy according to the invention differs from the alloy of DE 19524564 in that it contains 11.5-12% by weight of silicon and 0.05-0.4% by weight of copper.

[0037] The content of the alloying elements in the alloy according to the invention is related to the obtained mechanical properties of the alloy. These mechanical properties clearly vary with small changes in the composition. This can be seen in the alloys of the example, which shows changes of the properties with minor composition variations.

[0038] The alloy according to the invention differs from EP 1978120A1 in that it contains 11.5-12% by weight of silicon and that it does not contain C.

[0039] The alloy according to the invention differs from EP 2771493A2 in that it contains 0.05-0.4% by weight of copper. The concentration of copper in the alloy according to the invention lead to an increase in the elongation, in comparison with the values mentioned in EP 2771493A2, which discloses that an increasing Cu content can increase the strength due to higher amount of θ'-Al2Cu and Q' precipitates but reducing ductility.

[0040] A thermal treatment of the alloy according to the invention is not necessary, due to the appearance of a very fine eutectic and a quite globular dendrite structure in the alloy. The reduced content of Cu and Zn in comparison with the alloy of document JPH093610 (A) avoids the use of secondary aluminum as disclosed in JPH093610 (A).

[0041] The alloy according to the invention differs from the alloy of document EP2657360 in that it contains less than 0.35% by weight of Zn. An increase in the Zn percentage leads to a lower corrosion resistance, and because of that, the Zn percentage has been limited in the alloy according to the invention, in order to obtain parts that don't need extra surface treatments. Also, the alloy according to the invention has high ductility.

[0042] The alloy according to the invention differs from document EP 1612286 in that it does not contain Mo.

BRIEF DESCRIPTION OF DRAWINGS

[0043]

Figure 1. HPDC alloy 3 microstructure at x25 augmentations.

1: Intermetallics
2: Semi-globular dendrites
3: Fine eutectic structure

Figure 2. HPDC alloy 2 microstructure at x400 augmentations.

4: Eutectic Silicon
5: Al
6: Mg_2Si
7: $Al_{11.7\text{-}16.5}(Fe,Mn,Cr)_{2.3\text{-}3.3}Si_2$

DESCRIPTION OF EMBODIMENTS

Example 1. Aluminium casting alloys (preparation, composition and mechanical properties)

[0044] Aluminium compositions have been prepared by melting a standard EN-AC 43000 alloy in a holding furnace at 690°C and later poured into the injection vessel, being injected into the mold cavity of a 950 tonnes closing force HPDC machine at 685°C. No vacuum conditions were applied.

[0045] A serial of 30 specimens were produced, for each composition. Casted specimens were cooled down in air. Specimens dimensions and later mechanical characterization were set and carried out following, respectively, UNE-EN ISO 6892-1 B:2010 standards.

[0046] Several compositions were tested, the content is specified in Table 1. Alloy 1 is a comparative example, not according to the invention. Alloys 2 and 3 are according to the invention. The obtained results are also specified in Table 1.

Table 1

	Alloy 1	Alloy 2	Alloy 3
Si (% by weight)	9.02	11.82	11.64
Fe (% by weight)	1.05	0.96	0.96
Cu (% by weight)	0.294	0.106	0.078
Mn (% by weight)	0.81	0.108	0.078
Mg (% by weight)	0.382	0.52	0.53
Zn (% by weight)	0.063	0.175	0.125
Ti (% by weight)	0.171	0.109	0.267

(continued)

	Alloy 1	Alloy 2	Alloy 3
Cr (% by weight)	0.066	0.141	0.162
Ni (% by weight)	0.207	0.109	0.075
Pb (% by weight)	0.21	0.11	0.083
Sn (% by weight)	0.02	0.046	0.033
Sr (% by weight)	0.048	0.023	0.01
Rp0.2 (MPa)	145	177	178.4
Rm (MPa)	236	260	263.5
A (%)	2	2.7	2.4
Hardness Brinell (HB)	76	81.0	86.8

[0047] Alloys 2 and 3 have Brinell hardness (HB) values equal or above 81 HB, yield strength (Rp0.2) values above 177 Mpa and ultimate tensile strength values (Rm) above 260 MPa and elongation values above 2.4%. Small variations of the alloy composition out of the claimed values give values out of the objectives. For comparison, Alloy 1 with a composition out the one of the invention and having Mn wt.% higher than 0.75 wt.% (0.81 wt.%) has Rp0.2, Rm and Hb smaller values that the minimum to be obtained in the presented invention.

[0048] Document EP2657360 (B1) discloses the use of eutectic modificators, as Sr, Na and Sb, alone or in combination, and grain refiners as Ti, Zr, V. The alloy according to the invention has less than 0.3% by weight of titanium and less than 0.05% by weight of strontium. The use of Sr in the alloys of the example don't shown a significant benefit over the elongation, with for example the modified Alloy 1 with much higher Sr content wt. % than Alloy 3 but with a smaller elongation value. In the case of Ti, the alloys of the example don't show a significant benefit over the elongation, with similar values. This can be explained as much as the grain refining and a modification of the structure can be obtained by a rapid cooling (up to 100°c/s) of the injected part and a multiplication pressure (up to 120 Mpa) applied over the metal in the solidification in the high pressure die casting process (HPDC).

Claims

1. Aluminium casting alloy, **characterized in that** said alloy is consisting of:

11.5-12% by weight of silicon,
0.3-1% by weight of iron,
0.05-0.4% by weight of copper,
less than 0.75% by weight of manganese,
less than 0.35% by weight of zinc,
0.45-0.8% by weight of magnesium,
less than 0.3% by weight of titanium,
0.05-0.2% by weight of chrome,
less than 0.3% by weight of nickel,
less than 0.05% by weight of strontium,
less than 0.05% by weight of lead,
less than 0.05% by weight of tin,
and aluminum as the remainder.

Patentansprüche

1. Aluminiumgusslegierung, **dadurch gekennzeichnet, dass** die genannte Legierung besteht aus:

11,5-12 Gew.-% Silizium,
0,3-1 Gew.-% Eisen,

0,05-0,4 Gew.-% Kupfer,
weniger als 0,75 Gew.-% Mangan,
weniger als 0,35 Gew.-% Zink,
0,45-0,8 Gew.-% Magnesium,
weniger als 0,3 Gew.-% Titan,
0,05-0,2 Gew.-% Chrom,
weniger als 0,3 Gew.-% Nickel,
weniger als 0,05 Gew.-% Strontium,
weniger als 0,05 Gew.-% Blei,
weniger als 0,05 Gew.-% Zinn
und Aluminium als Restbestandteil.

Revendications

1. Alliage de fonderie d'aluminium, **caractérisé en ce que** ledit alliage est constitué de :

   11,5-12 % en poids de silicium,
   0,3-1 % en poids de fer,
   0,05-0,4 % en poids de cuivre,
   moins de 0,75 % en poids de manganèse,
   moins de 0,35 % en poids de zinc,
   0,45-0,8 % en poids de magnésium,
   moins de 0,3 % en poids de titane,
   0,05-0.2 % en poids de chrome,
   moins de 0,3 % en poids de nickel,
   moins de 0,05 % en poids de strontium,
   moins de 0,05 % en poids de plomb,
   moins de 0,05 % en poids d'étain,
   et le reste en aluminium.

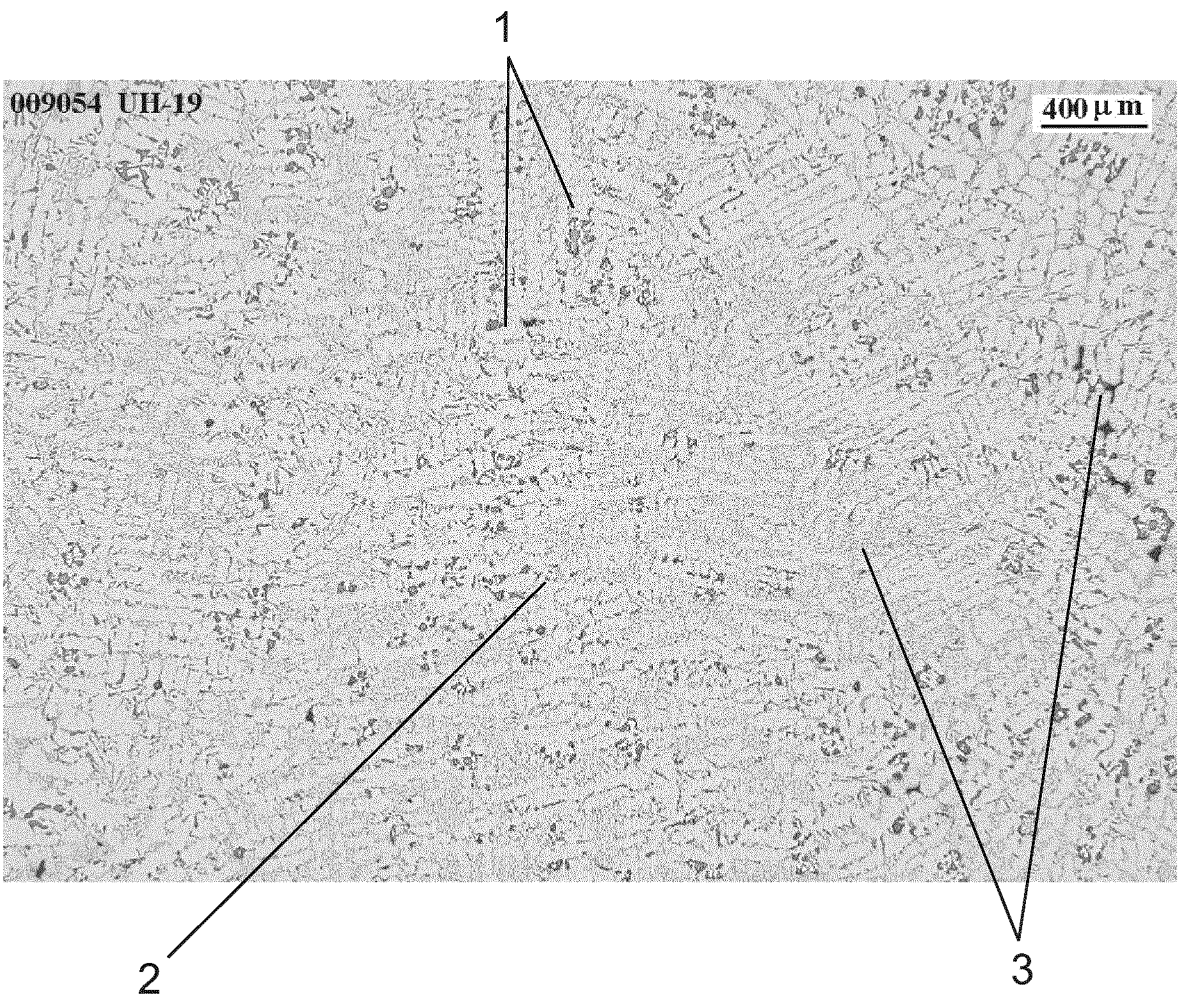

Fig. 1

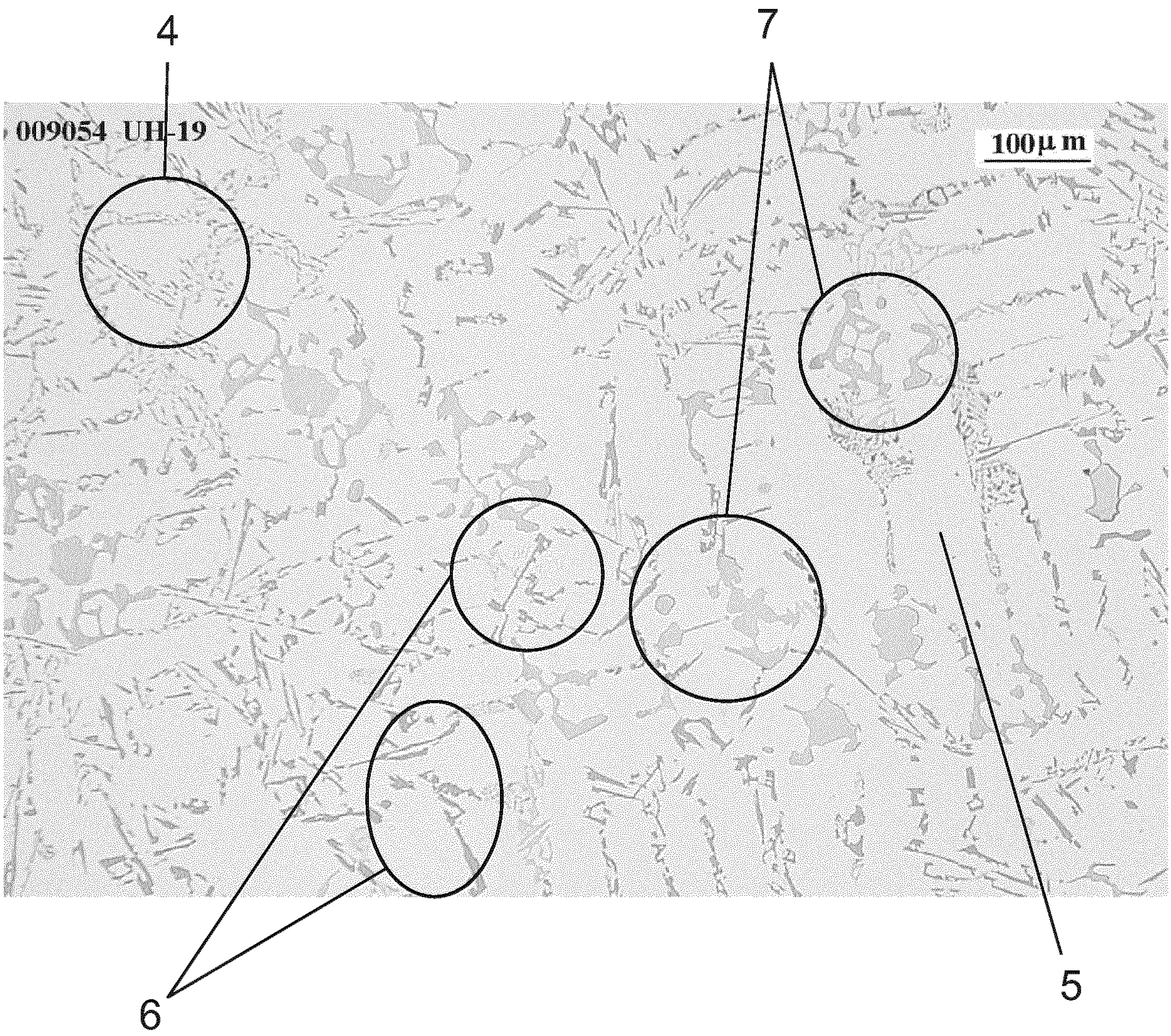

Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 20060066314 A **[0010] [0031] [0035]**
- DE 19524564 **[0011] [0036]**
- EP 1978120 A1 **[0014] [0038]**
- US 5573606 A **[0016]**
- EP 2771493 A2 **[0017] [0039]**
- JP H093610 A **[0018] [0040]**
- EP 2657360 A **[0019] [0041]**
- EP 1612286 A **[0020] [0042]**
- EP 2653579 A1 **[0020]**
- EP 2657360 B1 **[0048]**