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

(11) EP 4 215 634 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
26.07.2023 Bulletin 2023/30

(21) Application number: **21869849.6**

(22) Date of filing: **15.09.2021**

(51) International Patent Classification (IPC):
C22C 21/00 *(2006.01)*

(86) International application number:
PCT/RU2021/050295

(87) International publication number:
WO 2022/060253 (24.03.2022 Gazette 2022/12)

(84) Designated Contracting States:
AL 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 RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **16.09.2020 RU 2020130578**

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(54) ALUMINIUM CASTING ALLOY

(57) The invention refers to the field of metallurgy, in particular to aluminum-based alloys, and can be used to manufacture thin-walled complex-shaped castings by casting in a metal mold, in particular for automotive components, parts of electronic devices, etc. The aluminum-based casting alloy contains, wt.%: calcium 1.5-5.1; iron up to 0.7; silicon up to 1.0; zinc 0.1-1.8 and, optionally, one or more manganese 0.2-2.5; titanium 0.005-0.1; zirconium 0.05-0.14; chrome 0.05-0.15, with calcium and zinc present in the alloy structure primarily as eutectic particles. The technical result is to provide the required combination of process properties in casting and corrosion resistance. 3 patent claims, 3 tables, 4 attachments, 2 figures.

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Description

Technical field

[0001] The invention refers to the field of metallurgy, in particular, to aluminum-based alloys characterized by high corrosion resistance. The alloy can be used in the manufacture of thin-walled complex-shaped castings by casting in a metal mold.

Prior art

[0002] Industrial non-heat-treatable alloys of the A-Si system, such as A413.2 or AK12pch (GOST1583), are characterized by high processability when casting and a relatively low level of strength properties; in particular, the yield strength usually does not exceed 60-80 MPa, depending on the thickness of the castings. A higher level of strength properties of castings already in the as-cast condition is provided by the addition of copper; in particular, alloys such as AA383.1 or AK12M2 are known. The increase in mechanical properties in this case is accompanied by a significant decrease in elongation and deterioration of corrosion resistance.

[0003] Non-heat-treatable and corrosion-resistant alloys include the solid solution alloys based on the Al-Mg system, for example, AMg6L, AMg5K, AMg5Mz (GOST1583), Magsimal®59 (Rheinfelden Alloys) and others characterized by satisfactory processability when casting, good corrosion resistance, a high level of strength properties and elongation. The disadvantages of alloys of this system include high linear shrinkage and insufficient tightness of thin-walled castings.

[0004] The combination of a high level of strength properties, elongation, and corrosion resistance is implemented in Al-Si alloys with 0.2-0.5 wt% magnesium; in particular, AK9 (GOST1583), Silafont®36 (Rheinfelden Alloys), trimal®37 (Trimet), and other alloys are known. Hardening significantly complicates the casting production cycle, as it can cause warping of castings (especially when using water quenching), dimensional changes, and cracks.

[0005] NITU MISIS invention disclosed in patent RU2660492 is known. Material for use in the as-cast condition contains (wt. %): 5.4-6.4% calcium, 0.3-0.6% silicon, and 0.8-1.2% iron. The disadvantages of the proposed invention include low relative elongation, which did not exceed 2.6%, which limits the use of the material in critical cast parts.

[0006] Al-Ni-Mn casting alloy for structural components for automotive and aerospace applications is known as an alternative to branded silumins, developed by Alcoa and disclosed in patent US6783730B2 (published on 31.08.2004). This alloy can be used to produce castings with a good combination of casting and mechanical properties in the case of (wt. %) 2-6% Ni, 1-3% Mn, 1% Fe, less than 1% silicon, as well as in the case of other unavoidable impurities. The disadvantages of the proposed invention include the fact that the high level of casting and mechanical properties is ensured by using high-purity aluminum grades and with a high nickel content, which significantly increases the cost of the castings produced. Besides, the proposed material is non-heat-treatable in the entire concentration range, which limits its use. At the same time, the corrosion resistance of the castings decreases significantly in the area of high nickel concentrations.

[0007] Cast aluminum alloys based on Al-Ni and Al-Ni-Mn systems and a method of producing cast parts from them are known, which are described in Alcoa invention US8349462B2 (published on 08.01.2013) and application EP2011055318 of Rheinfelden Alloys GmbH & Co. KG. The invention proposes alloy compositions for casting applications. Common in the proposed inventions is a high nickel content of 1-6%, which determines the main disadvantage - a significant decrease in corrosion resistance. With a relatively low nickel and manganese content, cast alloys have a low level of strength characteristics.

[0008] Known is the material based on the Al-Ni-Mn system proposed by NITU MISIS and disclosed in Russian patent 2478131C2 published on 27.03.2013. The material contains (wt%): 1.5-2.5%Ni, 0.3-0.7%Fe, 1-2%Mn, 0.02-0.2%Zr, 0.02%-0.12%Sc, and 0.002-0.1%Ce. Castings made of the alloy after annealing (without using the quenching operation) are characterized by an ultimate resistance of at least 250 MPa with an elongation of at least 4%. The first disadvantage of this alloy is its increased tendency to form concentrated porosity, which makes it difficult to achieve high-quality, relatively large castings. The second disadvantage is the need to use higher casting temperatures, which cannot always be achieved in the conditions of foundries.

[0009] The closest material to the proposed one is the material containing (wt.%) Al-3.5%Ca-0.9%Mn-0.5%Fe-0.1%Zr-0.1%Sc disclosed in the publication available at https://doi.org/10.1016/j.msea.2019.138410. The authors of the publication consider the material as a deformed alloy, the process chain of which excludes water quenching. The publication shows the non-obviousness of using the alloy mentioned in the publication for castings and use in the as-cast condition. The disadvantages of the proposed invention include the presence of expensive scandium, as well as the need to use heat treatment to achieve the hardening effect of the joint addition of zirconium and scandium.

Invention disclosure

[0010] The object of the invention is to create a new casting aluminum alloy designed to produce thin-walled castings by various methods of casting into a metal mold, in particular, gravity casting, high-pressure casting, low-pressure casting, liquid forging, but not limited to, satisfying the specified requirements for a set of process and corrosion characteristics.

[0011] The technical result of the invention is to provide a given combination of process characteristics in casting and corrosion resistance.

[0012] The technical result is achieved by proposing an aluminum-based casting alloy with the following concentrations of alloying elements, wt. %:

Calcium	1.5-5.1
Zinc	0.1-1.8
Iron	up to 0.7
Silicon	up to 1.0

optionally, at least one element selected from the group

Manganese	0.2-2.5
Titanium	0.005-0.1
Zirconium	0.05-0.14
Chromium	0.05-0.15

[0013] Aluminum and unavoidable impurities - the rest

In the particular version, calcium and zinc are predominantly represented in the structure in the form of eutectic particles. The alloy is made in the form of castings.

[0014] Various modifications and improvements, which do not go beyond the scope of the invention as defined by the first claim, are permissible.

Summary of the invention

[0015] Thanks to the chosen combination of alloying elements, the proposed alloy is characterized by a narrow crystallization interval, which in combination with a large amount of eutectic phase provides a good level of casting characteristics, and thanks to the elements dissolved in aluminum solid solution - a satisfactory level of strength properties in the as-cast condition. At the same time, with various combinations of selected alloying elements, the corrosion resistance within the claimed area is maintained at a good level.

[0016] The basic criterion for the acceptable choice of alloying elements was the formation of the desired structure, excluding the presence of coarse primary crystals and/or coarsening of the eutectic phase; the justification of the concentration range is given below.

[0017] Concentrations (wt. %) of calcium in the range 1.5-5.1% and zinc in the range 0.1-1.8% provide good casting properties because calcium and zinc predominantly form a sufficient amount of the eutectic phase. The main effect of the joint introduction of calcium and zinc is the formation of a joint eutectic phase $Al_4(Ca,Zn)$, where the zinc atom replaces that of calcium. As a result, the level of strength properties is further increased. If the calcium content is less than the declared level, it will lead to a decrease in casting characteristics. If zinc is reduced below the declared level, no significant increase in strength properties will be observed. Calcium and zinc content above the declared level will lead to the formation of a coarse structure and a significant decrease in mechanical properties.

[0018] The iron and silicon content is primarily determined by the purity of the aluminum used to make the alloy. However, iron and silicon can also be used as alloying elements because silicon in amounts of up to 1.0 wt. % is redistributed between solid solution and eutectics, which, on the one hand, provides an increase in strength properties due to additional solid-solution hardening in the as-cast condition and, on the other hand, positively affects the alloy casting characteristics by increasing the eutectics. With a higher silicon content, the morphology of the eutectic phase deteriorates, which generally reduces the strength characteristics. Iron in amounts of up to 0.5 wt. % predominantly forms phases of eutectic origin, which positively affects the casting characteristics of the alloy by increasing the amount of eutectics. An increase in iron concentration above 0.5 wt. % may lead to coarsening of the eutectic phase and, as a consequence, a decrease in mechanical properties.

[0019] Manganese in amounts of up to 2.5 wt. % is necessary to increase the strength properties, primarily in the as-cast condition, by providing solid-solution hardening. With manganese content above 2.5 wt. %, primary crystals of the $Al_6(Fe,Mn)$ phase can be formed in the structure, which can lead to a decrease in mechanical characteristics. A manganese content of less than 0.2 wt. % will not result in significant solid-solution hardening and, as a consequence, a weak increase in strength characteristics.

[0020] Zirconium and chromium in the declared limits (wt. %) of 0.05-0.14% and 0.05-0.15%, respectively, are necessary to provide solid-solution hardening. Lower concentrations of these elements do not result in a significant increase in strength characteristics in the as-cast condition. Larger quantities would require higher casting temperatures than typical, which would reduce the stability of the casting molds; otherwise, there would be a high probability of forming primary crystals of the Al_7Cr and Al_3Zr phase, which would not increase the level of mechanical properties from the introduction of these elements.

[0021] Titanium in an amount of 0.005-0.1 wt. % is needed to modify the aluminum solid solution. A higher titanium content in the structure may result in the appearance of primary crystals, which will reduce the overall level of mechanical properties, while a lower titanium content will not achieve the positive effect of this element. Titanium can be introduced as a multicomponent ligature, such as Al-Ti-B and/or Al-Ti-C, so that the alloy may contain boron and carbon in compounds with titanium in quantities proportional to the content of the corresponding ligature. Boron and carbon, as independent elements, had no significant effect on the mechanical and casting properties for the range in question. Besides, in the presence of titanium, a decrease in the propensity to form hot cracks during casting was noted in some cases.

Embodiment

[0022] The following charge materials were used to prepare the alloys (wt. %): Aluminum grade A99 and A8, zinc grade C0, calcium as metallic calcium and ligature Al-6Ca, manganese as ligature Al-10%Mn, ligature Al-10%Zr, Al-10%Cr, Al-5%Ti.

EXAMPLE 1

[0023] To assess the effect of alloying elements on the structure and properties, 13 alloy compositions were prepared under laboratory conditions (Table 1).

Table 1 - Chemical composition of experimental alloys (wt. %)

N o.	Si	Fe	Ca	Zn	Mn	Ti	Cr	Zr
1	1.0	0.08	1.5	0.1	<0.001	<0.001	<0.001	<0.001
2	0.05	0.2	3.5	0.8	<0.001	<0.001	<0.001	<0.001
3	0.08	0.7	5.1	1.8	<0.001	<0.001	<0.001	<0.001
4	0.08	0.5	2.8	0.1	1.2	<0.001	<0.001	<0.001
5	0.22	0.08	3.8	1.3	0.9	<0.001	<0.001	<0.001
6	1.0	0.2	5.0	1.6	0.2	<0.001	<0.001	<0.001
7	0.08	0.1	5.1	1.5	0.9	0.01	<0.001	<0.001
8	0.01	0.01	1.5	0.1	2.5	0.005	<0.001	<0.001
9	0.5	0.5	2.0	0.4	1.5	0.05	<0.001	<0.001
10	0.08	0.1	4.8	1.8	0.8	<0.001	0.05	0.12
11	0.61	0.5	5.0	1.4	0.9	0.002	0.15	0.14
12	0.16	0.19	2.3	0.32	1.2	0.1	0.10	0.09
13	0.05	0.08	1.5	0.45	1.5	0.01	0.05	0.05

[0024] The content of other elements typically did not exceed 0.05 wt. %. The chemical composition of the alloy was chosen from the condition of obtaining a structure consisting of an aluminum solid solution and eutectic component. Specimens were cast gravitationally in a metal mold "Separately Cast Sample". The mold temperature could vary in the range of 20-60 °C. The casting was a tensile specimen 10 mm in diameter with an estimated length of 50 mm, which was tensile tested (with a determination of yield strength, tensile strength, and elongation) immediately after casting without machining. The structure of the specimens was evaluated from the specimen heads.

Table 2 - Mechanical properties in the as-cast condition (gravity casting into a metal mold)

No.*	σ_t, MPa	$\sigma_{0.2}$ (MPa)	δ, %
1	165	74	4.5
2	181	101	3.9
3	176	123	2.0
4	191	118	2.4
5	202	143	3.1
6	212	166	2.1
7	179	155	1.0
8	152	109	3.1
9	150	90	2.0
10	235	179	2.0
11	229	204	1.2
12	201	130	3.1
13	191	124	3.6
* - compositions of Table 1			

[0025] Analysis of the structure of the alloys studied showed that the structure of the considered compositions of Table 1 mainly consists of aluminum solid solution and eutectic phases formed by the corresponding elements. At the same time, calcium and zinc in all experimental alloys are predominantly represented in the form of eutectic particles.

[0026] Compositions 2, 5, and 12 are preferred because of their good yield strength to elongation ratio for use in the as-cast condition. The most desirable alloy structure, using the example of composition 5 (Table 1), is shown in Fig. 1.

EXAMPLE 2:

[0027] The corrosion resistance by the example of compositions 2, 5, 8, and 11 of the claimed alloy (Table 1) was evaluated by the method of accelerated corrosion tests conducted by exposure to neutral salt fog under the following program: 1 cycle - soaking in a salt fog chamber at spraying of 5% NaCl solution for 8 hours at a temperature of 25±1 °C, then soaking at 35±3 °C without spraying the solution for 16 hours, a total of 7 cycles. The result was evaluated by changing the surface appearance of the specimens and the depth of corrosion damage (metallographic method). The ADC6 type alloy was used as a reference, which is characterized by the highest corrosion resistance among cast aluminum alloys.

[0028] From the comparative analysis of the results, it follows that during the test, the surface color of the examined compositions and the standard changed from silver to silver-yellow, as well as single surface damage up to 10 microns without significant corrosion damage.

EXAMPLE 3

[0029] Casting characteristics were evaluated using the hot brittleness (HB) parameter using the "harp casting", where the best indicator is to obtain a casting with the maximum "rod" length (Fig. 2). The propensity for hot cracks was assessed using alloys 2, 4, and 12 as examples (Table 1). ADC6 type alloy was used as a comparison. The absence of cracks in alloys 2, 4, and 12 was shown (Table 1), which is a good indicator at the level of most Al-Si alloys, in contrast to the ADC6 alloy, the casting from which about 40% of the rods failed starting from the maximum length.

EXAMPLE 4

[0030] To evaluate the mechanical properties of alloy 12 (Table 1), 2-mm-thick plates were cast by injection molding (HPDC). Casting was done with vacuumization of the mold. The mold temperature was about 150 °C. The temperature of the melt was 710 °C. The results of the tensile test of specimens cut from the cast plate are shown in Table 3.

Table 3 - Tensile test results of a 2 mm HPDC-cast plate (as-cast condition)

σ_t, MPa	$\sigma_{0.2}$ (MPa)	δ, %
212	112	9.5

Claims

1. Aluminum-based casting alloy with the following distribution of alloying elements, wt. %:

Calcium	1.5-5.1
Zinc	0.1-1.8
Iron	up to 0.7
Silicon	up to 1.0

optionally, at least one element selected from the group

Manganese	0.2-2.5
Titanium	0.005-0.1
Zirconium	0.05-0.14
Chromium	0.05-0.15

Aluminum and unavoidable impurities - the rest

2. Alloy according to claim 1, **characterized in that** it contains alloying elements in the following redistribution, wt. %:

Calcium	2.8-5.0
Manganese	0.2-1.2
Iron	up to 0.5
Silicon	up to 1.0
Zinc	0.1-1.6

3. Alloy according to claims 1 or 2, **characterized in that** calcium and zinc are therein predominantly in the form of eutectic particles.

4. Alloy according to any of claims 1-3, **characterized in that** it is made in the form of a casting.

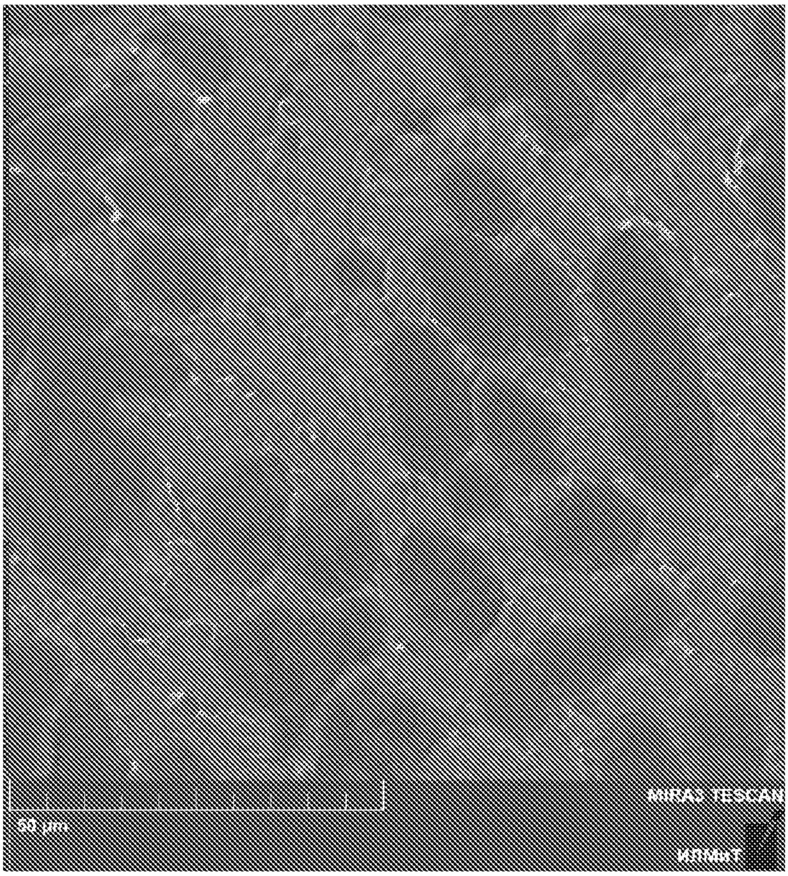

Fig.1

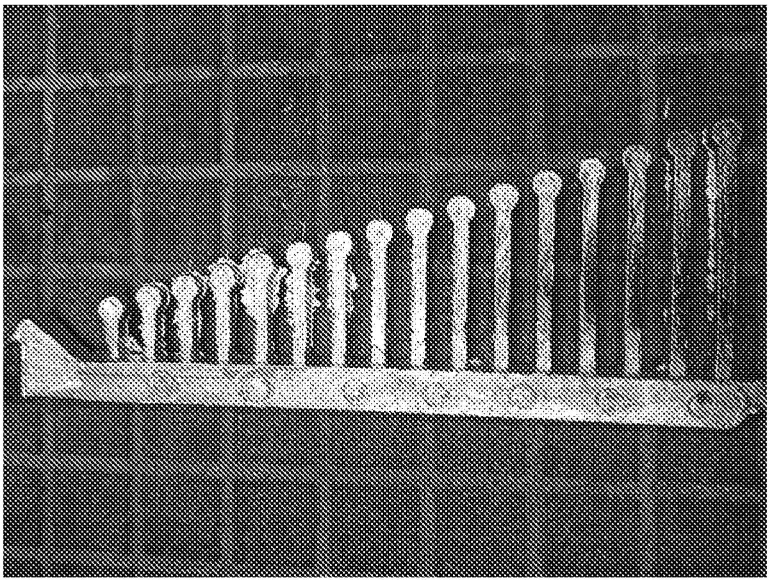

Fig.2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2021/050295

A. CLASSIFICATION OF SUBJECT MATTER

C22C 21/00 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 21/00

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 practicable, search terms used)

Espacenet, PatSearch, PAJ, WIPO, USPTO, RUPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D, A	RU 2660492 C1 (FEDERALNOE GOSUDARSTVENNOE AVTONOMNOE OBRAZOVATELNOE UCHREZHDENIE VYSSHEGO OBRAZOVANIYA «NATSIONALNY ISSLEDOVATELSKY TEKHNOLOGICHESKY UNIVERSITET «MISIS») 06.07.2018	1-4
A	RU 2672653 C1 (FEDERALNOE GOSUDARSTVENNOE AVTONOMNOE OBRAZOVATELNOE UCHREZHDENIE VYSSHEGO ORAZOVANIYA «NATSIONALNY ISSLEDOVATELSKY TEKHNOLOGICHESKY UNIVERSITET «MISIS») 16.11.2018	1-4
A	GB 546899 A (THE NATIONSL SMELTING COMPANY) 04.08.1942	1-4
A	RU 2683399 C1 (OBSHCHESTVO S OGRANICHENNOY OTVETSTVENNOSTJU «OB'EDINENNAYA KOMPANIYA RUSAL INZHENERNO-TEKHNOLOGICHESKY TSENTR) 28.03.2019	1-4
A	US 5573606 A (GIBBS DIE CASTING ALUMINUM) 12.11.1996	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
26 November 2021 (26.11.2021)	02 December 2021 (02.12.2021)
Name and mailing address of the ISA/ RU Facsimile No.	Authorized officer Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2660492 **[0005]**
- US 6783730 B2 **[0006]**
- US 8349462 B2 **[0007]**
- EP 2011055318 A **[0007]**
- RU 2478131 C2 **[0008]**