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(54) **Titre :** ADDITION DE CALCIUM ET DE VANADIUM A DES ALLIAGES ALMG
(54) **Title:** ADDITION OF CALCIUM AND VANADIUM TO ALMG ALLOYS

(57) **Abrégé/Abstract:**

A Process for the production of an aluminium-magnesium alloy with a content of at least 1% Mg, preferably 1 - 7% Mg is suggested, where in a molten state 0.01 - 2% Ca and 0.01 - 0.3% V are added to the alloy.

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Abstract:

A Process for the production of an aluminium-magnesium alloy with a content of at least 1% Mg, preferably 1 – 7% Mg is suggested, where in a molten state 0.01 – 2% Ca and 0.01 – 0.3% V are added to the alloy.

Addition of Calcium and Vanadium to AlMg Alloys

Field of disclosure

The present invention relates to a process for producing an aluminium-magnesium alloy and to an alloy produced by the process.

5 Background, prior art

Usually, aluminum melts form a closed oxide layer. A thin oxide skin is formed relatively quickly, which usually does not increase significantly over a longer period of time. If the aluminum alloy contains magnesium (AlMg alloy), the formation of this closed oxide layer (passivation layer) is impeded and a stronger oxidation occurs, which progresses over a
10 long period. The resulting cauliflower-like dross consists mainly of spinel ($\text{MgO} - \text{Al}_2\text{O}_3$) and can become very thick. After some time, particles in the melt sink down and the furnace becomes contaminated if the dross is not removed in time. A high furnace temperature favours this process.

It is known that the addition of beryllium (Be) can positively influence the oxidation tendency of AlMg melts. In earlier patents of the applicant, beryllium is mentioned for reducing the oxidation tendency of AlMg melts. One example is EP3159422 A1. Here 10-50 Be
15 ppm is added to an $\text{AlMg}_5\text{Si}_2\text{Mn}$ alloy.

It has also been known for a long time that an increased addition of beryllium to a metal melt is undesirable because of the carcinogenic properties of beryllium and therefore a reduced addition should be aimed for. In EP1090156 B1, a method is proposed for the addition of vanadium (V) and beryllium to an AlMg alloy. It was found that by adding vanadium, the amount of beryllium could be reduced and a corresponding reduction in the amount of dross could be observed.

Summary of disclosure

It is the object of the present invention to provide a process which further improves processes known from the prior art. This improvement is aimed in particular at the formation of the oxide layer forming on the melt surface.

One object is to provide a process which provides for the addition of an element or a combination of elements which cause a catalytic reaction and thus promote the formation of a passivation layer on the aluminium melt. By forming the passivation layer, further oxidation of the molten metal and thus undesirable formation of dross is prevented.

The process according to the invention is directed towards the production of an aluminium-magnesium alloy with a content of at least 1 % Mg, preferably 1 – 7 % Mg, more preferably at least 2 % Mg, preferably 2 – 7 % Mg. To this alloy 0.01 – 2 % calcium (Ca) and 0.01 – 0.3 % V are added in the molten state.

In a first embodiment, 0.05 % – 1 % Ca is added to the alloy in the molten state.

In a second embodiment, 0.07 % – 0.5 % Ca is added to the alloy in the molten state.

In a third embodiment, 0.02 – 0.15% V is added to the alloy in the molten state.

In a fourth embodiment, 0.02 – 0.08% V is added to the alloy in the molten state.

In a preferred version of the first embodiment, 0.02 – 0.15% V is added to the alloy in the molten state.

- 5 In a further preferred version of the first embodiment, 0.02 – 0.08% V is added to the alloy in the molten state.

In a preferred version of the second embodiment, 0.02 – 0.15% V is added to the alloy in the molten state.

- 10 In a further preferred version of the second embodiment, 0.02 – 0.08% V is added to the alloy in the molten state.

In the process according to the invention, Ca and V are added as aluminium master alloy during the production of the aluminium-magnesium alloy, preferably the first master alloy contains 10% Ca and 90% Al and the second master alloy contains 10% V and 90% Al.

- 15 In the process according to the invention, Ca and V are added at a melt temperature of 680 – 750°C.

In the process according to the invention, at least one of the following elements is added to the alloy in the molten state: Iron (Fe), Manganese (Mn), Strontium (Sr), Phosphorus

(P), Nickel (Ni), Zinc (Zn), Copper (Cu), Silicon (Si), Titanium (Ti), Chromium (Cr), Molybdenum (Mo), Zirconium (Zr), Hafnium (Hf), Gallium (Ga), Boron (B).

In the process according to the invention, the following elements are added to the alloy in the molten state in addition to Al, Mg, Ca and V, either individually or as a master alloy:

5 0.8 – 3.0 % Fe, preferably 0.8 – 2.0 % Fe

0 – 2.5 % Mn

0 – 0.5 % Ti

0 – 0.4 % Si

0 – 0.8 % Sr

10 0 – 500 ppm P

0 – 4.0 % Cu

0 – 10.0 % Zn

Up to 0.5 % of an element or group of elements selected from the group consisting of Cr, Ni, Mo, Zr, Hf, Ga and B.

15 Where reference is made in this application to percentages, this is to be understood as percentages by weight (wt%; w%).

Where the present application refers to the molten state, this defines a molten metal with a temperature of preferably 680 to 750°C, in which Ca and V can dissolve completely and all other alloying elements are completely dissolved.

20 The alloy produced by the process according to the invention is a die-cast alloy.

An Al-Mg alloy produced by the process according to the invention consists of the following elements:

0.8 – 3.0% Fe, preferably 1.0 – 2.4% Fe, more preferably 1.4% – 2.2% Fe

2.0 – 7.0% Mg, preferably 3.0% – 5.0% Mg

5 0.01 – 2% Ca

0.01 – 0.3% V, preferably 0.02 – 0.15%, particularly preferred 0.02 – 0.08%

Up to 2.5% Mn, preferably 0 – 0.6% Mn

Up to 0.5% Ti

Up to 0.4% Si

10 Up to 0.8% Sr, preferably 0 – 0.03% Sr

Up to 500 ppm P, preferably 0 – 50 ppm P

Up to 4.0% Cu, preferably 0 – 0.2% Cu

Up to 10.0% Zn, preferably 0 – 0.5% Zn

Up to 0.5% of an element or element group selected from the group consisting of Cr, Ni,
15 Mo, Zr, Hf, Ga and B, and the balance Al and unavoidable impurities.

Examples

An AlMg alloy which is to be protected against oxidation, is left in ambient air at a defined temperature for a certain time in an open crucible. Then the formation of the oxide layer is determined. In Al alloys with a Mg content of 4 – 6%, a visible oxide layer appears after a
20 few days, the strength of which is significantly higher than in Al alloys without a Mg content.

The following 15 test trials were carried out at the Tech Center Rheinfelden. The alloys were produced in an open, electrically heated crucible furnace. At a melt temperature of 700°C, high-pressure die casting trials were carried out and the melt was left in ambient air. The casting tests were carried out on a 400 to die casting cell and the produced test plates had the dimensions 260 x 60 x 3 mm. Tensile specimens were taken from these test plates and the mean values of six specimens were determined. For the tests left in ambient air, 8 kg of melt per test trial was transferred to a small, open crucible. Three of these small crucibles were placed in a larger, electrically heated crucible furnace and left to stand at 700°C for 3 or 10 days.

10 The investigated compositions V1 to V15, shown in the following table, are compositions without beryllium. Beryllium is known as an element for improving the oxidation tendency of an AlMg alloy and would falsify the evaluation of the effect of Ca and V.

The formation of the oxide layer, which could be improved with the addition of Ca and V, was assessed on the basis of three predefined classes. The aim is an oxide layer according to type A. Type B is classified as a poor result and type C as a very poor result for the formation of the oxide layer. This classification, as used in the following examples, is explained in more detail below.

Type A: Very thin oxide layer, which moves with the molten metal. It does not resist mechanical action.

20 Type B: Thin, semi-solid oxide layer that breaks into pieces when the melt moves. Little resistance to mechanical action.

Type C: Solid oxide layer that does not move with the melt. Considerable resistance to mechanical action.

No	Si	Fe	Cu	Mn	Mg	Ca	V	Ti
V1	0,04	1,6	0,001	0,006	4,25	0,00	0,025	0,002
V2	0,04	1,6	0,002	0,005	4,25	0,10	0,025	0,002
V3	0,04	1,6	0,002	0,005	4,25	0,20	0,025	0,003

No	Rm	Rp0,2	A	Oxide layer	
	[MPa]	[MPa]	[%]	3 days	10 days
V1	255	123	14,2	Typ C	Typ C
V2	254	122	14,1	Typ B	Typ B
V3	255	123	13,8	Typ A	Typ A

No	Si	Fe	Cu	Mn	Mg	Ca	V	Ti
V4	0,04	1,2	0,001	0,005	3,8	0,15	0,025	0,004
V5	0,04	1,2	0,002	0,005	3,8	0,15	0,050	0,005
V6	0,04	1,2	0,002	0,005	3,8	0,25	0,050	0,005

No	Rm	Rp0,2	A	Oxide layer	
	[MPa]	[MPa]	[%]	3 days	10 days
V4	246	113	15,2	Typ A	Typ B
V5	246	112	15,2	Typ A	Typ A
V6	246	113	14,2	Typ A	Typ A

No	Si	Fe	Cu	Mn	Mg	Ca	V	Ti
V7	0,04	1,15	0,001	0,002	3,79	0,00	0,010	0,005
V8	0,05	1,15	0,001	0,002	3,78	0,11	0,024	0,005
V9	0,05	1,16	0,001	0,003	3,83	0,11	0,024	0,005

No	Rm	Rp0,2	A	Oxide layer	
	[MPa]	[MPa]	[%]	3 days	10 days
V7	241	110	17,2	Typ B	Typ C
V8	242	111	15,2	Typ A	Typ A

V9	242	111	15,4	Typ A	Typ A
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No	Si	Fe	Cu	Mn	Mg	Ca	V	Ti
V10	0,05	1,59	0,001	0,002	5,18	0,07	0,030	0,005
V11	0,05	1,60	0,001	0,002	5,39	0,07	0,030	0,005
V12	0,05	1,57	0,001	0,003	5,96	0,07	0,030	0,005

No	Rm	Rp0,2	A	Oxide layer	
	[MPa]	[MPa]	[%]	3 days	10 days
V10	270	128	13,0	Typ A	Typ A
V11	277	131	13,5	Typ A	Typ A
V12	284	139	11,8	Typ A	Typ A

No	Si	Fe	Cu	Mn	Mg	Ca	V	Ti
V13	0,05	1,66	0,002	0,007	4,33	0,20	0,01	0,002
V14	0,05	1,67	0,002	0,008	4,32	0,30	0,01	0,002
V15	0,05	1,65	0,002	0,007	4,27	0,40	0,01	0,003

No	Rm	Rp0,2	A	Oxide layer	
	[MPa]	[MPa]	[%]	3 days	10 days
V13	259	119	13,6	Typ C	Typ C
V14	255	120	11,8	Typ A	Typ B
V15	257	122	10,5	Typ A	Typ A

A melt left in ambient air at 0% Ca and 0% Be resulted in a solid oxide layer of type C after only 3 days. The addition of Ca and V significantly reduced the formation of the oxide layer. The combination of both elements showed a better effect than one of the elements alone.

Claims

1. Process for the production of an aluminium-magnesium alloy with a content of at least 1% Mg, preferably 1 – 7%, characterized in that 0.01 – 2% Ca and 0.01 – 0.3% V are added to the alloy in the molten state.
- 5 2. Process for the production of an aluminium-magnesium alloy according to claim 1, characterized in that 0.05 – 1% Ca is added to the alloy in the molten state.
3. Process for the production of an aluminium-magnesium alloy according to claim 1, characterised in that 0.07 – 0.5% Ca is added to the alloy in the molten state.
4. Process for the production of an aluminium-magnesium alloy according to claim 1
10 or 2 or 3, characterized in that 0.02 – 0.15% V is added to the alloy in the molten state.
5. Process for the production of an aluminium-magnesium alloy according to claim 1 or 2 or 3, characterized in that 0.02 – 0.08% V is added to the alloy in the molten state.
- 15 6. Process for the production of an aluminium-magnesium alloy having a content of at least 2% Mg, preferably 2 – 7%, according to any one of the preceding claims 1 to 5.
7. Process for the production of an aluminium-magnesium alloy according to any one of the preceding claims, characterized in that Ca and V are added as two Al master

alloys, preferably the first master alloy contains 10% Ca and 90% Al and the second master alloy contains 10% V and 90% Al.

8. Process for the production of an aluminium-magnesium alloy according to any one of the preceding claims, characterized in that the addition of Ca and V is carried out at a melt temperature of 680 – 750°C.
9. Process for the production of an aluminium-magnesium alloy according to any one of the preceding claims, wherein at least one of the following elements is added to the alloy in the molten state: Fe, Mn, Sr, P, Ni, Zn, Cu, Si, Ti, Cr, Mo, Zr, Hf, Ga, B.
10. Process according to any one of the preceding claims, wherein the following elements are added to the alloy in the molten state, in addition to Al, Mg, Ca and V, either individually or as a master alloy:

0.8 – 3.0 % Fe, preferably 0.8 – 2.0%

0 – 2.5% Mn

0 – 0.5% Ti

0 – 0.4% Si

0 – 0.8% Sr

0 – 500 ppm P

0 – 4.0 % Cu

0 – 10.0% Zn

up to 0.5% of an element or element group selected from the group consisting of chromium, nickel, molybdenum, zirconium, hafnium, calcium, gallium and boron.

11. Process according to any one of the preceding claims, characterised in that the aluminium-magnesium alloy is a die-cast alloy.

5 **12.** Alloy produced by a process according to any one of the preceding claims, wherein the alloy consists of the following composition:

0.8 – 3.0% Fe, preferably 1.0 – 2.4% Fe, more preferably 1.4% – 2.2% Fe

2.0 – 7.0% Mg, preferably 3.0% – 5.0% Mg

0.01 – 2% Ca

10 0.01 – 0.3% V, preferably 0.02 – 0.15% V, particularly preferably 0.02 – 0.08% V

Up to 2.5% Mn, preferably 0 – 0.6% Mn

Up to 0.5% Ti

Up to 0.4% Si

15 Up to 0.8% Sr, preferably 0 – 0.03% Sr

Up to 500 ppm P, preferably 0 – 50 ppm P

Up to 4.0% Cu, preferably 0 – 0.2% Cu

Up to 10.0% Zn, preferably 0 – 0.5% Zn

20 Up to 0.5% of an element or group of elements selected from the group consisting of chromium, nickel, molybdenum, zirconium, hafnium, gallium and boron, and the balance aluminium and unavoidable impurities.