

(19)



(11)

**EP 4 050 115 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**31.08.2022 Bulletin 2022/35**

(51) International Patent Classification (IPC):

**C22C 21/00 (2006.01) C22C 21/06 (2006.01)**  
**C22C 21/08 (2006.01) C22F 1/047 (2006.01)**

(21) Application number: **21159556.6**

(52) Cooperative Patent Classification (CPC):

**C22C 21/06; C22C 21/08; C22F 1/047**

(22) Date of filing: **26.02.2021**

(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**

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(54) **DURABLE ALUMINIUM ALLOY SHEET FOR DECORATIVE APPLICATIONS**

(57) The invention relates to improved sheets for decorative and formable parts made of an aluminium alloy which comprises, in wt.%, Mg : 0.8 - 1.3, Mn : 0.8 - 1.2, Cu: 0.05 - 0.30, Cr : 0.05 - 0.30, Fe : ≤ 0.4, Si : ≤ 0.3, Zn : ≤ 0.25, Ti : ≤ 0.15, impurities < 0.05 each and < 0.15 total, remainder aluminium. The method to make a sheet according to the invention comprises casting a slab with

a composition according to the invention, homogenizing, hot and cold rolling the slab, annealing and tension leveling. The sheet according to the invention are particularly useful to make a coated decorative part preferably a decorative part for an automobile, or a household appliance or a medical device.

**EP 4 050 115 A1**

**Description****Field of the invention**

5 [0001] The invention relates to the field of decorative parts made of aluminium alloys which are formable. These parts are coated before forming for decorative purposes and/or to be durable. The alloy after the curing of the coating must be hard enough to present a good dent or scratch resistance.

[0002] The invention relates more particularly to aluminium alloy sheets of the AA3XXX and AA5xxx series with a composition and manufacturing process that are particularly suitable for this type of application and offering,

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**State of the art**

[0003] Aluminium alloys are commonly used in the manufacturing of decorative parts, particularly for the automotive industry, but also in the household appliance and medical device industries, in competition with wood, steel and plastics. These parts are generally coated, typically with a varnish or a paint.

[0004] In the case of the automotive industry, interior decorative elements are produced, for example for high-usage door handles, gearbox trims, light-resistant and shockproof trim elements for the center console, trims and/or panels on the dashboard and/or doors, capacitive function elements and exterior elements are also produced such as, in particular, the window surrounds, body side or door trim strips, bellines, tailgate trim strips, radiator grille trim, bumper piping, hubcaps, wheel hub cover...

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Two types of products are currently available on the market: extruded profiles and shaped sheets.

[0005] The predominant alloy types used for sheets are AA 1XXX, AA3XXX, AA5XXX and 8XXX alloys. AA5005 aluminium alloy rolled products with different heat treatment states are widely used in conductors, kitchenware, dashboards, architectural decorations, building materials, vehicle interior and exterior materials.

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[0006] WO/2014/203077 relates to a method for manufacturing an outer moulding ring of a motor vehicle, in particular such as a window frame or body shell moulding, made of an aluminium alloy, by shaping and polishing a sheet or strip made by continuous vertical casting of a high-purity alloy sheet of series AA5xxx.

Several patents disclose Al-Mn-Mg alloys, mainly for packaging applications:

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EP0504077 relates to Al-based alloys intended for deep drawing and/or drawing and exhibiting high mechanical strength characteristics as well as good isotropy (low distortion wedge content) and good cold processability having the following compositions by weight (%): Fe  $\leq$  0.25 - Si  $\leq$  0.25 - Mn from 0.8 to 1.6 - Mg from 0.7 to 2.5 - Cu from 0.20 to 0.6 - Cr from 0 to 0.35 - Ti from 0 to 0.1 - V from 0 to 0.1 - others each  $\leq$  0,05, total  $\leq$  0,15, remainder Al.

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WO/2018/143376 relates to an aluminium alloy sheet which contains 0.05-0.60 mass% of Si, 0.05-0.80 mass% of Fe, 0.05-0.25 mass% of Cu, 0.80-1.50 mass% of Mn, 0.80-1.50 mass% of Mg, Al, and incidental impurities.

WO2015140833 relates to an aluminium alloy for can bodies containing Si: 0.10-0.60 mass%, Fe: 0.10-0.80%, Cu: 0.05-0.25%, Mn: 0.80-1.50%, Mg: 0.80-1.30% and the remainder being obtained from Al and unavoidable impurities.

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WO/2016/149061 relates to aluminium alloys for making packaging products such as bottles and cans comprising 0.1-1.6 wt. % Mn, 0.1-3 wt. % Mg, 0.1-1.5 wt. % Cu, 0.2-0.7 wt. % Fe, 0.10-0.6 wt. % Si, up to 0.3 wt. % Cr, up to 0.6 wt. % Zn, up to 0.2 wt. % Ti, 0.05 wt. % for each trace element, <0.15 wt. % for total trace elements and remainder Al.

WO/2016/100800 relates to compositions and methods comprising aluminium alloy system useful for aluminium bottle applications comprising about 0.15-0.50 % Si, 0.35-0.65 % Fe, 0.05-0.30 % Cu, 0.60-1.10 % Mn, 0.80-1.30 % Mg, 0.000-0.0080 % Cr, 0.000-0.500 % Zn, 0.000-0.080 % Ti, up to 0.15 % of impurities, with the remainder as Al.

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There are four main requirements for these products: good formability, in order to provide the desired shape, nice surface aspect without surface defects generated by forming such as Portevin Le Chatelier bands, Lüders bands or orange peel, sufficient durability such as corrosion resistance and scratch resistance. Current alloys used for such applications (such as 5005, 8014 or 1050) typically have the requested formability, corrosion resistance and surface aspect but they may however undergo scratches /dents. A product with an improved resistance to scratches or dents is requested by the industry, without degrading any of the other properties.

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**The problem**

[0007] The invention aims to provide sheets made of aluminium alloys that are particularly suitable to make decorative parts and offer a high scratch resistance, with simultaneously being formable, corrosion resistant and providing a nice surface aspect.

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**Subject of the invention**

**[0008]** A first subject of the invention is a sheet made of an aluminium alloy comprising, by weight %

- 5 Mg : 0.8 - 1.3,
- Mn : 0.8 - 1.2,
- Cu: 0.05 - 0.30,
- Cr : 0.05 - 0.30,
- Fe :  $\leq$  0.4,
- 10 Si :  $\leq$  0.3,
- Zn :  $\leq$  0.25,
- Ti :  $\leq$  0.15,

impurities < 0.05 each and < 0.15 total, remainder aluminium.

15 **[0009]** Another subject of the invention is a method to make a sheet according to the invention wherein,

(a) a slab is cast of an aluminium alloy comprising, by weight %

- 20 Mg : 0.8 - 1.3,
- Mn : 0.8 - 1.2,
- Cu: 0.05 - 0.30,
- Cr : 0.05 - 0.30,
- Fe :  $\leq$  0.4,
- Si :  $\leq$  0.3,
- 25 Zn :  $\leq$  0.25,
- Ti :  $\leq$  0.15,

impurities < 0.05 each and < 0.15 total, remainder aluminium,

- (b) the slab is homogenized at a temperature of at least 550 °C,
- 30 (c) the homogenized slab is hot rolled to an intermediate rolled product having a thickness from 3 to 10 mm,
- (d) the intermediate rolled product is cold rolled into a sheet, optionally with an intermediate annealing during cold rolling,
- (e) the sheet is annealed at a temperature from 300°C to 400 °C and undergoes tension leveling with a stretching of at least 1%.

35 **[0010]** Yet another subject of the invention is the use of a sheet according to the invention to make a coated decorative part preferably a decorative part for an automobile, or a household appliance or a medical device.

**Description of the invention**

40 **[0011]** Unless otherwise indicated, all indications concerning the chemical composition of alloys are expressed as a percentage by weight based on the total weight of the alloy. The expression 1.4 Cu means that the copper content expressed in % by weight is multiplied by 1.4. The designation of the alloys is made in accordance with the regulations of The Aluminium Association, known to those skilled in the art.

45 The static mechanical properties in tension, in other words the ultimate tensile strength UTS, the conventional yield strength at 0.2 % elongation TYS, and the elongation at break A%, are determined by a tensile test according to standard NF EN ISO 6892-1. The elongation (A%) at break was measured using a 50 mm base extensometer and is reported under A50. Scratch resistance was measured according to the method described in the example.

50 Unless stated otherwise, the definitions of standard EN 12258 (2012) apply. A sheet is a rolled product with a rectangular cross section, the uniform thickness of which is between 0.20 mm and 6 mm. In the context of the invention, a sheet is not a clad sheet.

**[0012]** A preferred thickness of the sheet of the invention is from 0.35 mm to 1.5 mm and more preferably from 0.50 mm to 1.0 mm.

55 The inventors have found a sheet composition which solves the problem. In particular, with the simultaneous addition of Cu and Cr to an Al-Mg-Mn alloy, the sheet of the invention provides higher scratch resistance with similar formability and corrosion resistance than the known products.

The present inventors had first considered to use a high Mg content such as 1.8 wt.% in order to improve scratch resistance, however the products obtained had surface defects related to Lüders bands / Portevin-Le Chatelier bands

observed during forming. In order to avoid these bands, the magnesium content has to be at most 1.3 wt.%. A minimum Mg content of 0.8 wt.% is needed to obtain sufficient strength and scratch resistance. Preferably the minimum Mg content is 0.9 wt.%. Preferably the maximum Mg content is 1.2 wt.% and more preferably 1.1 wt.%. In a preferred embodiment by wt.%, Mg : 0,9 - 1.1.

Mn is used to improve strength and scratch resistance. The Mn content is from 0.8 to 1.2 wt.%. Preferably the minimum Mn content is 0.85 wt.%, more preferably 0.90 wt.% and preferentially 0.95 wt.%. Preferably the maximum Mn content is 1.15 wt.% and more preferably 1.10 wt.% and preferentially 1.05 wt.%. In a preferred embodiment by wt.%, Mn : 0.85 - 1.15 and preferably Mn : 0.95 - 1.05.

Cu is added to improve strength and scratch resistance. The Cu content is from 0.05 to 0.30 wt.%. Preferably the minimum Cu content is 0.10 wt.%, more preferably 0.15 wt.%. Preferably the maximum Cu content is 0.25 wt.% and more preferably 0.20 wt.%. In a preferred embodiment by wt.%, Cu : 0.10 - 0.25 and preferably Cu : 0.15 - 0.20.

Cr is added to improve strength and scratch resistance. The Cr content is from 0.05 to 0.30 wt.%. Preferably the minimum Cr content is 0.10 wt.%, more preferably 0.15 wt.%. Preferably the maximum Cr content is 0.27 wt.% and more preferably 0.25 wt.%. In a preferred embodiment by wt. % Cr : 0.10 - 0.30 and preferably Cr : 0.15 - 0.25.

Fe and Si have to be limited to a maximum of 0.4 wt.% and 0.3 wt.%, respectively, to obtain the desired formability. A minimum content is however beneficial for surface aspects by limiting, for example, orange peel aspect on formed parts. The inventors believe that Fe and Si additions increase the Particle Stimulated Nucleation effect during recrystallization compared to a purer chemistry, which leads to smaller grains and limits the orange peel on formed parts. Preferably the minimum Fe content is 0.15 wt.%, more preferably 0.20 wt.%. Preferably the maximum Fe content is 0.35 wt.% and more preferably 0.30 wt.%. In a preferred embodiment by wt.%, Fe : 0.15 - 0.35 and/or Si : 0.10 - 0.25.

Preferably the minimum Si content is 0.10 wt.%, more preferably 0.15 wt.% and even more preferably 0.18 wt.%. Preferably the maximum Si content is 0.25 wt.% and more preferably 0.23 wt.%.

With the selected preferred Fe and Si contents recyclability of the alloy is quite satisfactory.

The Zn content is limited to a maximum of 0.25 wt.%. Further limiting the zinc content usually degrades recyclability. In an embodiment the Zn content is at least 0.01 wt.%.

In another embodiment the Zn content is however limited to an impurity level of less than 0.01 wt.% to improve surface aspect.

The Ti content is limited to a maximum of 0.15 wt.%. Ti may be added to improve grain size control, in particular during casting. In an embodiment the Ti content is at least 0.01 wt.%. Preferably the maximum Ti content is 0.10 wt.% and more preferably 0.05 wt.%.

Other elements are impurities whose content is less than 0.05 wt.% each and 0.15 wt.% total.

The method to make a sheet according to the invention comprises casting a slab with a composition according to the invention, homogenizing, hot and cold rolling the slab, annealing and tension leveling.

The slab is homogenized at a temperature of at least 550 °C, preferably of at least 575 °C. The maximum homogenizing temperature is defined to avoid incipient melting, it is typically 630 °C or 620 °C. Preferably, the homogenization is carried out during at least one hour and at most 72 hours. Before or after homogenization, the slab is usually scalped.

The homogenized slab is then hot rolled to an intermediate rolled product having a thickness from 3 to 10 mm. Preferably the initial hot rolling temperature is at least 430 °C.

The intermediate rolled product is then cold rolled into a sheet, optionally with an intermediate annealing during cold rolling. In an embodiment the intermediate rolled product is first cold rolled to a first thickness between 1.5 and 8.0 mm, then annealed at a temperature from 300 °C to 450 °C and then cold rolled to a second thickness between 0.20 mm and 6 mm. In another embodiment, the intermediate rolled product is directly cold rolled into a sheet with a thickness between 0.20 mm and 6 mm.

**[0013]** The sheet is then annealed at a temperature from 300 °C to 450 °C. The annealing is designed to obtain full recrystallization. The temper after annealing is named O-temper. Finally, the sheet undergoes tension leveling with a stretching of at least 1 %. Tension leveling is needed to improve flatness of the product. Advantageously, a minimum stretching during tension leveling of 1.8 % and more preferably 2 %, is performed in order to improve the yield strength after curing of the coating, typically of 1 to 10 minutes at 150 to 230 °C. In order to prevent surface defects and preserve good formability a maximum stretching of 3.5 %, more preferably 3 %, during tension leveling is performed.

The sheets of the invention have preferably, after tension leveling a TYS in the longitudinal direction of at least 130 MPa and A% of at least 16 % and after further thermal treatment of 4 minutes at 195 °C, typically corresponding to curing of the coating, a TYS in the longitudinal direction of at least 110 MPa and A% of at least 16 %. The sheets according to the invention are preferably used to make a coated decorative part, preferably for an automobile, or a household appliance or a medical device. Preferably they are used to make an automobile interior finishing element selected in the list consisting of a door handle, a gearbox trim, a trim element for a center console, a trim for a dashboard, a panel for a dashboard, a trim for a door, a panel for a door and a capacitive function element or an automobile exterior element selected in the list consisting of a window surrounds, a body side or door trim strip, a tailgate trim strip, a radiator grille trim, wheel hub cover, a beltline and a bumper piping.

## EP 4 050 115 A1

**[0014]** The details of the invention will be understood better with the help of the example below, which is not, however, restrictive in its scope.

### Example

**[0015]** The alloys disclosed in Table 1 where cast in the form of small ingots of dimension 70 mm x 190 mm x 1500 mm. Alloy C is according to the invention.

Table 1: Composition in wt. %

Alloy	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Zn	Ti
<b>A</b>	0.11	0.20	0.17	0.97	1.1	< 0.01	<0.01	0.01
<b>B</b>	0.10	0.19	< 0.01	1.02	1.3	0.18	<0.01	0.01
<b>C</b>	0.11	0.20	0.16	1.00	1.1	0.21	<0.01	0.01

**[0016]** The ingots were scalped and homogenized 3 hours at 600 °C. The ingots were hot rolled with a starting temperature above 500 °C down to a thickness of 7.6 mm and cold rolled to a thickness of 2.5 mm. An intermediate annealing of 1 hour at 340 °C was carried out and the cold rolling was continued to sheets with a thickness of 0.76 mm. The sheets were annealed 1 hour at 340 °C to obtain a fully recrystallized grain structure. The sheets were then tension-levelled with a stretching of 2.5 % in the rolling direction.

In order to obtain representative mechanical properties of the finished part, which is formed and coated, a coating curing simulation of 4 min at 195 °C was carried out. Mechanical properties characterized in the longitudinal direction L are provided in Table 2.

Table 2: Mechanical properties of the sheets

Alloy	Recrystallized	+ stretching 2.5 % by tension leveling		+ 4 min at 195°C			
	TYS (MPa)	TYS (MPa)	A50 (%)	TYS (MPa)	UTS (MPa)	TYS/UTS (-)	A50 (%)
<b>A</b>	65	126	17.2	105	182	0.57	15.8
<b>B</b>	64	127	18.2	102	177	0.58	18.3
<b>C</b>	68	135	17.8	113	191	0.59	17.0

**[0017]** All samples were also coated with the same varnish thickness and scratch resistance was tested with a scratch hardness tester (Erichsen Model 435 pen).

The test range used is 0 to 20N (range 3 of the apparatus). The test wheel used is the provided steel disc. The hardness tester is placed perpendicularly onto the surface to be tested and is pressed down so that the guide wheels touch the surface. In this way the preset force acting upon the test disc is fully effective on the test surface. The instrument is then moved, the wheel being over the specimen to be tested.

**[0018]** The scratch resistance is related to maximum force at which the test body does not leave any trace on the test surface. The results are presented in Table 3 in a comparative manner compared to a typical requirement "+" slightly above requirement, "++" significantly above requirement.

Table 3: Scratch resistance of the sheets

Alloy	scratch resistance
<b>A</b>	+
<b>B</b>	+
<b>C</b>	++

**[0019]** With the composition according to the invention, an improved scratch resistance is obtained, without degrading elongation before or after the curing.

**Claims**

1. Sheet made of an aluminium alloy comprising, by weight %

5 Mg : 0.8 - 1.3,  
Mn : 0.8 - 1.2,  
Cu: 0.05 - 0.30,  
Cr : 0.05 - 0.30,  
Fe :  $\leq$  0.4,  
10 Si :  $\leq$  0.3,  
Zn :  $\leq$  0.25,  
Ti :  $\leq$  0.15,

impurities < 0.05 each and < 0.15 total, remainder aluminium.

15 2. Sheet according to claim 1 comprising by wt. % Cr : 0.10 - 0.30 and preferably Cr : 0.15 - 0.25.

3. Sheet according to claim 1 or claim 2 comprising, by wt.%, Fe : 0.15 - 0.35 and/or Si : 0.10 - 0.25.

20 4. Sheet according to anyone of claims 1 to 3 comprising, by wt.%, Mg : 0.9 - 1.1.

5. Sheet according to anyone of claims 1 to 4 comprising, by wt.%, Mn : 0.85 - 1.15 and preferably Mn : 0.95 - 1.05.

25 6. Sheet according to anyone of claims 1 to 5 comprising, by wt.%, Cu : 0.10 - 0.25 and preferably Cu : 0.15 - 0.20.

7. Sheet according to anyone of claims 1 to 6 wherein TYS in the longitudinal direction is at least 130 MPa and A% in the longitudinal direction is at least 16%.

30 8. Sheet according to anyone of claims 1 to 7 wherein, after a thermal treatment of 4 min at 195 °C TYS in the longitudinal direction is at least 110 MPa and A% in the longitudinal direction is at least 16%.

9. Method to make a sheet according to anyone of claims 1 to 8 wherein,

(a) a slab is cast of an aluminium alloy comprising, by weight %

35 Mg : 0.8 - 1.3,  
Mn : 0.8 - 1.2,  
Cu: 0.05 - 0.30,  
Cr : 0.05 - 0.30,  
40 Fe :  $\leq$  0.4,  
Si :  $\leq$  0.3,  
Zn :  $\leq$  0.25,  
Ti :  $\leq$  0.15,

45 impurities < 0.05 each and < 0.15 total, remainder aluminium,

(b) the slab is homogenized at a temperature of at least 550 °C,

(c) the homogenized slab is hot rolled to an intermediate rolled product having a thickness from 3 to 10 mm,

(d) the intermediate rolled product is cold rolled into a sheet, optionally with an intermediate annealing during cold rolling,

50 (e) the sheet is annealed at a temperature from 300°C to 400 °C and undergoes tension leveling with a stretching of at least 1%.

10. Use of a sheet according to anyone of claims 1 to 9 to make a coated decorative part preferably a decorative part for an automobile, or a household appliance or a medical device.

55 11. Use according to claim 10 to make an automobile interior finishing element selected in the list consisting of a door handle, a gearbox trim, a trim element for a center console, a trim for a dashboard, a panel for a dashboard, a trim for a door, a panel for a door and a capacitive function element or an automobile exterior element selected in the

**EP 4 050 115 A1**

list consisting of a window surrounds, a body side or door trim strip, a tailgate trim strip, a radiator grille trim, wheel hub cover, a beltline and a bumper piping.

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EUROPEAN SEARCH REPORT

Application Number  
EP 21 15 9556

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The present search report has been drawn up for all claims			
Place of search <b>The Hague</b>		Date of completion of the search <b>15 July 2021</b>	Examiner <b>Ugarte, Eva</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 21 15 9556

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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