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(54) **Heat-resistant alloy for production of aerosol cans**

(57) Heat-resistant alloy for production of aerosol cans from a material having the following contents of alloying additions in percent by weight:
according to the standards EN 573-3
EN AW 1050A
Si ≤ 0.25 ; Fe ≤ 0.40 ; Cu ≤ 0.05 ; Mn ≤ 0.05 ; Mg ≤ 0.05 ; Zn ≤ 0.07 ; Ti ≤ 0.05 ;
EN AW 3102
Si ≤ 0.40 ; Fe ≤ 0.70 ; Cu ≤ 0.10 ; Mn 0.05-0.40; Zn ≤ 0.30 ; Ti ≤ 0.10 ;
EN AW 3207
Si ≤ 0.30 ; Fe ≤ 0.45 ; Cu ≤ 0.10 ; Mn 0.40-0.80; Mg ≤ 0.10 ; Zn ≤ 0.10 ;

or with more specific compositions

- Si = $0.05 \div 0.09$; Fe = $0.15 \div 0.27$; Cu ≤ 0.005 ; Mn ≤ 0.005 ; Mg ≤ 0.005 ; Zn ≤ 0.015 ; Ti = $0.01 \div 0.03$;
- Si = $0.05 \div 0.09$; Fe = $0.23 \div 0.27$; Cu ≤ 0.005 ; Mn = $0.28 \div 0.32$; Mg ≤ 0.005 ; Zn ≤ 0.015 ; Ti = $0.01 \div 0.03$;
- Si = $0.05 \div 0.09$; Fe = $0.23 \div 0.27$; Cu ≤ 0.005 ; Mn = $0.58 \div 0.62$; Mg ≤ 0.005 ; Zn ≤ 0.015 ; Ti = $0.01 \div 0.03$;

where each composition contains added Zr in the amount ranging between 0.05 and 0.20% by weight, the sum of the contained amounts of all the secondary elements being $\leq 0.10\%$ by weight and Al content is remainder.

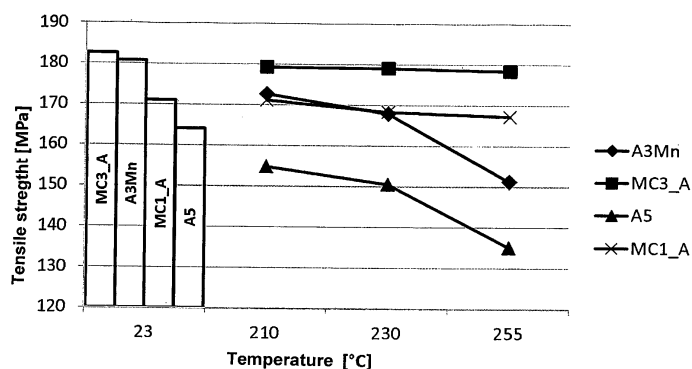


Fig.1

Description

Background of the invention

5 **[0001]** At the present time, aerosol cans are manufactured either from pure aluminium or from aluminium alloys. In the former case, 1000-series aluminium according to the European standard EN 573-3 is mostly used. The most common aluminium grades are EN AW 1050A having the minimum Al content of Al 99.5% and EN AW 1070A having the minimum Al content of 99.7%.

10 **[0002]** In the latter case, aerosol cans are mostly made of 3000-series aluminium alloys according to the European standard EN 573-3. The most common aluminium alloy grades are EN AW 3102 having the Mn content of approximately 0.3% and EN AW 3207 having the Mn content of approximately 0.6%.

[0003] For the manufacture of aerosol cans, aluminium and its alloys are mostly supplied in the form of slugs.

[0004] Such slugs are manufactured in a continuous two-phase process comprising the following steps.

15 a.) Phase 1 - Manufacture of strips

[0005]

- Melting down ingots in melting furnaces.
- 20 • Transfer of molten aluminium into a holding furnace.
- Continuous casting of a strip.
- Hot rolling of the cast strip.
- Cold rolling of the cast strip.
- Coiling the rolled strip.

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b.) Phase 2 - Manufacture of slugs

[0006]

- 30 • Uncoiling the rolled strip.
- Punching the slugs in a blanking press.
- Annealing of the slugs.
- Cooling down of the slugs.
- Surface finishing of the slugs (tumbling, sand blasting, vibration).
- 35 • Packaging of the slugs.

[0007] The method of manufacturing aerosol cans can be described as follows:

- Applying a lubricant to the slugs.
- 40 • Backward impact extrusion.
- Wall ironing of the can.
- Brushing of the can.
- Degreasing of the can.
- Application of the inner varnish layer + curing in a polymerization oven
- 45 • Application of the basecoat + curing in oven.
- Application of the decorative inks + curing in oven.
- Application of the overcoat + curing in oven.
- Shaping the cans on the necking press.

50 **[0008]** The above described materials according to the standards EN AW 1050A and EN AW 1070A respectively exhibit significant levels of formability and work hardening which make them ideal for the manufacture of aerosol cans in a backward impact extrusion process. Aluminium alloys EN AW 3102 and EN AW 3207 offer enhanced mechanical properties (strength) and hence better rigidity and pressure resistance of finished aerosol cans. Nevertheless, the mechanical properties of these materials are changed when the cans pass through a curing oven in which polymerization of the inner varnish layer takes place. The curing (polymerization) temperatures of the inner varnish layers range between 210 and 255°C, the respective curing process lasting about 10 minutes. Under such temperatures, partial annealing of the can bodies occurs causing the mechanical strength of the same to decrease.

55 **[0009]** In order to eliminate the above undesirable effect, thicker walls of the aerosol cans must be selected which are

necessary for achieving the required safety and technological specifications, particularly a sufficient pressure resistance, of the cans. This leads to an significant increase of the consumption of input materials.

Summary of the invention

[0010] The above drawbacks are eliminated by the heat-resistant alloy for the production of aerosol cans having the features defined in the characterizing part of claim 1.

Brief description of the drawings

[0011] The invention will be further explained with reference to the accompanying drawings in which Fig. 1 shows the temperature dependences of the strengths of the new alloys in comparison with those of standard alloys by means of a graphical representation.

[0012] The subject matter of the present invention is a new, modified heat resistant aluminium based alloy provided for eliminating the effect of weakening the material of the cans passing through a curing oven. Thereby, the desired enhancement of the mechanical properties of aerosol cans is achieved in comparison with standard (conventionally used) materials, along with the reduction of the wall thickness and increase of the pressure resistance of the same. Particularly, the above favourable effect is achieved by adding an anti-recrystallization admixture formed by Zr (zirconium) for the purpose of modifying the compositions of aluminium and its alloys: EN AW 1050A, EN AW 3102, EN AW 3207.

[0013] The chemical compositions of the commonly used, non-modified alloys have the following limit values in accordance with EN 573-3 in percent by weight:

EN AW 1050A

Si $\leq$ 0.25; Fe $\leq$ 0.40; Cu $\leq$ 0.05; Mn $\leq$ 0.05; Mg $\leq$ 0.05; Zn $\leq$ 0.07; Ti $\leq$ 0.05; Al 99.5 min.

EN AW 3102

Si $\leq$ 0.40; Fe $\leq$ 0.70; Cu $\leq$ 0.10; Mn 0.05-0.40; Zn $\leq$ 0.30; Ti $\leq$ 0.10; Al remainder

EN AW 3207

Si $\leq$ 0.30; Fe $\leq$ 0.45; Cu $\leq$ 0.10; Mn 0.40-0.80; Mg $\leq$ 0.10; Zn $\leq$ 0.10; Al remainder

[0014] The alloys according to the invention have new chemical compositions with added Zr, the proportion of the new constituent ranging between 0.05 and 0.20% by weight. The addition of Zr gives rise to completely new alloys which cannot be categorized in the existing classes according to the standard EN 573-3. Therefore, the new alloys will be referred to as MC alloys hereinafter, namely MC1 (EN AW 1050A + Zr), MC3 (EN AW 3102 + Zr) and MC4 (EN AW 3207 + Zr). The compositions of the new alloys (in percent by weight) are as follows:

Alloy MC1

Si $\leq$ 0.25; Fe $\leq$ 0.40; Cu $\leq$ 0.05; Mn $\leq$ 0.05; Mg $\leq$ 0.05; Zn $\leq$ 0.07; Ti $\leq$ 0.05; Zr = 0.05÷0.20; Al remainder; (sum of all secondary elements $\leq$ 0.10)

Alloy MC3

Si $\leq$ 0.40; Fe $\leq$ 0.70; Cu $\leq$ 0.10; Mn 0.05÷0.40; Zn $\leq$ 0.30; Ti $\leq$ 0.10; Zr = 0.05÷0.20; Al remainder; (sum of all secondary elements $\leq$ 0.10)

Alloy MC4

Si $\leq$ 0.30; Fe $\leq$ 0.45; Cu $\leq$ 0.10; Mn 0.40÷0.80; Mg $\leq$ 0.10; Zn $\leq$ 0.10; Zr = 0.05÷0.20; Al remainder; (sum of all secondary elements $\leq$ 0.10)

[0015] Preferably, the new alloys have the following chemical compositions (in percent by weight) which are optimized for the technology of production aerosol cans:

Alloy MC1

Si = 0.05÷0.09; Fe = 0.15÷0.27; Cu $\leq$ 0.005; Mn $\leq$ 0.005; Mg $\leq$ 0.005; Zn $\leq$ 0.015; Ti = 0.01÷0.03; Zr = 0.05÷0.20; Al remainder; (sum of all secondary elements $\leq$ 0.10)

Alloy MC3

Si = 0.05÷0.09; Fe = 0.23÷0.27; Cu $\leq$ 0.005; Mn = 0.28÷0.32; Mg $\leq$ 0.005; Zn $\leq$ 0.015; Ti = 0.01÷0.03; Zr =

0.05÷0.20; Al remainder; (sum of all secondary elements ≤ 0.10)

Alloy MC4

Si = 0.05÷0.09; Fe = 0.23÷0.27; Cu ≤ 0.005; Mn = 0.58÷0.62; Mg ≤ 0.005; Zn ≤ 0.015; Ti = 0.01÷0.03; Zr = 0.05÷0.20; Al remainder; (sum of all secondary elements ≤ 0.10)

[0016] In order to verify the anti-recrystallization effect during the aerosol can production process, the new alloys were compared with the known, commonly used materials. The outcome is graphically represented in Fig. 1 where the first standard material according to EN AW 1050A, herein specifically referred to as alloy A5, is compared with the new alloy MC1_A and the second standard material according to EN AW 3102, herein specifically referred to as alloy A3Mn, is compared with the new alloy MC3_A containing the added anti-recrystallization constituent Zr. The cans, which were made of the above materials under the same technological conditions, had identical wall specifications.

[0017] The standard alloys used for comparison purposes of anti-recrystallization effect are designated as follows:

Alloy A5 (aluminium according to EN AW 1050A) having the following chemical composition in percent by weight:

Si = 0.08; Fe = 0.24; Cu ≤ 0.005; Mn ≤ 0.005; Mg ≤ 0.005; Zn = 0.01; Ti = 0.02; Al remainder

Alloy A3Mn (aluminium alloy according to EN AW 3102) having the following chemical composition in percent by weight:

Si = 0.07; Fe = 0.25; Cu ≤ 0.005; Mn = 0.29; Mg ≤ 0.005; Zn = 0.01; Ti = 0.02; Al remainder

[0018] The newly developed alloys used for comparison purposes of anti-recrystallization effect are designated as follows:

Alloy MC1_A having the following chemical composition in percent by weight:

Si = 0.08; Fe = 0.24; Cu ≤ 0.005; Mn ≤ 0.005; Mg ≤ 0.005; Zn = 0.01; Ti = 0.02; Zr = 0.11; Al remainder

Alloy MC3_A having the following chemical composition in percent by weight:

Si = 0.06; Fe = 0.23; Cu ≤ 0.005; Mn = 0.30; Mg ≤ 0.005; Zn = 0.01; Ti = 0.03; Zr = 0.12; Al remainder

[0019] Table 1 shows the mechanical properties of the cans made of the above materials. During the comparison, the values of the tensile strength (Rm) of the cans measured before and after the curing oven, in which the inner varnish layer was polymerized, were evaluated. Moreover, the hardness (HB) of the input semifinished products (slugs) was measured.

Table 1

Alloy	Hardness of the slug	Tensile strength Rm [MPa]			
		After the backward extrusion	After the curing (polymerization) oven of inner varnish		
			210°C/10min	230°C/10min	255°C/10min
A5	20.8	164.1	154.8	150.5	135.1
A3Mn	22	180.7	172.6	167.9	151.2
MC1_A	22	171.0	171.1	168.3	167.2
MC3_A	23.5	182.5	179.2	179.0	178.3

[0020] The results listed in Table 1 clearly show that the standard materials lose their tensile strength when being subject to the temperature of 255°C in the oven, the strength being decreased by 17.7% for aluminium A5 and by 16.3% for the alloy A3Mn. In contrast to that, the loss of strength of the alloys containing Zr is significantly lower, namely only 2.2% for the alloy MC1_A and 2.3% for the alloy MC3_A. In several cases, even an increase of the tensile strength of the new alloys was observed after they had passed through the curing oven.

[0021] The comparison of aluminium A5 with the alloy MC1_A shows that the value of the tensile strength of the latter

alloy was by 32.1 MPa higher after the passage through the polymerization oven under the temperature of 255°C.

[0022] The comparison of aluminium alloys A3Mn and MC3_A shows that the value of the tensile strength of the latter alloy was by 27.1 MPa higher after the passage through the polymerization oven under the temperature of 255°C.

[0023] Also advantageous proves to be the fact that although the alloy MC1_A containing the added Zr constituent has its tensile strength after the backward extrusion by 9.7 MPa lower in comparison with the alloy A3Mn, the passage of the alloy MC1_A through the polymerization oven under temperatures over 226°C causes the strength of this alloy to exceed the strength of the A3Mn alloy, even though the MC1_A alloy does not contain Mn.

[0024] The main advantages of the new alloys MC1, MC3 and MC4 particularly include:

- a.) Owing to the admixture of Zr, the alloys MC1, MC3 and MC4 contain a fine dispersion of Al_3Zr .
- b.) The presence of manganese in the alloys MC3 and MC4 additionally results in an increase of the strength of these alloys after undergoing a shaping process, this being due to the formation of the particles of Al_6Mn , $Al_6(FeMn)$ and $\alpha-Al(Mn,Fe)Si$.
- c.) The above particles become caught in the subgrain boundaries, thus preventing any recovery, formation of recrystallization nuclei or growth of recrystallized grains from occurring (increasing the recrystallization resistance).

Claims

1. Heat-resistant alloy for production of aerosol cans from a material having the following contents of alloying additions in percent by weight:

according to the standards EN 573-3

EN AW 1050A

$Si \leq 0.25$; $Fe \leq 0.40$; $Cu \leq 0.05$; $Mn \leq 0.05$; $Mg \leq 0.05$; $Zn \leq 0.07$; $Ti \leq 0.05$;

EN AW 3102

$Si \leq 0.40$; $Fe \leq 0.70$; $Cu \leq 0.10$; $Mn 0.05-0.40$; $Zn \leq 0.30$; $Ti \leq 0.10$;

EN AW 3207

$Si \leq 0.30$; $Fe \leq 0.45$; $Cu \leq 0.10$; $Mn 0.40-0.80$; $Mg \leq 0.10$; $Zn \leq 0.10$;

or with more specific compositions

- $Si = 0.05 \div 0.09$; $Fe = 0.15 \div 0.27$; $Cu \leq 0.005$; $Mn \leq 0.005$; $Mg \leq 0.005$; $Zn \leq 0.015$; $Ti = 0.01 \div 0.03$;

- $Si = 0.05 \div 0.09$; $Fe = 0.23 \div 0.27$; $Cu \leq 0.005$; $Mn = 0.28 \div 0.32$; $Mg \leq 0.005$; $Zn \leq 0.015$; $Ti = 0.01 \div 0.03$;

- $Si = 0.05 \div 0.09$; $Fe = 0.23 \div 0.27$; $Cu \leq 0.005$; $Mn = 0.58 \div 0.62$; $Mg \leq 0.005$; $Zn \leq 0.015$; $Ti = 0.01 \div 0.03$;

characterized in that each composition contains added Zr in the amount ranging between 0.05 and 0.20% by weight, the sum of the contained amounts of all the secondary elements being $\leq 0.10\%$ by weight and Al content is remainder.

2. Modified heat resistant aluminium alloy according to claim 1, **characterized in that** the content of added Zr ranges between 0.10 and 0.15% by weight.

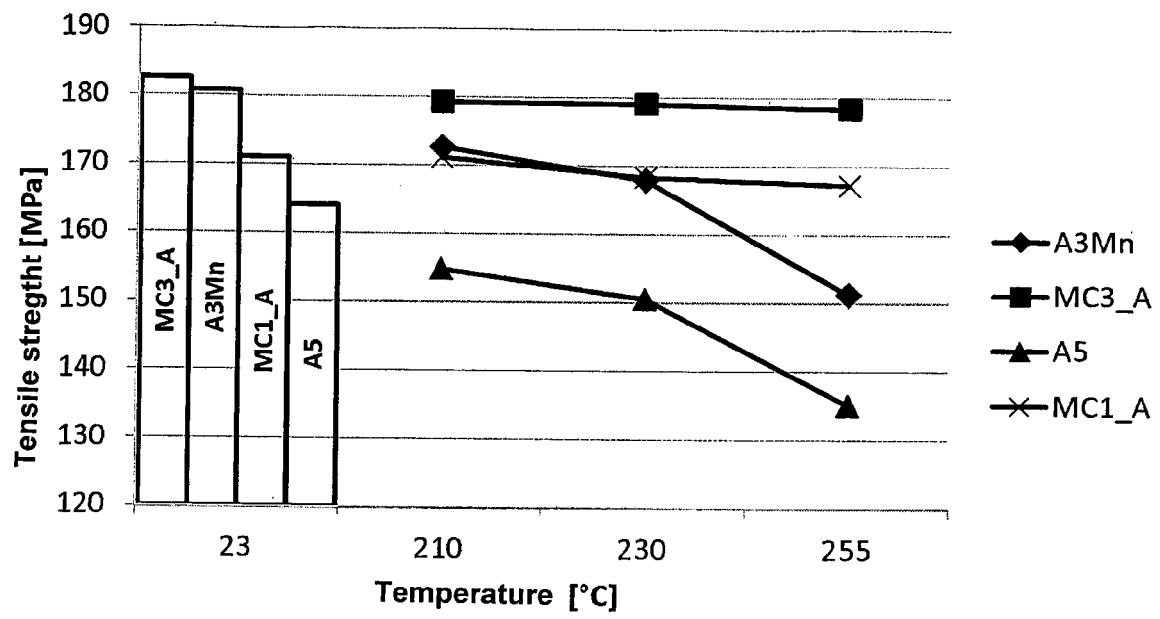


Fig.1



EUROPEAN SEARCH REPORT

Application Number
EP 13 46 6032

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
			C22C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 11 August 2014	Examiner Brown, Andrew
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			

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EPO FORM 1503 03/82 (P04C01)



Application Number

EP 13 46 6032

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 13 46 6032

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1, 2(partially)

Heat resistant alloy (EN AW 1050A)

2. claims: 1, 2(partially)

Heat Resistant Alloy (EN AW 3012)

3. claims: 1, 2(partially)

Heat Resistant Alloy (EN AW 3207)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 13 46 6032

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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11-08-2014

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