Title: ALUMINUM ALLOYS WITH ENHANCED FORMABILITY AND ASSOCIATED METHODS

Abstract: Disclosed is an aluminum alloy for aluminum bottle applications, including methods of producing highly shaped aluminum products, such as bottles or cans, comprising the aluminum alloy. In some cases, the aluminum alloy has improved high strain rate formability at elevated temperatures and improved earing, which results in reduced spoilage rates. In one non-limiting example, the disclosed alloys have stable values greater than or equal to 0.035, where $\varepsilon_{\text{stable}} = \varepsilon_{\gamma} \cdot \varepsilon_{\delta}$ and $\varepsilon_{\gamma}$ represents the strain at which work hardening stage IV starts and $\varepsilon_{\delta}$ represents the strain at which diffuse necking ends. In some cases, the disclosed alloys have an earing balance from about $-3.5\%$ to about $2\%$ and a mean earing of less than or equal to $5.5\%$. [Continued on next page]
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ALUMINUM ALLOYS WITH ENHANCED FORMABILITY AND ASSOCIATED METHODS

REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 62/330,554, filed on May 2, 2016 and entitled ALUMINUM ALLOYS WITH ENHANCED FORMABILITY AND ASSOCIATED METHODS, the content of which is hereby incorporated in its entirety by this reference.

FIELD OF THE INVENTION

[0002] The invention relates to aluminum alloys with enhanced formability and methods of producing highly shaped aluminum products, such as bottles or cans.

BACKGROUND

[0003] Many modern methods of aluminum can or bottle manufacture require highly shapeable aluminum alloys. For shaped bottles, the manufacturing process typically involves first producing a cylinder using a drawing and wall ironing (DWI) process. The resulting cylinder is then formed into a bottle shape using, for example, a sequence of full-body necking steps, blow molding, or other mechanical shaping, or a combination of these processes. The demands on any alloy used in such a process or combination of processes are complex.

[0004] As one example, the Bottle Container Manufacturing System (BCMS) can be used to form the bottle through a number of necking and finishing progressions. In the BCMS process, the brim roll (BR) step is the last step of the finishing process during which a curl is formed above the thread on the top of the bottles. The split of the curl (i.e. BR split) is one of the largest contributors to the number of bottles rejected during inspection, such as by a vision camera inspection system. In some cases, more than 90% of the bottles rejected by the camera inspection system have BR splits. While manufacturers strive for an overall spoilage rate that is as low as possible, preferably less than 1%, the overall spoilage rate for the BCMS system can be 60% or more due to BR splits.

[0005] The forming of the curl in the BR step is a difficult forming process because forming the curl involves bending the metals outward, which is illustrated in FIG. 1A, and simultaneously expanding slightly the diameter of the cut edge, which is illustrated in FIG. 1B. In addition, because the BR step is the last step of the shaping processes, the metals are already in highly deformed conditions with little formability left to accommodate further straining.
SUMMARY

[0006] The terms “invention,” “the invention,” “this invention” and “the present invention” used in this patent are intended to refer broadly to all of the subject matter of this patent and the patent claims below. Statements containing these terms should be understood not to limit the subject matter described herein or to limit the meaning or scope of the patent claims below. Embodiments of the invention covered by this patent are defined by the claims below, not this summary. This summary is a high-level overview of various embodiments of the invention and introduces some of the concepts that are further described in the Detailed Description section below. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used in isolation to determine the scope of the claimed subject matter. The subject matter should be understood by reference to appropriate portions of the entire specification of this patent, any or all drawings and each claim.

[0007] Provided are alloys that display high strain rate formability at elevated temperatures. The alloys can be used for producing highly shaped aluminum products, including bottles and cans, while reducing the incidence of splitting. The disclosed alloys can sustain high levels of deformation during mechanical shaping or blow molding for the bottle shaping processes and function well during the DWI process.

[0008] In one example, the aluminum alloy has a spoilage rate due to BR split that is less than or equal to 0.025 (or 25 %), such as less than or equal to 0.015 (or 15 %) or less than or equal to 0.010 (or 10 %). In some examples, a combination of good earing and stable strain provides the reduced spoilage rate. In certain aspects, the aluminum alloys have a stable strain, ε_{stable}, greater than or equal to 0.035 (or 3.5 %). In some examples, the stable strain, ε_{stable}, is greater than or equal to 0.042 (or 4.2 %), greater than or equal to 0.045 (or 4.5 %), or greater than or equal to 0.060 (or 6.0 %). In some examples, the aluminum alloys have an earing balance between -3.5 % and 2.0 %, such as between -3.0 % and 2.0 % or between -2.5 % and 2.0 %. In some examples, the aluminum alloys have a mean earing of less than or equal to 5.5 %, such as less than 5 %.

[0009] Other objects and advantages of the invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE FIGURES

[0010] The features and components of the following figures are illustrated to emphasize the general principles of the present disclosure. Corresponding features and components throughout the figures can be designated by matching reference characters for the sake of consistency and clarity.
FIG. 1A illustrates the initial stage of curling of an aluminum bottle during the BR step of the BCMS process.

FIG. 1B illustrates the final stage of curling of an aluminum bottle during the BR step of the BCMS process.

FIG. 2 is a graph comparing the stress-strain relationship of two alloys according to an aspect of the current disclosure.

FIG. 3 is a graph comparing the work hardening rates of the alloys of FIG. 2 according to an aspect of the current disclosure.

FIG. 4 is a chart comparing example coils according to an aspect of the current disclosure.

DETAILED DESCRIPTION

The subject matter of examples of the present invention is described here with specificity to meet statutory requirements, but this description is not necessarily intended to limit the scope of the claims. The claimed subject matter may be embodied in other ways, may include different elements or steps, and may be used in conjunction with other existing or future technologies. This description should not be interpreted as implying any particular order or arrangement among or between various steps or elements except when the order of individual steps or arrangement of elements is explicitly described.

In this description, reference is made to alloys identified by aluminum industry designations, such as "series." For an understanding of the number designation system most commonly used in naming and identifying aluminum and its alloys, see "International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys" or "Registration Record of Aluminum Association Alloy Designations and Chemical Compositions Limits for Aluminum Alloys in the Form of Castings and Ingot," both published by The Aluminum Association.

The aluminum alloys referenced herein are described in terms of their elemental composition in weight percentage (wt. %) based on the total weight of the alloy. In certain examples of each alloy, the remainder is aluminum, with a maximum wt. % of 0.15 % for the sum of the impurities. All ranges disclosed herein encompass any and all subranges subsumed therein. For example, a stated range of "1 to 10" includes any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more, e.g. 1 to 6.1, and ending with a maximum value of 10 or less, e.g., 5.5 to 10.

Reference is made in this application to alloy temper or condition. For an understanding of the alloy temper descriptions most commonly used, see "American
National Standards (ANSI) H35 on Alloy and Temper Designation Systems.” An H condition or temper refers to an aluminum alloy after strain hardening.

[0020] As used herein, the meaning of "room temperature" can include a temperature of from about 15 °C to about 30 °C, for example about 15 °C, about 16 °C, about 17 °C, about 18 °C, about 19 °C, about 20 °C, about 21 °C, about 22 °C, about 23 °C, about 24 °C, about 25 °C, about 26 °C, about 27 °C, about 28 °C, about 29 °C, or about 30 °C.

[0021] Disclosed is an aluminum alloy system for aluminum bottle applications, where the alloys exhibit desirable high strain rate formability at elevated temperatures. Because of the high strain rate formability, the disclosed alloys are highly formable and usable in high-speed production processes for manufacturing highly shaped cans and bottles.

[0022] In some examples, the disclosed aluminum alloys have a reduced rate of spoilage due to reduced BR split during the processes used to form the cans or bottles. FIG. 1A illustrates the initial stage of curling of an aluminum bottle during the BR step of the BCMS process. FIG. 1B illustrates the final stage of curling of an aluminum bottle during the BR step of the BCMS process.

[0023] In particular, in various examples, the aluminum alloys have a spoilage rate due to BR split that is less than or equal to about 0.025 (or 25 %), such as less than or equal to about 0.015 (or 15 %) or less than or equal to about 0.010 (or 10 %).

[0024] The aluminum alloys also have increased stable strain and improved earing, as described in greater detail below. The increased stable strain and the improved earing of the aluminum alloys reduce the spoilage rate due to reduced BR split.

[0025] Stable strain, ε_{stable}, is related to stage IV work hardening strain, ε_{IV}, and diffused necking strain, ε_{DF}. In certain aspects, the disclosed aluminum alloys have a stable strain, ε_{stable}, greater than or equal to about 0.035 (or 3.5 %). In some non-limiting examples, the stable strain, ε_{stable}, is greater than or equal to about 0.042 (or 4.2 %), greater than or equal to about 0.045 (or 4.5 %), or greater than or equal to about 0.060 (or 6.0 %).

[0026] The stable strain, ε_{stable}, of an aluminum alloy can be calculated from the derivative of an engineering stress-strain curve of that alloy. As one non-limiting example, FIG. 2 illustrates the engineering stress-strain curves (work hardening curves) for an Alloy A and an Alloy B. In this non-limiting example, Alloy A is an aluminum alloy with a composition of about 0.193 wt. % Si, about 0.416 wt. % Fe, about 0.096 wt. % Cu, about 0.895 wt. % Mn, about 0.938 wt. % Mg, about 0.012 wt. % Cr, about 0.060 wt. % Zn, about 0.012 wt. % Ti, and up to about 0.15 wt. % impurities, with the remainder as Al. Alloy B is an aluminum alloy with a composition of about 0.304 wt. % Si, about 0.492 wt. % Fe, about 0.125 wt. % Cu, about 0.882 wt. % Mn, about 0.966 wt. % Mg, about 0.019 wt. % Cr, about 0.071 wt. % Zn, about 0.020 wt. % Ti, and up to about 0.15 wt. % impurities, with the remainder as Al.
[0027] In FIG. 2, the stress $\sigma$ is shown along the y-axis in MPa and the strain $\varepsilon$ is shown along the x-axis. The derivative is normalized by the stress values of the work hardening curve, and is represented by the parameter $H$, which can be represented as:

$$H = \frac{1}{\sigma} \left( \frac{d\sigma}{d\varepsilon} \right)$$

where $\varepsilon$ represents the strain and $\sigma$ represents the stress.

[0028] FIG. 3 illustrates a plot of the normalized derivative $H$ values versus the true strain $\varepsilon$. Referring generally to FIG. 3, the start strain, $\varepsilon_{Sx}$, for each alloy is the strain at which work hardening stage IV starts. Work hardening stage IV refers to the further dynamic recovery (which releases the stored energy by removal or rearranging the defects, primarily dislocation in the crystal structure during the deformation) taking place for the alloy after work hardening stage III (where the work hardening rate sharply decreases), leading to an eventual actual saturation (when dynamic recovery can balance the work hardening during the deformation) of the flow stress. The start strain $\varepsilon_0$ is obtained by drawing a tangent line parallel to the initial normalized work hardening rate and taking the intercepts of the line at $H=0$. Referring specifically to Alloy A and Alloy B, the start strain $\varepsilon_{Sx}$ for Alloy A is represented by $\varepsilon_{S1}$ and the start strain $\varepsilon_{Sx}$ for Alloy B is represented by $\varepsilon_{S2}$. As illustrated in FIG. 3, a first tangent line 502 for Alloy A intercepts the line $H=0$ at a first true strain $\varepsilon_{S1}$ and a second tangent line 504 for Alloy B intercepts the line $H=0$ at a second true strain $\varepsilon_{S2}$.

[0029] A diffuse necking starting strain, $\varepsilon_d$, represents the strain where diffuse necking starts for the alloy. Diffuse necking refers to the phase when the alloy’s spatial extension is much larger than the sheet thickness and strain hardening is no longer able to compensate for the weakening due to the reduction of the cross section. This diffuse necking starting strain $\varepsilon_d$ is obtained from the intercept of the work hardening rate curve at $H=1$. Referring to FIG. 3, the diffuse necking starting strain $\varepsilon_d$ was the same for both Alloy A and Alloy B.

[0030] Referring generally to FIG. 3, the diffuse necking ending strain $\varepsilon_e$ is obtained from the intercept of the work hardening rate curve at $H=0.5$. Referring specifically to Alloy A and Alloy B, the diffuse necking ending strain $\varepsilon_e$ was the same for both Alloy A and Alloy B.

[0031] The stable strain, $\varepsilon_{stable}$, is the sum of the stage IV work hardening strain, $\varepsilon_{IV}$, and the diffuse necking strain, $\varepsilon_{DF}$. In other words, the stable strain is:

$$\varepsilon_{stable} = \varepsilon_{IV} + \varepsilon_{DF}$$
The stage IV work hardening strain $\varepsilon_{w4}$ is the strain in the work hardening stage IV, which can be calculated from $\varepsilon_4$, $\varepsilon_5$. The diffused necking strain $\varepsilon_{DF}$ is the strain during the diffuse necking, which can be calculated from $\varepsilon_F - \varepsilon_G$. Therefore, the stable strain $\varepsilon_{stable}$, which equals the sum of $\varepsilon_{IV}$ and $\varepsilon_{DF}$, can also be expressed as:

$$\varepsilon_{stable} = \varepsilon_F - \varepsilon_G.$$ 

Referring specifically to Alloy A and Alloy B, the Alloy A $\varepsilon_{stable} = \varepsilon_F - \varepsilon_{s1}$, and the Alloy B $\varepsilon_{stable} = \varepsilon_F - \varepsilon_{s2}$. Therefore, in general:

$$\text{Alloy B } \varepsilon_{stable} = \varepsilon_F - \varepsilon_{s2} > \text{Alloy A } \varepsilon_{stable} = \varepsilon_F - \varepsilon_{s1}$$

Both Alloy A and Alloy B were formed as bottles through the BCMS process. During the BCMS process, Alloy A had a spoilage rate due to BR split of about 60% while Alloy B had a spoilage rate due to BR split of about 13%. Therefore, Alloy B with the greater $\varepsilon_{stable}$ value had a reduced spoilage rate due to BR split.

In some cases, the disclosed aluminum alloys also have improved earing, which is determined by mean earing and earing balance. Earing is the formation of a wavy edge having peaks and valleys at the top edge of a drawn aluminum preform during processing. Earing is calculated by measuring the cup sidewall height around the circumference of the cup (from 0 to 360 degrees). Mean earing is calculated by the equation:

$$\text{Mean earing } (\%) = (\text{peak height} - \text{valley height}) / \text{cup height}.$$ 

Earing balance is calculated by the equation:

Earing balance $\text{(%) } = (\text{mean of two heights at 180 degree intervals} - \text{mean of four heights at 45 degree intervals})/\text{cup height}$.

In various examples, the aluminum alloys have an earing balance between about -3.5 % and about 2.0 %, such as between about -3.0 % and about 2.0 %, such as between about -2.5 % and about 2.0 %. In various aspects, the aluminum alloys have a mean earing of less than or equal to about 5.5 %, such as less than about 5 %.

In some examples, the aluminum alloys have a slab gauge before hot rolling of from about 1.1 in. to about 2.1 in., such as from about 1.2 in. to about 2.0 in. such as from
about 1.6 in. to about 2.0 in. In certain cases, the aluminum alloys have a hot band (HB) gauge of from about 0.12 in. to about 0.25 in., such as from about 0.13 in. to about 0.24 in., such as from about 0.18 in. to about 0.22 in. Hot band refers to the coil after hot rolling.

[0039] In various examples, the aluminum alloys have a yield strength (YS) of from about 185 Mpa to about 225 Mpa, such as from about 190 Mpa to about 220 Mpa. In some examples, the aluminum alloys have an ultimate tensile strength (UTS) of from about 205 Mpa to about 250 Mpa, such as from about 210 Mpa to about 240 Mpa. In various examples, as illustrated in FIG. 4, the earing, yield strength (YS), ultimate tensile strength (UTS), and stable strain can be utilized to get specific spoilage rates due to BR split.

[0040] As a non-limiting example, FIG. 4 is a table comparing the earing balance %, mean earing %, YS, UTS, stable strain %, and spoilage rate of five non-limiting example aluminum alloy coils A, B, C, D, and E formed from a 3104 aluminum alloy. The alloys are ranked in order from the alloy with the worst (highest) spoilage rate (the A coil) to the alloy with the best (lowest) spoilage rate (the E coil).

[0041] Strain in hot rolling is calculated by the equation:

\[
\text{Strain in hot rolling} = \ln(\text{entry gauge before hot rolling/exit gauge after hot rolling})
\]

[0042] Strain in cold rolling is calculated by the equation:

\[
\text{Strain in cold rolling} = \ln(\text{entry gauge before cold rolling/exit gauge after cold rolling})
\]

[0043] In FIG. 4, the ratio of finishing mill rolling reduction in hot rolling (FM reduction strain) to cold rolling reduction (CM reduction strain), which is also known as the ratio of FM reduction/CM reduction, is calculated by the equation:

\[
\text{Ratio of FM reduction strain/CM reduction strain} = \ln(\text{entry gauge before hot rolling/exit gauge after hot rolling})/ \ln(\text{entry gauge before cold rolling/exit gauge after cold rolling})
\]

[0044] Referring to FIG. 4, coil A had a -0.2 % earing balance, a 2.9 % mean earing, a YS of 199 Mpa, a UTS of 228 Mpa, a 3.2 % stable strain, and a spoilage rate of 65 %. Coil B had a -4.6 % earing balance, a 6.3 % mean earing, a YS of 204 Mpa, a UTS of 224 Mpa, a 4.6 % stable strain, and a spoilage rate of 20 %. Coil C had a -2.5 % earing balance, a 4.4 % mean earing, a YS of 191 Mpa, a UTS of 216 Mpa, a 6.2 % stable strain, and a 13 % spoilage rate. Coil D had a -1.29 % earing balance, a 4.0 % mean earing, a YS of 195 Mpa, a UTS of 218 Mpa, a 4.9 % stable strain, and an 11 % spoilage rate. Coil E had a -1.9 %
earing balance, a 4.6 % mean earing, a YS of 197 Mpa, a UTS of 218 Mpa, a 7.4 % stable strain, and a 2.6 % spoilage rate. In general, because coil E had the best combination of earing, yield strength, ultimate tensile strength, and stable strain within the ranges described above, coil E had the best spoilage rate.

[0045] The disclosed aluminum alloys have improved the materials' resistance to BR splits after extensive body necking stages such that the spoilage rate can be less than 10%. As such, alloys with higher stable strain $\varepsilon_{\text{stair}}$ and improved earing have lower spoilage rate.

[0046] In one example, the aluminum alloy comprises from about 0.15 wt. % to about 0.50 wt. % Si; from about 0.35 wt. % to about 0.65 wt. % Fe; from about 0.05 wt. % to about 0.30 wt. % Cu; from about 0.60 wt. % to about 1.10 wt. % Mn; from about 0.80 wt. % to about 1.30 wt. % Mg; from about 0.000 wt. % to about 0.080 wt. % Cr; from about 0.000 wt. % to about 0.500 wt. % Zn; from about 0.000 wt. % to about 0.080 wt. % Ti; and up to about 0.15 wt. % impurities, with the remainder as Al. In some examples, the aluminum alloy comprises about 0.304 wt. % Si, about 0.492 wt. % Fe, about 0.125 wt. % Cu, about 0.882 wt. % Mn, about 0.966 wt. % Mg, about 0.019 wt. % Cr, about 0.071 wt. % Zn, about 0.020 wt. % Ti, and up to about 0.15 wt. % impurities, with the remainder as Al. In other examples, the aluminum alloy comprises about 0.193 wt. % Si, about 0.416 wt. % Fe, about 0.096 wt. % Cu, about 0.895 wt. % Mn, about 0.937 wt. % Mg, about 0.012 wt. % Cr, about 0.06 wt. % Zn, about 0.012 wt. % Ti, and up to about 0.15 wt. % impurities, with the remainder as Al. Other examples of aluminum alloys are provided in U.S. Patent Application No. 14/974,661 filed December 18, 2015 and titled “Aluminum Alloy Suitable for the High Speed Production of Aluminum Bottle and the Process of Manufacturing Thereof,” which is hereby incorporated by reference in its entirety.

[0047] Aluminum alloys with lower spoilage rates can be produced by a combination of rolling and annealing processes. One exemplary method includes the sequential steps of: casting (such as direct chill (DC) casting); homogenizing; hot rolling; cold rolling (about 60–99 % thickness reduction); optional recrystallization annealing (about 290–500 °C/0.5–4 hrs.); further cold rolling (15–30 % reduction); and stabilization annealing (about 100–300°C/0.5–5 hrs.).

[0048] In another example, the method of making the aluminum alloy as described herein includes the sequential steps of: direct chill (DC) casting; homogenizing; hot rolling; cold rolling (about 60–99 % thickness reduction); optional recrystallization annealing (about 300–450 °C/1–2 hrs.); further cold rolling (about 15–30 % reduction); and stabilization annealing (about 120–260 °C/1–3 hrs.).
The final temper of the alloys can be, for example, either H2x (without inter-annealing) or H3x or H1x (with inter-annealing). Thus, the temper of the alloy can vary depending on the requirement of final products.

The alloys described herein can be cast into ingots using a direct chill (DC) process. The DC casting process is performed according to standards commonly used in the aluminum industry as known to one of ordinary skill in the art. Optionally, the casting process can include a continuous casting process. The continuous casting may include, but is not limited to, twin roll casters, twin belt casters, and block casters. In some cases, to achieve the desired microstructure, mechanical properties, and physical properties of the products, the alloys are not processed using continuous casting methods.

The cast ingot can then be subjected to further processing steps to form a metal sheet. In some examples, the further processing steps include subjecting a metal ingot to a homogenization step, a hot rolling step, a cold rolling step, an optional recrystallization annealing step, a second cold rolling step, and a stabilization annealing step.

The homogenization step can involve a one-step homogenization or a two-step homogenization. In some examples of the homogenization step, a one-step homogenization is performed in which an ingot prepared from the alloy compositions described herein is heated to attain a peak metal temperature (PMT). The ingot is then allowed to soak (i.e., held at the indicated temperature) for a period of time during the first stage. In other examples of the homogenization step, a two-step homogenization is performed where an ingot prepared is heated to attain a first temperature and then allowed to soak for a period of time. In the second stage, the ingot can be cooled to a temperature lower than the temperature used in the first stage and then allowed to soak for a period of time during the second stage.

Following the homogenization, a hot rolling process can be performed. In some examples, the ingots can be hot rolled to about a 5 mm thick gauge or less. For example, the ingots can be hot rolled to about a 4 mm thick gauge or less, about a 3 mm thick gauge or less, about a 2 mm thick gauge or less, or about a 1 mm thick gauge or less.

To obtain an appropriate balance of texture in the final materials, the hot rolling speed and temperature can be controlled such that full recrystallization of the hot rolled materials is achieved during coiling at the exit of the hot mill.

The hot rolled products can then be cold rolled to a final gauge thickness. In some examples, a first cold rolling step produces a reduction in thickness of from about 60–99 % (e.g. about 50–80 %, about 60–70 %, about 50–90 %, or about 60–80 %). For example, the first cold rolling step produces a reduction in thickness of about 65 %, about 70 %, about 75 %, about 80 %, about 85 %, about 90 %, or about 99%. In some examples, a
second cold rolling step produces a further reduction in thickness of from about 15–30 % (e.g., from about 20–25 %, about 15–25 %, about 15–20 %, about 20–30 %, or about 25–30 %). For example, the second cold rolling step produces a further reduction in thickness of about 15 %, 20 %, 25 %, or 30 %.

[0056] In some examples, an annealing step is a recrystallization annealing (e.g., after the initial cold rolling). In one example, the recrystallization annealing is at a metal temperature from about 290–500 °C for about 0.5–4 hrs. In one example, the recrystallization annealing is at a metal temperature from about 300–450 °C. In one example, the recrystallization is for about 1–2 hrs.

[0057] The recrystallization annealing step can include heating the alloy from room temperature to a temperature from about 290 °C to about 500 °C (e.g., from about 300 °C to about 450 °C, from about 325 °C to about 425 °C, from about 300 °C to about 400 °C, from about 400 °C to about 500 °C, from about 330 °C to about 470 °C, from about 375 °C to about 450 °C, or from about 450 °C to about 500 °C).

[0058] In certain aspects, an annealing step is stabilization annealing (e.g., after the final cold rolling). In one example, the stabilization annealing is at a metal temperature from about 100–300 °C for about 0.5–5 hrs. In another example, the stabilization annealing is at a metal temperature from about 120–280 °C for about 1–3 hrs. In a further example, the stabilization annealing is at a metal temperature of about 240 °C for about 1 hour.

[0059] The stabilization annealing step can include heating the alloy from room temperature to a temperature from about 100 °C to about 300 °C (e.g., from about 120 °C to about 250 °C, from about 125 °C to about 200 °C, from about 200 °C to about 300 °C, from about 150 °C to about 275 °C, from about 225 °C to about 300 °C, or from about 100 °C to about 175 °C).

[0060] The alloys and methods described herein can be used to prepare highly shaped metal objects, such as aluminum cans or bottles. The cold rolled sheets described above can be subjected to a series of conventional can and bottle making processes to produce preforms. The preforms can then be annealed to form annealed preforms. Optionally, the preforms are prepared from the aluminum alloys using a drawing and wall ironing (DWI) process and the cans and bottles are made according to other shaping processes as known to those of ordinary skill in the art.

[0061] The shaped aluminum bottles may be used for beverages including but not limited to soft drinks, water, beer, energy drinks and other beverages.

[0062] A collection of exemplary embodiments, including at least some explicitly enumerated as “ECs” (Example Combinations), providing additional description of a variety of embodiment types in accordance with the concepts described herein are provided below.
These examples are not meant to be mutually exclusive, exhaustive, or restrictive; and the invention is not limited to these example embodiments but rather encompasses all possible modifications and variations within the scope of the issued claims and their equivalents.

[0063] EC 1. A method comprising: direct chill casting an aluminum alloy ingot; homogenizing the aluminum alloy ingot for form a homogenized aluminum alloy ingot; hot rolling the homogenized aluminum alloy ingot to form a hot rolled aluminum alloy product; cold rolling the hot rolled aluminum alloy product in a cold rolling step to form a cold rolled aluminum alloy product, wherein the cold rolling step produces an about 60 – 99% thickness reduction; and stabilization annealing the cold rolled aluminum alloy product at a metal temperature from about 100–300 °C for about 0.5–5 hours, wherein the hot rolling, the cold rolling, and the stabilization annealing steps result in the cold rolled aluminum alloy product comprising an earing balance from about -3.5% to about 2%, a mean earing of less than or equal to about 5.5%, a yield strength of from about 185 Mpa to about 225 Mpa, an ultimate tensile strength of from about 205 Mpa to about 250 Mpa, a start strain $\varepsilon_S$ at which work hardening stage IV starts, and an end strain $\varepsilon_F$ at which diffuse necking ends, wherein an $\varepsilon_{slab-e}$ is greater than or equal to about 0.035, where $\varepsilon_{slab-e} = \varepsilon_F - \varepsilon_S$, wherein the earing balance is a difference between a mean of two heights of a cup formed from the cold rolled aluminum alloy product measured at 180° positions around a circumference of the cup and a mean of four heights of the cup measured at 45° positions around the circumference, and the difference is divided by a cup height, and wherein the mean earing is a difference between a peak height and a valley height, and the difference is divided by the cup height.

[0064] EC 2. The method of any preceding or subsequent example combination, wherein the cold rolling is a first cold rolling step, wherein the cold rolled product is a first cold rolled product, and wherein the method further comprises rolling the first cold rolled product in a second cold rolling step to form a second cold rolled product, wherein the second cold rolling produces an about 15 – 30% thickness reduction.

[0065] EC 3. The method of any preceding or subsequent example combination, further comprising: prior to the second cold rolling step, recrystallization annealing the first cold rolled product, wherein the metal temperature of the recrystallization annealing is from about 290 – 500 °C for about 0.5 – 4 hours.

[0066] EC 4. The method of any preceding or subsequent example combination, wherein the metal temperature of the recrystallization annealing is from about 300 – 450 °C for about 1 – 2 hours.

[0067] EC 5. The method of any preceding or subsequent example combination, wherein the metal temperature of the stabilization annealing is from about 120 – 260 °C for about 1 – 3 hours.
[0068] EC 6. The method of any preceding or subsequent example combination, further comprising: shaping the cold rolled aluminum alloy product to form a shaped product, wherein shaping the preform comprises brim rolling, and wherein the brim rolling step results in the shaped product comprising a spoilage rate less than or equal to about 25 % due to a brim roll split.

[0069] EC 7. The method of any preceding or subsequent example combination, wherein the spoilage rate is less than or equal to about 15 %.

[0070] EC 8. The method of any preceding or subsequent example combination, wherein the spoilage rate is less than or equal to about 10 %.

[0071] EC 9. The method of any preceding or subsequent example combination, wherein the shaped product is an aluminum bottle.

[0072] EC 10. The method of any preceding or subsequent example combination, wherein the shaped product is an aluminum can.

[0073] EC 11. The method of any preceding or subsequent example combination, wherein the $\varepsilon_{\text{strain}}$ is greater than or equal to about 0.042.

[0074] EC 12. The method of any preceding or subsequent example combination, wherein the $\varepsilon_{\text{strain}}$ is greater than or equal to about 0.050.

[0075] EC 13. The method of any preceding or subsequent example combination, wherein the earing balance is from about -3.0 % to about 2 %.

[0076] EC 14. The method of any preceding or subsequent example combination, wherein the earing balance is from about -2.5 % to about 2 %.

[0077] EC 15. The method of any preceding or subsequent example combination, wherein the mean earing is less than or equal to about 5.0 %.

[0078] EC 16. The method of any preceding or subsequent example combination, wherein the yield strength is from about 190 Mpa to about 220 Mpa.

[0079] EC 17. The method of any preceding or subsequent example combination, wherein the ultimate tensile strength is from about 210 Mpa to about 240 Mpa.

[0080] EC 18. The method of any preceding or subsequent example combination, wherein prior to hot rolling, the aluminum alloy has a slab gauge of from about 1.1 inches to about 2.1 inches.

[0081] EC 19. The method of any preceding or subsequent example combination, wherein the slab gauge is from about 1.2 inches to about 2.0 inches.

[0082] EC 20. The method of any preceding or subsequent example combination, wherein the slab gauge is from about 1.6 inches to about 2.0 inches.
EC 21. The method of any preceding or subsequent example combination, wherein the hot rolled aluminum alloy product has a hot band (HB) gauge of from about 0.12 inches to about 0.25 inches.

EC 22. The method of any preceding or subsequent example combination, wherein the HB gauge is from about 0.13 inches to about 0.24 inches.

EC 23. The method of any preceding or subsequent example combination, wherein the HB gauge is from about 0.18 inches to about 0.22 inches.

EC 24. The method of any preceding or subsequent example combinations, wherein the cold rolled aluminum alloy product has a ratio of hot rolling strain/cold rolling strain of from about 0.50 to about 1.55.

EC 25. The method of any preceding or subsequent example combination, wherein the ratio of hot rolling strain/cold rolling strain is from about 0.60 to about 1.15.

EC 26. The shaped product of any preceding or subsequent example combination, wherein the ratio of hot rolling strain/cold rolling strain is from about 0.80 to about 1.05.

EC 27. A shaped product comprising: an aluminum sheet comprising an alloy having an earing balance from about -3.5 % to about 2 %, a mean earing of less than or equal to 5.5 %, a yield strength of about 185 – 225 Mpa, an ultimate tensile strength of about 205 – 250 Mpa, a start strain $\varepsilon_S$ at which work hardening stage IV starts, and an end strain $\varepsilon_F$ at which diffuse necking ends; wherein an $\varepsilon_{stable}$ is greater than or equal to 0.035, where $\varepsilon_{stable} = \varepsilon_F - \varepsilon_S$, wherein the earing balance is a difference between a mean of two heights of a cup formed from the aluminum sheet measured at 180° positions around a circumference of the cup and a mean of four heights of the cup measured at 45° positions around the circumference, and the difference is divided by a cup height, and wherein the mean earing is a difference between a peak height and a valley height, and the difference is divided by the cup height.

EC 28. The shaped product of any preceding or subsequent example combination, wherein the shaped product is an aluminum bottle.

EC 29. The shaped product of any preceding or subsequent example combination, wherein the shaped product is an aluminum can.

EC 30. The shaped product of any preceding or subsequent example combination, wherein the $\varepsilon_{stable}$ is greater than or equal to about 0.042.

EC 31. The shaped product of any preceding or subsequent example combination, wherein the $\varepsilon_{stable}$ is greater than or equal to about 0.060.

EC 32. The shaped product of any preceding or subsequent example combination, wherein the earing balance is from about -3.0 % to about 2 %.
[0095] EC 33. The shaped product of any preceding or subsequent example combination, wherein the earing balance is from about -2.5% to about 2%.

[0096] EC 34. The shaped product of any preceding or subsequent example combination, wherein the mean earing is less than or equal to about 5.0%.

[0097] EC 35. The shaped product of any preceding or subsequent example combination, wherein the yield strength is from about 190 Mpa to about 220 Mpa.

[0098] EC 36. The shaped product of any preceding or subsequent example combination, wherein the ultimate tensile strength is from about 210 Mpa to about 240 Mpa.

[0099] EC 37. The shaped product of any preceding or subsequent example combination, wherein the aluminum sheet has a slab gauge of from about 1.1 inches to about 2.1 inches.

[0100] EC 38. The shaped product of any preceding or subsequent example combination, wherein the slab gauge is from about 1.2 inches to about 2.0 inches.

[0101] EC 39. The shaped product of any preceding or subsequent example combination, wherein the slab gauge is from about 1.6 inches to about 2.0 inches.

[0102] EC 40. The shaped product of any preceding or subsequent example combination, wherein the aluminum sheet has a hot band (HB) gauge of from about 0.12 inches to about 0.25 inches.

[0103] EC 41. The shaped product of any preceding or subsequent example combination, wherein the HB gauge is from about 0.13 inches to about 0.24 inches.

[0104] EC 42. The shaped product of any preceding or subsequent example combination, wherein the HB gauge is from about 0.18 inches to about 0.22 inches.

[0105] EC 43. The shaped product of any preceding or subsequent example combination, wherein the aluminum sheet has a ratio of hot rolling strain/cold rolling strain of from about 0.50 to about 1.55.

[0106] EC 44. The shaped product of any preceding or subsequent example combination, wherein the ratio of hot rolling strain/cold rolling strain is from about 0.60 to about 1.15.

[0107] EC 45. The shaped product of any preceding or subsequent example combination, wherein the ratio of hot rolling strain/cold rolling strain is from about 0.80 to about 1.05.

[0108] EC 46. A method of making the alloy of any preceding or subsequent example combination comprising: direct chill casting an aluminum ingot; homogenizing the aluminum ingot for form a homogenized ingot; hot rolling the homogenized ingot to form a hot rolled product; cold rolling the hot rolled product in a cold rolling step to form a cold rolled product, wherein the cold rolling step produces an about 60 – 99% thickness reduction; and
stabilization annealing the cold rolled product at a metal temperature from about 100 – 300 °C for about 0.5 – 5 hours.

[00109] EC 47. The method of any preceding or subsequent example combination, wherein the cold rolling is a first cold rolling step, wherein the cold rolled product is a first cold rolled product, and wherein the method further comprises rolling the first cold rolled product in a second cold rolling step to form a second cold rolled product, wherein the second cold rolling produces an about 15 – 30 % thickness reduction.

[00110] EC 48. The method of any preceding or subsequent example combination, further comprising: prior to the second cold rolling step, recrystallization annealing the first cold rolled product, wherein the metal temperature of the recrystallization annealing is from about 290 – 500 °C for about 0.5 – 4 hours.

[00111] EC 49. The method of any preceding or subsequent example combination, wherein the metal temperature of the recrystallization annealing is from about 300 – 450 °C for about 1 – 2 hours.

[00112] EC 50. The method of any preceding or subsequent example combination, wherein the metal temperature of the stabilization annealing is from about 120 – 260 °C for about 1 – 3 hours.

[00113] EC 51. A method of manufacturing the shaped product of any preceding or subsequent example combination comprising: forming the aluminum sheet into a preform; annealing the preform; and shaping the preform to form the shaped product, wherein shaping the preform comprises brim rolling, and wherein a spoilage rate due to a brim roll split during brim rolling is less than or equal to about 25 %.

[00114] EC 52. The method of manufacturing of any preceding or subsequent example combination, wherein the spoilage rate is less than or equal to about 15 %.

[00115] EC 53. The method of manufacturing of any preceding or subsequent example combination, wherein the spoilage rate is less than or equal to about 10 %.

[00116] The above-described aspects are merely possible examples of implementations, merely set forth for a clear understanding of the principles of the present disclosure. Many variations and modifications can be made to the above-described example(s) without departing substantially from the spirit and principles of the present disclosure. All such modifications and variations are included herein within the scope of the present disclosure, and all possible claims to individual aspects or combinations of elements or steps are intended to be supported by the present disclosure. Moreover, although specific terms are employed herein, as well as in the claims that follow, they are used only in a generic and descriptive sense, and not for the purposes of limiting the described invention, nor the claims that follow.
CLAIMS

That which is claimed is:

1. A method comprising:
   casting an aluminum alloy ingot;
   homogenizing the aluminum alloy ingot for form a homogenized aluminum alloy ingot;
   hot rolling the homogenized aluminum alloy ingot to form a hot rolled aluminum alloy product;
   cold rolling the hot rolled aluminum alloy product in a cold rolling step to form a cold rolled aluminum alloy product, wherein the cold rolling step produces an about 60 – 99 % thickness reduction; and
   stabilization annealing the cold rolled aluminum alloy product at a metal temperature from about 100 – 300 °C for about 0.5 – 5 hours,

   wherein the hot rolling, the cold rolling, and the stabilization annealing steps result in
   the cold rolled aluminum alloy product comprising an earing balance from about -3.5 % to about 2 %, a mean earing of less than or equal to 5.5 %, a yield strength of about 185 – 225 Mpa, an ultimate tensile strength of about 205 – 250 Mpa, a start strain \( \varepsilon_B \) at which work hardening stage IV starts, and
   an end strain \( \varepsilon_F \) at which diffuse necking ends,

   wherein an \( \varepsilon_{stable} \) is greater than or equal to 0.035, where \( \varepsilon_{stable} = \varepsilon_F - \varepsilon_B \),

   wherein the earing balance is an earing balance difference between a mean of two heights of a cup formed from the cold rolled aluminum alloy product measured at 180° positions around a circumference of the cup and a mean of four heights of the cup measured at 45° positions around the circumference, and
   the earing balance difference is divided by a cup height, and

   wherein the mean earing is a mean earing difference between a peak height and a valley height, and the mean earing difference is divided by the cup height.

2. The method of claim 1, wherein the cold rolling is a first cold rolling step, wherein the cold rolled product is a first cold rolled product, and wherein the method further comprises rolling the first cold rolled product in a second cold rolling step to form a second cold rolled product, wherein the second cold rolling produces an about 15 – 30 % thickness reduction.
3. The method of claim 1 or 2, further comprising, prior to the second cold rolling step, recrystallization annealing the first cold rolled product, wherein the metal temperature of the recrystallization annealing is from about 290 – 500 °C for about 0.5 – 4 hours.

4. The method of any one of the preceding claims, wherein the metal temperature of the recrystallization annealing is from about 300 – 450 °C for about 1 – 2 hours.

5. The method of any one of the preceding claims, wherein the metal temperature of the stabilization annealing is from about 120 – 260 °C for about 1 – 3 hours.

6. The method of any one of the preceding claims, further comprising shaping the cold rolled aluminum alloy product to form a shaped product, wherein shaping the cold rolled aluminum alloy product comprises brim rolling, and wherein the brim rolling step results in the shaped product comprising a spoilage rate less than or equal to 25 % due to a brim roll split.

7. The method of claim 6, wherein the spoilage rate is less than or equal to 15 %.

8. The method of manufacturing of claim 6, wherein the spoilage rate is less than or equal to 10 %.

9. The method of any one of claims 1 to 6, wherein the $\varepsilon_{\text{stable}}$ is greater than or equal to 0.042.

10. The method of claim 9, wherein the $\varepsilon_{\text{stable}}$ is greater than or equal to 0.060.

11. The method of any one of claims 1 to 6, wherein the earing balance is about -3.0 – 2 %.

12. The method of claim 10, wherein the earing balance is about -2.5 – 2 %.

13. The method of any one of claims 1 to 6, wherein the mean earing is less than or equal to 5.0 %.

14. The method of any one of claims 1 to 6, wherein the yield strength is about 190 – 220 Mpa.
15. The method of any one of claims 1 to 6, wherein the ultimate tensile strength is about 210 – 240 Mpa.

16. The method of any one of claims 1 to 6, wherein prior to hot rolling, the aluminum alloy ingot has a slab gauge of about 1.1 – 2.1 inches.

17. The method of any one of claims 1 to 6, wherein the hot rolled aluminum alloy product has a hot band (HB) gauge of about 0.12 – 0.25 inches.

18. The method of any one of claims 1 to 6, wherein the cold rolled aluminum alloy product has a ratio of hot rolling strain/cold rolling strain of about 0.50 – 1.55.

19. A shaped product formed by the method of claim 1.

20. The shaped product of claim 19, wherein the shaped product is at least one of an aluminum bottle and an aluminum can.
FIG. 3
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<th>Earing Bal. %</th>
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**FIG. 4**
INTERNATIONAL SEARCH REPORT

1. CLASSIFICATION OF SUBJECT MATTER

INV. C22C21/06 C22C21/08 C22F1/047
ADD.

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 C22F

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 database and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"S" document member of the same patent family

Date of the actual completion of the international search: 22 August 2017

Date of mailing of the international search report: 30/08/2017

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tél. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Brown, Andrew

Form PCT/ISA/210 (second sheet) (April 2005)
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