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

(11) Publication number: 0 154 702
B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **06.02.91**

(51) Int. Cl.[5]: **C 22 C 21/16,** C 22 C 21/08

(21) Application number: **84115197.0**

(22) Date of filing: **12.12.84**

(54) Aluminum alloy sheet for containers excellent in corrosion resistance and method of producing same.

(30) Priority: **05.03.84 JP 40494/84**

(43) Date of publication of application: **18.09.85 Bulletin 85/38**

(45) Publication of the grant of the patent: **06.02.91 Bulletin 91/06**

(84) Designated Contracting States: **DE FR GB**

(56) References cited:
EP-A-0 059 812
EP-A-0 097 319
EP-A-0 121 620
GB-A-2 027 743
GB-A-2 027 744
US-A-4 318 755

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EP 0 154 702 B1

Courier Press, Leamington Spa, England.

Description

The invention relates to corrosion resistant aluminum alloy sheets for containers and a method for producing the same. More particularly, the present invention is directed to aluminum alloy sheets useful as metallic can stock, especially as can end stock, for various saline beverages, such as health drinks, tomato juice, etc., food or the like.

From GB—A—2 027 743 a method for continuous strip casting of aluminum alloy for container components is known. With this known method aluminum scrap including consumer scrap, is recycled into aluminum sheet and aluminum containers. Aluminum scrap is melted in a furnace, and the melt is adjusted to form an alloy composition, consisting of silicon 0.1—1.0%, iron 0.1—0.9%, manganese 0.4—1.0%, magnesium 1.3—2.5%, copper 0.05—0.4%, and titanium 0—0.2%; balance essentially aluminum. The total amounts of Mg+Mn is 2—3.3%, and the Mg:Mn ratio between 1.4:1 and 4.4:1. The composition is cast and fabricated into sheet having strength and formability properties making it suitable for container manufacture.

A similar method is known from GB—A—2 027 744. Also with this known composition optional ingredients can include up to 0.1% chromium, up to 0.25% zinc and up to 0.2% titanium. With the known composition also copper and iron are included because they are indicated to be inevitable impurities in consumer scrap. It is also indicated that the presence of copper between 0.05 and 0.2% increases the strength and enhances the low earing properties of the alloy.

From EP—A—0 059 812 an aluminum alloy for forming sheets is known. A high strength, good formability of the aluminum alloy sheet particularly suitable for forming can-body parts and can-end parts which has received a final cold rolling reduction of at least 50% can be obtained if the alloy consists essentially of Mn 0.30 to 1.50 wt.%, Mg 0.50 to 2.00 wt.%, preferably 0.50 to 1.25 wt.%, Si 0.52 to 1.00 wt.% and the balance being aluminum and incidental impurities. If required, this known aluminum alloy forming sheet may also, in addition to the above elements, contain at least one component selected from the group consisting of Fe, Cu, Cr, Zn and Ti in the specified ranges.

From EP—A—0 097 319 a cold-rolled aluminum-alloy sheet having a high strength and a good formability as required for producting a DI can and also a process for producing the same is known. The sheet contains 0.1—2.0% Mn, 0.1—2.0% Mg, and 0.1 to 0.5% Si and has a thickness of 0.4 mm or less. The process for producing these sheets is characterized by holding the product at a temperature between 80 and 150°C, after the heat treatment at 400—580°C and prior to the final cold-rolling step.

Furthermore conventionally, mild steel materials, such as tin-free steel sheets or tinplate sheets, have been extensively employed in end parts of cans for the above-mentioned saline beverages and other foods. However, it is very difficult to open can ends made of the conventional mild sheet sheets because of its high strength and thus there is a risk that the user's hands will be wounded when opening can.

On the other hand, when aluminum alloy sheets having an easy open property are employed in manufacturing of can ends, the sheets are fabricated from Al-Mg type aluminum alloys, for example, JIS A 5052 and 5082 (throughout this specification, aluminum alloy numbers are represented under Japanese Industrial Standard designations unless otherwise indicated) and a resin coating with a sufficient thickness is applied onto the sheets with a view to protecting the aluminum alloy sheet ends from being corroded by the saline contents. However, it is very difficult for such coating treatment to provide a complete protection coating in industrial production and, thus, it has been for a long time highly desirable to develop corrosion resistant aluminum alloy sheets not suffering corrosion even if the applied protection coatings are incomplete.

As types of corrosions encountered with the conventional cans, there are known a microscopic self-corrosion related to the metallurgical structure of the material themselves and a macroscopic galvanic corrosion caused from a contact potential between a can end material and can body material. The contact potential arises when different materials are employed in can ends and bodies. Particularly, when a body is formed of mild steel and an end is made of aluminum alloy, such galvanic corrosion phenomenon considerably occurs. Therefore, the galvanic corrosion cannot be completely prevented unless the same material is employed in both parts of can bodies and can ends. When tin-free steel, tin plate or the similar mild steels ae employed in bodies and ends, the galvanic corrosion is slight, but these mild steels present difficulty as regards the easy opening property of the ends. On the other hand, in the case of using aluminum alloys in can bodies and can ends, for example, JIS A 3004 for bodies and the other different aluminum alloys, such as JIS A 5052 or A 5082, for ends, galvanic corrosion is not negligible.

Further, Al-Mg type aluminum alloys, for example, A 5052, A 5082, A 5182, or the like are employed as can end materials in can manufacturing for low salt content beverages, such as carbonated drinks and beer. In this case, galvanic corrosion is caused by the contact potential between the can end and the mild steel can body with increase in salt content and, thus, the aluminum alloy sheets cannot be emplolyed as can end stock unless coating having sufficient protection against galvanic corrosion are applied onto them.

Summary of the Invention

It is therefore an object of the present invention to overcome difficulties or problems encountered in conventional cans for saline beverages and other foods, and particularly to provide high corrosion resistant aluminum alloy sheets for containers which exhibit a considerable effect in reducing galvanic corrosion and other corrosions caused by saline contents when employed as can materials for saline beverages, food and other goods, especially as can end materials in combination with mild steel can body materials.

Another object of the present invention is to provide a method of producing the foregoing aluminum alloy sheets with an excellent corrosion resistance in a high yield.

In the first feature, the present invention resides in an aluminum alloy sheet with an excellent corrosion-resistance which consists of, in weight percentages:

Mg: from 0.50 to 2.0%

Si: from 0.10 to 0.70%

Mn: from 0.30 to 1.5%

Cu: from 0.52 to 1.0%

and the balance being, except for incidental impurities, aluminum, the spontaneous electrode potential of the sheet being in the range of from −700 to −630 mV in a 0.1% sodium chloride solution at 25°C, against an AgCl reference electrode.

The further aspect of the present invention is in a method of producing the aluminum alloy sheet set forth above, the method comprising the steps of:

hot rolling a cast ingot composed of an aluminum alloy in the usual manner, the cast ingot consisting of, in weight percentages:

Mg: from 0.50 to 2.0%

Si: from 0.10 to 0.70%

Mn: from 0.30 to 1.5%

Cu: from 0.52 to 1.0%

and the balance being, except for incidental impurities, aluminum; cold rolling to a sheet with a thickness of at least one and a half times a final thickness;

heating to a temperature of 500°C or higher and then rapidly cooling from said heating temperature; and final cold rolling.

Detailed Description of the Preferred Embodiments

The first feature of the present invention resides in an aluminum alloy sheet with an excellent corrosion-resistance, the sheet consisting of (by weight percentages):

Mg: from 0.50 to 2.0%

Si: from 0.10 to 0.70%

Mn: from 0.30 to 1.5%

Cu: from 0.52 to 1.0%

and the balance being aluminum except for incidental impurities which may be expected from the production of ingot.

The alloying elements enumerated above are selected with the objects of (1) preventing galvanic corrosion caused in combination with mild steel sheets and (2) ensuring both of strength and formability at sufficient levels as can end materials.

More specifically, Mg and Si are added to ensure strength at a desired level. When a Mg content is less than 0.50%, sufficient strength cannot be obtained in a finished alloy. On the other hand, an addition exceeding 2.0% will significantly lower galvanic corrosion resistance.

Si forms a fine-grained Mg_2Si compound in combination with Mg and thereby improved strength. However, an addition of less than 0.1% does not afford a sufficient strength due to an insufficient formation of Mg_2Si, while addition of more than 0.70% excessively increases strength thereby impairing formability.

Mn has a strengthening effect without lowering galvanic corrosion resistance and further enhances the strengthening effect imparted by Mg and Si. Amounts less than 0.30% do not afford a sufficient effect, while an addition exceeding 1.5% forms unfavorable coarse compounds, resulting in an unfavourable lowering of formability.

Further it has been found that an excess addition of Mn beyond 1.5% has no further effect and, thus, an upper limit of 1.5% was taken for an Mn content.

The principal reason for Cu addition is to bring the spontaneous electrode potential of the invention aluminum alloy sheet to the same level as that of the mild steel and whereby galvanic corrosion caused by the contact potential between the invention aluminum alloy and the mild steel may be effectively prevented. The prevention effect cannot be expected in an amount of less than 0.10%, while an amount exceeding 1.0% increases the difference in spontaneous electrode potential against the mild steel in the reverse direction and the mild steel is liable to dissolve due to galvanic corrosion on the mild steel side. Thus, the excessive addition of Cu must be avoided. Further, aluminum alloy sheets containing a large amount of Cu exceeding 1.0% exhibit a reduced resistance to self corrosion resistance in a sodium chloride solution which makes them unsuitable for use as container materials for salt-containing food. Still further, Cu has also an effect in improving strength and formability.

Now, galvanic corrosion of aluminum alloy sheets caused by the spontaneous electrode potential difference from that of mild steel sheet will be explained hereinafter.

When two different metallic materials which differ from one another in spontaneous potential are contacted, a corrosive current will flow depending on the contact potential difference and the circuit resistances of the two materials. Galvanic corrosion is the dissolution of an anode caused by the corrosive current and the dissolution amount ΔW is calculated in accordance to Faraday's law expressed below.

$$\Delta W(g/cm^2) = 9.3 \times 10^{-5} \times [\text{corrosive current}(A/cm^2)] \times [\text{time(sec.)}]$$

When the dissolution amounts exceed a certain level, metallic sheets are pierced and no longer serve as containers.

According to the inventors' experimental analysis, it has been found that with respect to easy open type aluminum can ends, a corrosive current at room temperature should be suppressed within the range of not more than 3 $\mu A/cm^2$, in order to avoid the thinnest portion (not more than 100 µm thiuck) of the can ends from being pierced for a period of at least one year.

More specifically, in order to suppress galvanic corrosion occurring in an aluminum alloy can end material employed together with a mild steel can body material to an acceptable level for practical uses, it is requested that corrosive current between the foregoing two different materials which are joined to each other in an area ratio of 1:1 be in the range of ± 3 $\mu A/cm^2$ and, accordingly, the spontaneous electrode potential difference between the two sheets be controlled within the range of −30 mV to +30 mV.

The spontaneous electrode potential of the aluminum alloy sheet of the present invention is in the range of −700 to −630 mV in a 0.1% sodium chloride solution at 25°C and the potential range satisfies the requirements set forth above.

For the production of the aluminum alloy sheets according to the present invention, cast ingot with the foregoing composition is prepared and homogenized in accordance to the conventional procedures. Thereafter, the homogenized alloy is hot-rolled and cold-rolled. Particularly, after the hot-rolling, the alloy sheet is cold rolled to an intermediate thickness which is at least one and a half times a thickness of a finally cold-rolled sheet, and thus intermediate cold-rolled sheet is heated to a temperature of 500°C or higher, and then rapidly cooled from the temperature, for example, by forced air-cooling. Following the heat treatment, final cold rolling is carried out to finish the desired aluminum alloy sheet product. By virtue of the foregoing production steps, there can be obtained final products having highly improved properties, particularly in strength and formability, without causing their spontaneous electrode potentials to depart from the level set forth above.

The foregoing intermediate thickness to be subjected to the heat treatments closely relates to the strength of the finished sheet products. When the intermediate thickness is below one and a half times the thickness of the final sheet products, it is difficult to achieve a sufficient strength for the use as container material. Particularly, where a higher strength is desired for use as can end materials, the intermediate thickness is preferable to be at least 2.5 times the thickness of the final cold-rolled sheets.

The present invention will now be described in detail hereinafter with reference to the examples.

Example 1

Eight kinds of aluminum alloys with the compositions given in Table 1 were molten, cast into ingots and then homogenized. Thereafter, the ingots were hot rolled and cold rolled to a sheet form with a thickness of 0.8 mm. With respect to the alloy sheets thus fabricated, the spontaneous electrode potential was measured in a 0.1% sodium chloride at 25°C, using an AgCl electrode as a reference electrode, and indicated in the right column of Table 1. For reference, the spontaneous electrode potentials of a mild steel sheet and a tin free steel were also given. The spontaneous electrode potentials were continuously measured over a period of 60 minutes and their variation ranges in spontaneous electrode potential for time are shown.

Table 1

No.	Alloy Composition (by weight%)				Spontaneous Electrode Potential (mV)
	Si	Cu	Mn	Mg	
1	0.25	0.52	0.82	1.27	-650 to -680
2	0.18	0.83	0.59	1.29	-640 to -670
3	0.75	1.68	0.02	0.38	-610 to -640
4	0.07	0.01	0.03	2.67	-680 to -730
5	0.09	0.02	0.14	4.68	-700 to -750
6	Mild Steel Sheet				-670 to -690
7	Tin Free Steel Sheet				-660 to -680

Nos. 1 and 2: Alloy Sheets according to the Present Invention

Nos. 3 to 5: Comparative Alloy Sheets

Nos. 6 to 7: Reference Sheets

As is clear from Table 1, it was proved that the alloy sheets Nos. 1 and 2 according to the present invention had almost the same spontaneous electrode potential levels as compared to those of the reference sheets made of the mild steel and the tin-free steel. The spontaneous electrode potential of the comparative sheet No. 3 was too noble due to an excessive Cu content and exhibited a large potential difference with respect to the steel sheet. The comparative sheets Nos. 4 and 5 were made of aluminum alloys corresponding to A 5052 alloy and A 5082 alloy, respectively which have been both heretofore extensively used as beverage can end materials. The potential difference between such conventional alloy materials and steel sheets are not less than 50 mV and detrimentally large from the viewpoint of the prevention of the aforementioned galvanic corrosion problem.

Example 2

Ingots of alloys Nos. 1 to 3 given in Table 1 were homogenized, hot rolled and then intermediate cold rolled to provide 0.8 mm thick sheets. Following intermediate cold rolling, the alloy sheets were heated to 520°C and compulsorily air-cooled. Subsequently, the sheets were finally cold-rolled to a thickness of 0.3 mm.

The thus formed sheets were subjected to coating and baking treatments which are usually conducted in can end manufacturing. Baking was carried out by repeating twice heating at 205°C for 10 minutes. The thus obtained sheets were each examined on mechanical properties and the results are listed in Table 2.

Further, the aluminum alloy sheets were jointed to the mild steel sheet in an area ratio of 1:1 and immersed in a 0.1% sodium chloride solution at 25°C. Corrosive current in the sodium chloride solution was measured and given in Table 2.

Table 2

No.	Yield Strength N/m² [Pa]	Tensile Strength N/m² [Pa]	Elongation %	Earing Ratio %	Erichsen Value mm	Corrosive Current* μA/cm²
1	$313.8 \cdot 10^6$	$355.0 \cdot 10^6$	10	1.0	5.2	<±1
2	$326.5 \cdot 10^6$	$369.7 \cdot 10^6$	11	1.0	5.4	<±1
3	$240.26 \cdot 10^6$	$266.7 \cdot 10^6$	7	3.5	4.7	-1 ∼ -2
4	$245.1 \cdot 10^6$	$283.4 \cdot 10^6$	6	4.0	5.0	2 ∼ 7
5	$304.0 \cdot 10^6$	$359.9 \cdot 10^6$	9	3.5	4.8	5 ∼ 8

* Measured in a 0.1 % Sodium Chloride Solution

Nos. 1 and 2: Alloy Sheets according to the present Invention

Nos. 3 to 5: Comparative Alloy Sheets

It can be seen in Table 2 that the aluminum alloy sheets Nos. 1 and 2 in accordance to the present invention have a high strength and an excellent Erichsen value which are both equivalent or superior to the conventional can end materials made of the comparative alloys No. 4 and No. 5 and exhibits a lower earing ratio (anisotoropy for deep drawing) than those of the comparative sheets.

Further, in the case of the comparative sheets Nos. 4 and 5, a greater corrosive current exceeding 3 μA/cm² flows, while in the invention aluminum alloy sheets of Nos. 1 and 2, a very little corrosive current of ±1 to ±2 μA/cm² flows and, thus, it is obvious that galvanic corrosion is prevented.

Further, the spontaneous electrode potentials of the aforementioned aluminum alloy sheets were measured at 25°C in a 0.5% sodium chloride solution instead of the above 0.1% sodium chloride solution against an AgCl reference electrode and, further, in the same sodium chloride solution, the corrosive current was also measured for combination of each of the alloy sheets and the mild steel sheet joined in an area ratio of 1:1. After the measurement at 25°C, the 0.5% sodium chloride solution was heated to 120°C and at the temperature, corrosive current was measured. The results are shown in Table 3.

Table 3

No.	Spontaneous Potential*1 mV	Electrode	Corrosive Current*1 μA/cm²	Corrosive Current*2 μA/cm2	Evaluation*3
1	-650 to	-700	$< \pm 1$	100 to 200	o
2	-620 to	-660	$< \pm 1$	50 to 100	o
3	-600 to	-620	$< \pm 1$	10 to 40	(o)
4	-670 to	-720	2 to 5	600 to 1300	x
5	-770 to	-800	5 to 7	300 to 800	x

*1: Measured in a 0.5 % Sodium Chloride Solution at 25°C

*2: Measured in a 0.5 % Sodium Chloride Solution at 120°C

*3: o: very good, x: bad (impracticable)

(o): very good (poor in self corrosion)

Nos. 1-2: Alloy Sheets according to the Present Invention

Nos. 3-5: Comparative Alloy Sheets

In the case of a high salt content, the alloy sheets Nos. 1 and 2 of the present invention were found to have the optimum composition.

On the other hand, when the sodium chloride solution was heated to 120°C, the corrosive current of the invention alloy sheet increased to the level of 50 to 200 μA/cm², but the increase was far less than that of conventional materials Nos. 4 and 5 and therefore it is obvious that even if the alloy sheets of the present invention are subjected to a sterilizing thermal treatment for food cans, they will maintain sufficient resistance to galvanic corrosion. Further, the mild steel sheet and the tin-free steel had the spontaneous electrode potentials in the ranges of −620 to −640 mV and −600 to −620 mV, respectively, in the 0.5% sodium chloride solution at 25°C and, further at the elevated temperature of 120°C, the potentials were more noble.

As previously described, galvanic corrosion due to the contact potential difference between the invention alloy sheets and the mild steel sheets is very slight and thus the aluminum alloy sheets of this invention are useful as can end materials in combination with the mild steel can bodies for saline food. Further, since the aluminum alloy sheets according to the invention have also a significantly increased resistance to other corrosions, they can be used not only as can end materials but also as can body materials for the manufacturing of various aluminum cans.

The advantages derived from the present invention are summarized in the following.

(1) In all-steel cans, which are entirely made of steel, for saline beverages and the other foods, their can end materials can be replaced by the invention aluminum alloy materials suitable for use in manufacturing easy opening can end.

(2) Also, in all-aluminum can manufacturing, the aluminum alloy sheets of the present invention exhibits significantly better properties as can end materials.

(3) The alloy sheet of the present invention is useful not only as can end materials but also as can body materials.

(4) The invention alloy sheets make possible the production of unialloy cans in which can body stock and can end stock are both made on the same type aluminum alloy (Al-Mg-Mn-Cu-Si), hereby facilitating recycling process of empty cans after use.

Claims

1. An aluminum alloy sheet for containers excellent in resistance corrosion, said aluminum alloy sheet consisting of, in weight percentages:

Mg: from 0.50 to 2.0%

Si: from 0.10 to 0.70%

Mn: from 0.30 to 1.5%

Cu: from 0.52 to 1.0%

and the balance being except for incidental impurities, aluminum, the spontaneous electrode potential of the sheet being in the range of from −700 to −630 mV in a 0.1% sodium chloride solution at 25°C, against an AgCl reference electrode.

2. A method for producing an aluminum alloy sheet for container excellent in corrosion resistance, said method comprising the steps of:

hot rolling a cast ingot composed of an aluminum alloy in the usual manner, said aluminum alloy consisting of, in weight percentages:

Mg: from 0.50 to 2.0%

Si: from 0.10 to 0.70%

Mn: from 0.30 to 1.5%

Cu: from 0.52 to 1.0%

and the balance being, except for incidental impurities, aluminum;

cold rolling to a sheet with a thickness of at least one and a half times a final thickness;

heating to a temperature of 500°C or higher and then rapidly cooling from said heating temperature; and

final cold rolling.

Patentansprüche

1. Blech aus einer Aluminiumlegierung für Behälter mit hervorragender Korrosionswiderstandsfähigkeit, wobei das Blech aus der Aluminiumlegierung im Gewichtsprozenten enthält:

Mg: von 0.50 bis 2.0%

Si: von 0.10 bis 0.70%

Mn: von 0.30 bis 1.5%

Cu: von 0.52 bis 1.0%

und den Hauptanteil, abgesehen von unwesentlichen Verunreinigungen, Aluminium bedeutet, wobei das spontane Elektrodenpotential des Bleches innerhalb eines Bereiches von −700 bis −630 mV in einer 0,1%igen Sodiumchloridlösung bei 25°C gegen eine AgCl-Referenzelektrode ist.

2. Verfahren zur Herstellung eines Bleches aus einer Aluminiumlegierung für Behälter mit hervorragender Korrosionswiderstandsfähigkeit, wobei das Verfahren die folgenden Schritte umfaßt:

Heib-Walzen eines Schmelzenblöckchens aus einer Aluminiumlegierung in der Überlichen Weise, wobei die Aluminiumlegierung in Gewichtprozenten enthält:

Mg: von 0.50 bis 2.0%

Si: von 0.10 bis 0.70%

Mn: von 0.30 bis 1.5%

Cu: von 0.52 bis 1.0%

und der Hauptanteil, abgesehen von unwesentlichen Verunreinigungen, aus Aluminium besteht;

Kalt-Walzen zu einem Blech mit einer Dicke von zumindest ein und eine Halbes Mal einer Enddicke;

Aufzeihung auf eine Temperatur von 500°C oder höher und dann von der Heiztemperatur schnell abkühlen; und

schließlich Kalt-Walzen.

Revendications

1. Tôle d'alliage d'aluminium présentant une excellent résistance à la corrosion et qui consiste, en pourcentages en poids, en:

Mg: de 0,50 à 2,0%

Si: de 0,10 à 0,70%

Mn: de 0,30 à 1,5%

Cu: de 0,52 à 1,0%

et le complément étant, à l'exception d'éventuelles impuretés, de l'aluminium, le potentiel d'électrode spontané de la tôle étant compris dans la plage de −700 à −630 mV dans une solution de chlorure de sodium à 0,1% à 25°C, contre une électrode de référence en AgCl.

2. Procédé pour obtenir une tôle en alliage d'aluminium pour récipient présentant une excellent résistance à la corrosion, ledit procédé comprenant les étapes consistant à:

laminer à chaud un lingot coulé composé d'un alliage d'aluminium de la manière habituelle, l'alliage d'aluminium coulé consistant, en pourcentages en poids, en:

Mg: de 0,50 à 2,0%

Si: de 0,10 à 0,70%

Mn: de 0,30 à 1,5%

Cu: de 0,52 à 1,0%

et le complément étant, à l'exception d'éventuelles impuretés, de l'aluminium; laminer à froid jusqu'à l'obtention d'une tôle ayant une épaisseur d'au moins une fois et demi l'épaisseur finale;

chauffer à une température de 500°C ou plus et ensuite le refroider rapidement à partir de ladite température de chauffage; et

laminer finalement à froid.