Improved aluminum alloy composite sheet consisting of a core in a strain hardenable aluminum base alloy and a cladding in an alloy containing about 1.3 percent zinc, the balance being aluminum of at least 99 percent purity is especially useful as rigid container stock for use in containers featuring scored easy open or tear tab arrangements.

11 Claims, 4 Drawing Figures
ALUMINUM ALLOY CONTAINER END AND SEALED CONTAINER THEREOF

This is a continuation of application Ser. No. 123,778, filed Mar. 12, 1971, now abandoned.

This invention relates to an aluminum alloy composite and its embodiment in scored can ends and other container applications.

DESCRIPTION

In the description below reference is made to the drawings in which:

FIG. 1 is an enlarged cross sectional elevation of a portion of a container panel featuring the easy open provisions;

FIG. 2 is a graph plotting probability of failure versus alloy composition;

FIG. 3 is a cross sectional elevation of a portion of a container panel featuring the present improvement;

FIG. 4 is a cross sectional elevation greatly enlarged of a portion of FIG. 1.

BACKGROUND

Aluminum has become popular in the container field because of its ability to be fabricated into container ends and other panels featuring easy-open or pull-tab provisions of the general type depicted in U.S. Pat. No. 3,194,797 and 3,424,337. Referring to FIG. 1, a portion of a can end or other panel 10 features a weakened removable tear strip 12 defined by scored tear lines 14 and a pull tab or ring 18. The pull tab is usually secured to the tear strip by an integral rivet 20 drawn from the sheet forming the end. Opening the container merely requires pulling the tab or ring to rupture the container end and continuing the pulling action to remove the tear strip along the score lines. The portion of the container end removed can vary from a relatively small strip, as with beverages, to substantially the entire end, as with soups and foods. One popular example appears in beer can ends where the tear strip is of a key hole shape.

Easy-open aluminum container ends and other panels are usually fashioned from alloys which are not heat treatable but which can be imparted with substantial strength by cold working operations especially where the cold working imparts to the sheet a cold reduction of 90 percent or more in thickness to produce a highly strain hardened condition. Suitable alloys contain 4 to 5 percent magnesium with optional manganese additions of up to 0.7 percent. These alloys are relatively inexpensive to manufacture into sheet products which exhibit substantial strength levels of up to 57 ksi tensile and higher and 54 ksi yield strength and higher in the strain hardened temper and retain a substantial amount of this strength after thermal exposures encountered in finding their way to container ends.

In making the container ends the sheet is first coated on one or both sides with a protective organic coating. Suitable coatings include thermoset vinlyls or epoxy formulations. The sheet is then cut into blanks which are formed or converted to easy-open ends by scoring the outline of the removable tear strip on the outer surface of the end and, where an integral rivet is employed, the drawing and compression of the integral rivet. Referring again to FIG. 1, in those inside portions 24 under the integral rivet and 22 under the score area, the protective organic coating 26 is disturbed and the integrity of the protection often severely reduced because of the forces and metal movement associated with the scoring and rivet forming operations. This effect is not particularly disarrange in beer can ends because the chemical behavior of beer is not especially severe. However, there are several corrosive beverage and food products where the fractured and disturbed protective coating leads to failures of the container system. Such food products include carbonated soft drink beverages, vegetable and fruit juices, together with soups, vegetables and other retorted food products. These corrosive foods attack the metal exposed by the damaged coating beneath the score lines where the metal is quite thin having been reduced to only a few thousandths of an inch. A can end is typically about 0.010 inch to 0.014 inch thick and the scored portion about 0.004 inch thick; that is, less than half the thickness of the end. The result of the attack is premature perforation at these sites in as little as a few days of storage. In the case of thermally processed foods such as soups or vegetables which are typically retorted for about one hour at about 250°F, failures sometimes occur by the time the cans are removed from the retort or shortly thereafter. The perforations referred to are extremely small in that they are often not readily visible although they are adequate to completely relieve any internal pressure or vacuum in the can and expose the contents to the outside atmosphere. The corrosion picture is complicated somewhat by the fact that aluminum can ends are used on container bodies fashioned from protectively coated or bare "tin plate" (tin-coated steel) or coated tin-free steel or aluminum of a different alloy than the end and by the fact that the chemical nature of the can body exerts an influence on the corrosion effects of the aluminum container ends. To date there is no known economical organic coating suitable for use in food containers which can reliably sustain the scoring operation. One obvious solution to the problem is to repair coat the damaged areas. However, attempts to use repair coated easy-open container ends have proven difficult, expensive and, in the case of hot filled products such as juices and in the case of retortable products, they have proven unreliable. While the use of two or three repair coats offers some improvement in the picture, the costs become very unattractive. The use of electrochemical protective systems runs the risk of hydrogen generation which can cause swelling. The net result is an unreliable container end since prior attempts at electrochemical protection have failed to reliably prevent perforation and have also created an additional problem re swelling.

DETAILED DESCRIPTION

In accordance with the invention a highly specific aluminum composite sheet serves to effectively protect the container end metal exposed to the container contents in the areas of coating fracture or impairment while substantially avoiding excessive hydrogen generation. Referring to FIG. 3 it has been found that cladding the container end 10 sheet with an inside cladding layer 11 in an alloy consisting essentially of 1 to 1.5 percent zinc, preferably 1.1 to 1.4 percent zinc, the balance being substantially aluminum, accomplishes the desired purpose in a comparatively inexpensive and economical manner. The cladding faces the inside of the container when the sheet is fabricated into a container end. The core alloy is an aluminum alloy containing magnesium and preferably some amount of
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manganese. Suitable core alloys are listed in the table below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4 to 5.5</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>4 to 5.5</td>
<td>0.2 to 0.5</td>
</tr>
</tbody>
</table>

Thus, suitable core alloys may contain at least 90 percent preferably at least 92 percent aluminum and 4 to 6 percent Mg and up to 1 percent Mn, typically 0.2 to 0.7 or 1 percent Mn. A preferred embodiment features a core consisting essentially of at least 92.5 percent aluminum, 4 to 5.5 percent Mg, 0.2 to 0.7 percent Mn, together with incidental elements and impurities, and a cladding consisting essentially of 1.1 to 1.4 percent Zn, balance essentially aluminum.

Concerning the composition of the cladding reference is made to FIG. 2 which is a graphical representation of the results of extensive tests in the laboratory and in actual food containers. The graph plots probability of failure versus zinc content based on several container applications including vegetable juice, fruit juice and carbonated beverages. From the graph it can be seen that the incidence of failure of the package system by perforations through the easy opening can end is very high, about 100 percent, where the cladding contains no zinc. Very high probability of failure prevails until the zinc content approaches about 1 percent where the probability drops off markedly and reaches zero just short of 1.1 percent Zn. This represents the commercially necessary degree of reliability. Further increases in zinc do not necessarily retain this reliability, however, in that while perforations are still eliminated a marked tendency to develop hydrogen gas and swelling of the container develops in many food product applications, especially vegetable and fruit juices. Referring again to FIG. 2 and proceeding from right to left (decreasing zinc content) it can be seen that at 3 or 2% percent zinc there can be a 100 percent probability of failure. This probability is reduced somewhat at 2 percent zinc and approaches zero at about 1.5 percent zinc.

In addition to Zn another significant aspect of the improved cladding composition is purity of the aluminum base. While the invention contemplates an aluminum base purity of as low as 92.2 percent, better results are assured with a purity of 99.5 percent. A preferred embodiment contemplates a cladding composition in an aluminum alloy consisting essentially of 1.1 to 1.4 percent Zn, the balance aluminum of at least 98.8 percent or 99.9 percent; that is, elements other than aluminum and zinc are restricted to 0.1 percent or 0.2 percent in a substantially binary aluminum-zinc alloy.

The composite sheet product normally ranges in thickness from 0.008 to 0.0145 inches of which the cladding constitutes 2 to 10 percent. The cladding may be placed on both faces of the core if desired to absolutely assure that it faces the inside of the container.

The strength of the composite is not much less than for sheet of the same thickness in the unclad condition. For instance, considering an alloy containing normally 4.5 percent magnesium and 0.35 percent manganese the tensile strength is about 57 ksi. That same alloy clad with 4 percent of the cladding in accordance herewith is only reduced to a composite tensile strength of about 55 ksi. Accordingly, the improved composite can be employed with little or no additional metal thickness to compensate for its only slightly lower strength. That is, the improved sheet is about the same in thickness as previous container end sheet.

It is believed that the perforations are caused by a magnesium-aluminum precipitate, having the general formula Mg_xAl_{2-x}, which occurs in aluminum alloys containing over 1.5 percent Mg, especially those containing 2 percent Mg or more. The extent of the precipitate tends to increase with higher amounts of magnesium and with higher amounts of cold work. In addition, the presence of manganese tends to increase the extent of the precipitation. Modern practices, however, favor increased magnesium and increased cold work since both improve the strength of the sheet and accordingly permit the use of thinner sheet material. For instance, increasing the magnesium content from about 3 to 4.5 percent and increasing the amount of cold work from about a 75 percent cold reduction to a cold reduction of at least 85 percent and preferably at least 90 percent increase the tensile strength from about 45 to over 50 ksi. Modern practices also favor including manganese which tends to optimize strength and fabricability. The net result is that the current high strength easily fabricated alloys contain substantial amounts of magnesium and manganese and include a very substantial amount of cold work all of which tend to maximize the extent of the magnesium-aluminum precipitate. The picture gets even worse in that the alloy sheet is often heated to temperatures about 150° to 350°F in curing the protective coating or retorting the canned food product. Such thermal exposures are highly favorable to developing further precipitate. The precipitate occurs preferentially along grain boundaries and along <111> slip planes caused by the scoring operation in producing the tear tab of a can end. The scoring is essentially a stamping operation which produces a substantial deformation or discontinuity in the grain flow pattern as shown in FIG. 4 where it is quite apparent that the grain flow lines 28 are greatly disturbed. Also shown in FIG. 4 are <111> slip planes 29 developed in scoring. The magnesium-aluminum precipitate particles are anodic to the matrix in that the particles have a typical breakdown potential of ~875 millivolts whereas the typical matrix breakdown potential is only ~700 mv. Electrode potentials mentioned herein are referred to the saturated calomel electrode scale. Because of its anodic potential the precipitate particles tend to corrode preferentially to the matrix. This corrosion is especially favored in the area under the score line where precipitate particles are closely spaced and connecting paths between adjacent particles are extremely short and accordingly favorable to propagation of a particle corrosion path. In a typical perforation, corrosion is initiated in a precipitate particle 30 deposited near or at the metal surface beneath the disturbed coating. The path of corrosion proceeds from particle to neighboring particle typically along a <111> plane or along a grain flow line. This pattern of propagation continues until a perforation path 32 is completed, resulting in container failure, with attendant loss of the hermetic seal which is essential to protect food products.

The improved cladding can sustain the scoring operations without becoming drastically impaired and even if it is disturbed it continues to prevent perforations. The breakdown potential of the improved cladding is
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In the container end according to claim 1 the further improvement wherein the composite sheet is in a strain hardened and partially relaxed condition resulting from a cold rolling reduction of at least 90 percent in thickness followed by a thermal exposure which partially relaxes the strains.

6. In an aluminum alloy container end having a removable portion defined by at least one score line in the outer surface of said container end can end said score line describing a closed perimeter for said removable portion and extending sufficiently through its thickness to locally weaken it to render said portion defined thereby manually removable substantially by tearing to provide an access opening in said container end, the container end being produced from an aluminum alloy sheet, the improvement wherein said aluminum alloy sheet is provided as a composite sheet composed of a core layer containing at least 90 percent aluminum, 4 to 6 percent Mg and up to 1 percent Mn, an inside cladding layer composed of an alloy consisting essentially of 1 to 1.5 percent Zn, the balance Al of at least 99.2 percent purity, said container end having a protective organic coating applied to the underside surface beneath said score line, said coating being disturbed in the region beneath the score line, said improvement serving to improve resistance to perforation attack in the region of said score line.

7. In a container end of an aluminum alloy of the type containing 4 to 6 percent magnesium and having a removable portion defined by at least one score line in the outer surface of said container end can end said score line describing a closed perimeter for said removable portion and extending sufficiently through its thickness to locally weaken it to render said portion defined thereby manually removable substantially by tearing to provide an access opening in said container end, core layer having Mg-Al precipitate particles situated preferentially along grain boundaries and <111> planes in the region of said score line, said particles being more closely spaced in said region than in the remainder of said core alloy layer of said container end and being anodic with respect to the matrix of said core, the container end being produced from sheet of said type of aluminum alloy, the improvement wherein said sheet is provided as a composite sheet composed of a core layer consisting essentially of at least 92.5 percent Al, 4 to 6 percent Mg and 0.2 to 0.7 percent Mn and an inside cladding layer composed of an aluminum base alloy consisting essentially of aluminum and 1 to 1.5 percent Zn and not more than 0.8 percent of elements other than Al and Zn, said improvement serving to improve resistance to perforation attack in the region of said score line.

8. In a hermetically sealed container the contents of which are corrosive to aluminum, said container having end and side wall portions to define said container and including an aluminum alloy panel having a removable portion defined by at least one score line in the outer surface of said panel and extending sufficiently through its thickness to locally weaken it to render said portion defined thereby manually removable substantially by tearing to provide an access opening in said panel, said aluminum alloy panel being produced from an aluminum alloy sheet, the improvement wherein said sheet is provided as a composite sheet composed of a core alloy layer containing at least 90 percent aluminum, 4 to 6 percent magnesium and up to 1 percent manga-
and an inside cladding layer composed of an alloy consisting essentially of 1 to 1.5 percent zinc, the balance aluminum of at least 99.2 percent purity, said improvement serving to improve resistance to perforation attack in the region of said score line.

10. In the container according to claim 9 wherein a food or beverage commodity occupies the container.

11. In a hermetically sealed container, housing a food or beverage commodity corrosive to aluminum having end and side wall portions to define said container and including an aluminum alloy panel, said panel having a removable portion defined by at least one score line in the outer surface of said panel and extending sufficiently through its thickness to locally weaken it to render said portion defined thereby manually removable substantially by tearing to provide an access opening in said panel, said panel being produced from aluminum alloy sheet, the improvement wherein the said sheet is provided as an aluminum composite sheet composed of a core alloy layer containing at least 90 percent aluminum, 4 to 6 percent magnesium and up to 1 percent manganese and a cladding layer metallurgically bonded to the core alloy and composed of an alloy consisting essentially of 1 to 1.5 percent zinc, the balance aluminum of at least 99.2 percent purity, said improvement serving to improve resistance to perforation attack in the region of said score line.

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