

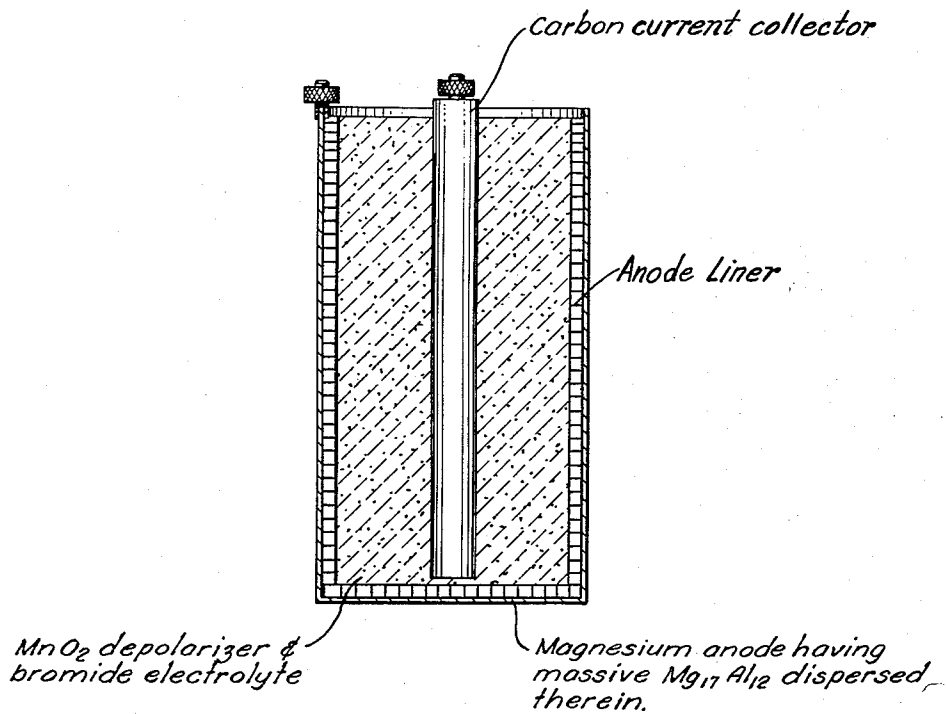
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R. C. KIRK ET AL

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ANODE FOR MAGNESIUM PRIMARY CELL

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INVENTORS.
Roy C. Kirk
John L. Robinson
BY

Griswold & Lurdick
ATTORNEYS

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2,952,727

ANODE FOR MAGNESIUM PRIMARY CELL

Roy C. Kirk and John L. Robinson, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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4 Claims. (Cl. 136—120)

This invention relates to an improved anode for use in a primary magnesium battery cell whereby the normal delayed action usually resulting from the employment of such a battery cell is decreased.

It has been well established that primary cells utilizing magnesium as the anode, carbon depolarized with manganese oxide as the cathode and a bromide of an alkali metal, alkaline earth metal or ammonium as an electrolyte have specific advantages in certain uses. For example, a greater capacity per unit of volume is generally achieved. One of their disadvantages, however, is that the cells do not always attain full working voltage immediately on attempting to reuse them following a rest period. This delayed action may vary from 0 to as much as 100 seconds or more depending upon the specific composition of the components of the cell, the amount of use that has been made of the cell, the intervening rest period, and the age of cell.

It is a principal object of the present invention to provide an anode material for a magnesium primary cell which results in a shorter delayed action when employed in the conventional magnesium primary cell. Still another object of the present invention is to provide an improved magnesium anode material containing substantial quantities of massive $Mg_{17}Al_{12}$ compound. A further object of the present invention is to provide an improved anode material for magnesium primary cells which is prepared by the rapid cooling of a magnesium aluminum alloy from a temperature above its solidus and below its liquidus temperatures. Another object of the present invention is to provide a magnesium anode material for primary cells containing from 0.5 to 12 percent aluminum, a substantial proportion of which is present as massive $Mg_{17}Al_{12}$ compound. Other objects will become apparent hereinafter.

The foregoing and additional objects have been accomplished by providing a magnesium cell having a magnesium anode in which a part of the magnesium is present as massive $Mg_{17}Al_{12}$ compound.

Magnesium batteries have been described in a number of U.S. patents including U.S. Patents 2,547,907, 2,616,940, 2,712,564, etc. These patents all rely upon a magnesium anode, a cathode into which has been mixed a depolarizing agent such as manganese dioxide and an alkaline metal, alkaline earth metal, or ammonium bromide electrolyte, an anode liner, and a carbon current collector. The present invention specifically relates to an improvement in the anode of such a cell whereby the delayed action is substantially reduced. Provision of such anode is accomplished by heating a magnesium alloy containing from 1 to 12 percent aluminum to a temperature above its solidus temperature but below its liquidus temperature and rapidly cooling this material so that a massive $Mg_{17}Al_{12}$ compound is formed. Representative alloy materials which are suitable are those magnesium base alloys containing at least 80 percent, preferably 90 percent magnesium and containing from 1 to 12 percent

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aluminum, preferably from 1 to 9 percent aluminum, from 0.0 to 3.0 percent zinc, from 0.0 to 0.5 percent calcium, the balance being commercial magnesium containing not over 0.005 percent iron, not over 0.002 percent nickel, and not over 0.6 percent manganese. This alloy is heated to a temperature above its solidus temperature, and below its liquidus temperature, both of which will vary depending upon the particular alloy being employed. After heating to this temperature, the alloy material is rapidly cooled as by quenching, etc., that is, at a rate of at least 500 Fahrenheit degrees per minute, preferably about 1000 Fahrenheit degrees per minute, and when so cooled, results in substantial quantities of massive $Mg_{17}Al_{12}$ compound being formed therein. The rapid cooling should be carried to a point below that which the massive $Mg_{17}Al_{12}$ compound will be stabilized and not converted to fine $Mg_{17}Al_{12}$ compound or another MgAl composition. This temperature is below the eutectic temperature, usually below 700 degrees Fahrenheit and preferably below 500 degrees Fahrenheit. Slower cooling techniques may result in fine particles of $Mg_{17}Al_{12}$ compound being formed. It has been established that these fine particles adversely affect the magnesium alloy when used as an anode in magnesium primary cells by increasing the delay time. Therefore, it is essential that the anodes of the present invention contain massive $Mg_{17}Al_{12}$ particles. Alternatively, the magnesium alloy may be heated to above its liquidus temperature and thereafter rapidly cooled, as in a die-cast technique. This constitutes a preferred embodiment for forming the anodes of the present invention. While die-casting is the preferred technique for forming the anodes of the present invention, quenching of the alloy after heating above its solidus but below its liquidus temperature, providing a mixture of magnesium and massive $Mg_{17}Al_{12}$ compound and forming the anode with powdered metallurgy techniques, etc., may be used, that is, any metal forming technique which allows the formation of or retains the presence of massive $Mg_{17}Al_{12}$ compound. Alternatively, stock containing massive $Mg_{17}Al_{12}$ present may be machined or otherwise formed to obtain the desired final shape for the anode, provided however, that such forming operations are not sufficiently drastic to eliminate the presence of the massive $Mg_{17}Al_{12}$ compound.

The anodes so prepared are used in a conventional manner in a magnesium primary cell. The advantages of employing such an alloy are many, but primarily are represented in the decreased delayed action of a cell employing such an anode.

The following examples are given to illustrate the anodes of the present invention but are not to be construed as limiting the invention thereto:

EXAMPLE I

Two alloy compositions, one of which contains 3 percent aluminum and 1 percent zinc, the remainder being commercial magnesium (AZ10A) and the second of which contains 1 percent aluminum and 0.4 percent zinc, the remainder being commercial magnesium (AZ10A) were both extruded and die-cast to form anodes for primary magnesium cells. Cells containing these alloys as anodes, a cathode of 91 percent manganese dioxide, 3 percent barium chromate and 6 percent acetylene black, and an electrolyte containing 250 grams per liter of magnesium bromide and 0.36 gram per liter of sodium chromate were employed. Different cells containing the extruded and die-cast anodes were tested in three standard tests: the "Railroad Lantern" test utilizing an alternate discharge time and rest time of 30 minutes during an 8-hour day with a subsequent rest time of 16 hours, 7 days per week, on a 32 ohm load for a 3-cell pack; the

general purpose test of 5 minutes discharge through 4 ohms per cell per day, 7 days per week and the BA-30 test of 4 minutes discharge through 6.75 ohms per cell out of 30 minutes for 10 hours per day, 5 days a week. The following table summarizes the results obtained from these tests.

cient to provide the improved anode of the present invention, alloy AZ31A was heated at various temperatures for 1 hour and quenched in water to provide a rapid cooling. The following table shows that heating above the solidus temperature is essential to provide the massive $Mg_{17}Al_{12}$ required by the present invention.

Table I
TESTS

Anode Com- position.	Slug Type	Cathode	Railroad Lantern Delay, Seconds				Gen. Purpose Delay, Seconds		BA-30 Delay, Seconds	
			AM		PM					
			Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.
AZ31A-----	Extruded---	91-3-6	6	4.6	15	10.6	5	2.9	2.8	1.8
AZ31A-----	Die-Cast---	91-3-6	2.3	1.8	8	4.7	3.2	1.5	0.8	0.3
AZ10A-----	Extruded---	91-3-6	2.8	1.8	5	3.5	3.0	1.4	2.0	1.3
AZ10A-----	Die-Cast---	91-3-6	1.8	1.3	4.8	3.4	1.8	0.2	0.2	0.2

NOTE.—In the above table, the AM delay is measured during the first discharge of that day's test, the PM delay is measured during the final discharge of that day's test.

Table I illustrates that massive $Mg_{17}Al_{12}$ compound is required to achieve the reduced delay time of the present invention. Die-cast forming causes massive $Mg_{17}Al_{12}$ compound to be present while extrusion does not cause its presence.

EXAMPLE II

The procedure of Example I was repeated with alloy AZ31A (3 percent aluminum, 1 percent zinc, remainder magnesium) and AZ91A (9 percent aluminum, 1 percent zinc, remainder magnesium) and a variety of fabrication methods used to form the anode. The following table summarizes the results obtained.

Table II
TESTS

Anode Compo- sition	Slug Type	Railroad Lantern Delay, Seconds				General Purpose Delay, Seconds	
		AM		PM		Max.	Ave.
		Max.	Ave.	Max.	Ave.		
AZ31A---	Impact extruded—Ex- truded slugs.	6	4.6	15	10.6	5	2.9
AZ31A---	Impact extruded—Die- cast slugs.	2.3	1.8	8	4.7	3.2	1.5
AZ31A---	Die-cast-----	2.0	1.2	5	2.4	0	-----
AZ31A---	Die-cast heat treat—800 F—16 Hrs.—Furnace cool.	5.5	4.6	10	7.2	3	2.1
AZ31A---	Die-cast heat treat—1120 F—2 hrs.—H ₂ O quench.	2.0	1.2	3	2.5	0	-----
AZ91A---	Die-cast-----	13	8.5	7	5.3	2	1.4
AZ91A---	Die-cast heat treat—800 F—16 hrs.—Furnace cool.	49	25.0	12	2.9	3	1.9

† Above the Solidus Temperature.

Table II illustrates that the die-cast anode shows a lowered delay action than impact extruded from extruded slug anodes, because the first method forms massive $Mg_{17}Al_{12}$ compound, while the second method does not form this material. Alternatively, impact extrusion of a die-cast slug retains sufficient massive $Mg_{17}Al_{12}$ compound to cause improved delay action. The table also illustrates that massive $Mg_{17}Al_{12}$ compound can be destroyed by solution heat treatment, with the loss of the improved delay properties.

EXAMPLE III

To illustrate that heat treatment by itself is not suffi-

Table III

Heat-Treat Temperature	General Purpose Test Delay, Seconds	
	Max.	Ave.
30 Blank-----	3	1.8
200 F-----	3	1.6
400 F-----	3	1.5
600 F-----	3	1.8
700 F-----	3	1.8
800 F-----	3	2.0
900 F-----	3	1.5
1000 F-----	2.8	1.2
1120 F.†-----	1.2	0.1

† Above the Solidus Temperature.

Various modifications may be made in the present invention without departing from the spirit and scope thereof and it is to be understood that we limit ourselves only in the appended claims.

We claim:

1. A process for preparing an anode for use in a primary magnesium cell which comprises heating a magnesium alloy containing from 1 to 12 percent aluminum to a temperature above its solidus temperature, but below its liquidus temperature, cooling the resulting heated alloy at a rate greater than 500 Fahrenheit degrees per minute.

2. A process for preparing an anode for use in a pri-

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mary magnesium cell which comprises heating a magnesium alloy containing from 1 to 9 percent aluminum to a temperature of about 1130 degrees Fahrenheit, cooling the resulting heated alloy at a rate greater than 1000 Fahrenheit degrees per minute.

3. A primary battery cell comprising an anode of magnesium having massive $Mg_{17}Al_{12}$ compound dispersed therein, a manganese dioxide depolarized cathode, and an electrolyte comprising an aqueous solution of an inorganic bromide selected from the group consisting of the alkali metal, alkaline earth metal and ammonium bromides.

4. An anode for a primary magnesium cell which comprises an alloy which has been formed by die casting, said alloy containing from 1 to 12 percent aluminum, from 0.0 to 3.0 percent zinc, from 0.0 to 0.5 percent

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calcium, the balance being commercial magnesium containing not over 0.005 percent iron, not over 0.002 percent nickel, and not over 0.6 percent manganese.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,952,727

September 13, 1960

Roy C. Kirk et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 58, for "AZ10A" read -- AZ31A --.

Signed and sealed this 16th day of May 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents