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SUPERIOR GALVANIC MAGNESIUM ANODE

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This invention relates to a magnesium galvanic anode and is more particularly concerned with a method of preparing such an anode.

Magnesium galvanic anodes have been used extensively to prevent galvanic action of various metals in contact with soil, such as pipe lines, steel supporting structures, etc. For many such applications it is desirable to have an anode which exhibits both high solution potential and high current efficiency without seriously affecting the other electrochemical properties. Prior art galvanic magnesium anodes in order to provide an acceptable current efficiency have required careful control of alloying impurities. In addition heat treating of the formed anode is sometimes used.

A principal object of the present invention is to provide a superior magnesium anode. Another object of the present invention is to provide a method of forming a galvanic magnesium anode directly from cell magnesium without the necessity of a subsequent heat treatment. A further object of the present invention is to provide a magnesium alloy galvanic anode containing from 0.2 to 2.0 percent manganese with certain normal alloying impurities, the remainder being magnesium. Another object of the present invention is to prepare such an anode by pouring a suitable molten alloy into a water-cooled mold, removing the alloy from this mold when its temperature is between 450 and 350 degrees centigrade, and, thereafter water-quenching or air-cooling to provide a galvanic magnesium anode. Other objects will become apparent hereinafter.

The foregoing and additional objects have been accomplished by heating a magnesium alloy containing from 0.2 to 2.0 percent manganese and from 0.0 to 1.0 percent other metallic alloying materials to a temperature above its molten temperature, pouring this molten magnesium alloy into a water-cooled mold, cooling at a rate of at least 65 degrees centigrade per minute to a temperature between 350 and 450 degrees centigrade, and thereafter removing the molded alloy from the mold and either water-quenching or air-cooling. This procedure has resulted in a galvanic magnesium anode which will produce between 500 and 600 ampere hours per pound at an anode current density of 72 milliamperes per square foot.

While a cooling rate of at least 65 centigrade degrees is operative for the initial cooling rate, it is preferred that a cooling rate of about 85 centigrade degrees per minute be employed and desirably a cooling rate of about 100 centigrade degrees per minute is used. These cooling rates may be readily obtained by utilizing a water-cooled mold. A convenient mold is a Junkers-type mold. The cooling rate will be dependent upon the amount of water passed through the mold and upon the amount of surface of the anode exposed to the cooling. After the anode has been cooled in the mold to below 450 degrees centigrade,

but above 350 degrees centigrade, preferably above 375 degrees centigrade, the anode is removed from the mold and either quenched in a water bath or air-cooled. Where a water-quench is employed, a cooling rate in excess of about 500 centigrade degrees per minute will result, and a rate of 1,000 centigrade degrees per minute sometimes results. On the other hand, when air-cooling is employed, rates as low as 1 centigrade degree per minute from the temperature on removal from the mold to 100 degrees centigrade will result, although an air-cooling rate of about 5 centigrade degrees per minute is usual. It is to be understood that other cooling exchange mediums than water may be used for the water-cooled mold, similarly the quenching may be accomplished in other liquid mediums than water, and also similarly other gases may be substituted for the air in air-cooling the choice of a specific heat exchanger or medium dependent on the particular situation presented. Generally, however, water or air will be employed. Cooling rates greater than about 10 C./minute below 350° C. yield galvanic anodes having a lower solution potential and lower current efficiency. A temperature range appears to exist lower than 350° C. through which we must cool either very slowly or very rapidly.

Following the two-stage cooling procedure of the present invention, it is possible to produce a magnesium galvanic anode which will supply more current to the cathode at a high current efficiency. Another advantage is that the anode may be formed directly from cell magnesium without requiring a subsequent heat treatment.

The following examples are given to illustrate the process of the present invention but are not to be construed as limiting.

Example I

Casting SQ was cast directly from a production cell at 650 degrees centigrade by pouring into a water-cooled mold and cooled at the rate of 65 centigrade degrees per minute. It was removed from the mold when it reached a temperature of 480 degrees centigrade and thereafter water-quenched. This casting when tested in a $CaSO_4$—$Mg(OH)_2$ electrolyte yielded between 500 and 600 ampere hours per pound at an anode current density of 72 milliamperes per square foot. This is the same range as would be obtained from the best commercial anode material on the market today. The casting also had a solution potential about 250 millivolts greater in laboratory evaluation than the same best commercial anode. This means that about 40 percent more current can be obtained from the water-cooled alloy. In saline soils, this alloy would be expected to yield over 100 ampere hours per pound more than AZ63A alloy from previous tests.

Composition	Percent Al	Percent Cu	Percent Fe	Percent Mn	Percent Ni	Percent Si
SQ	<.001	.0009	.032	0.76	<.001	<.005

Example II

A magnesium anode TC, containing 0.5 to 1.0 percent Mn, was cast in a water-cooled mold from 650 to 350 degrees centigrade in 4 minutes. The casting was removed from the mold at a temperature of about 350 degrees centigrade and air-cooled to room temperature. This casting, when tested in a $CaSO_4$—$Mg(OH)_2$ electrolyte, yielded between 500 and 550 ampere hours per

pound. Again, the magnesium-manganese alloy yielded solution potentials about 250 millivolts greater than the best commercial anode. This means much more current can be obtained from an anode of equal size.

Composition	Percent Al	Percent Cu	Percent Fe	Percent Mn	Percent Ni	Percent Si
TC	.0033	.0010	.033	0.73	.001	<.005

Example III

Casting TB, cast from an operating magnesium cell containing 0.61 percent manganese, was cast in a Junkers-type mold and cooled at 75 centigrade degrees per minute to 390 degrees centigrade. At this temperature, it was removed from the mold and air-cooled to room temperature. The average air-cooling rate was 5.3 centigrade degrees per minute. This casting had a solution potential of 1.800 volts with respect to a calomel reference electrode.

Various modifications may be made in the method of the present invention without departing from the spirit or scope thereof and it is to be understood that I limit myself only as defined in the appended claims.

I claim:

1. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and from 0.0 to 1.0 percent other materials and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, removing said alloy from said mold at said temperature and cooling said alloy at a different rate.

2. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and 0.0 to 1.0 percent metallic materials other than magnesium and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, and, thereafter cooling said alloy to a temperature below approximately 110 degrees centigrade by quenching.

3. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and 0.0 to 1.0 percent metallic materials other than magnesium and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, and, thereafter air-cooling said alloy to a temperature below approximately 100 degrees centigrade.

4. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and 0.0 to 1.0 percent metallic materials other than magnesium and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, and, thereafter air-cooling said alloy at a rate of approximately 5 centigrade degrees per minute to a temperature below about 100 degrees centigrade.

5. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and 0.0 to 1.0 percent metallic materials other than magnesium and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, and, thereafter quenching said alloy to cool at a rate of at least 500 centigrade degrees per minute to a temperature below about 100 degrees centigrade.

6. A process for preparing a magnesium alloy which contains from 0.2 to 2.0 percent manganese and 0.0 to 1.0 percent metallic materials other than magnesium and which has superior galvanic anode activity, comprising: cooling said alloy from its pourable temperature to a temperature between 450 and 350 degrees centigrade at a rate of at least 65 centigrade degrees per minute in a water-cooled mold, and, thereafter quenching said alloy to cool at a rate of at least 1000 centigrade degrees per minute to a temperature below about 100 degrees centigrade.

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