주조법에 의해 제조된 마그네슘 합금에서 칼슘 첨가가 전기화학적 특성에 미치는 영향

The Effect of Ca Addition on Electrochemical Properties of Mg-alloy by Casting

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Key words : Electrochemical property, Mg-Ca alloy, Sacrificial anode

요약

본 연구에서는 주조법으로 제조한 Mg-Ca 합금의 전기 화학적 특성을 알아보고자 하였다. 연구결과에 의하면 전기 화학적 특성이 불순물의 화학조성과 매우 밀접한 관계가 있으며, 칼슘 첨가 전·후 뚜렷한 미세구조 변화가 있음이 관찰되었다. 본 연구로부터 적은 양의 칼슘이 첨가되면 마그네슘 합금의 미세구조적 변화를 통하여 우수한 전기화학적 특성이 얻어질 수 있음이 확인되었다.

Abstract

It is the purpose of the present paper to report results of a preliminary electrochemical characterization of the as-cast Mg-Ca alloys. Electrochemical data will be correlated with chemical composition of impurities, and the microstructural change before and after Ca is added. This paper shows that small addition of Ca imparts beneficial effect in electrochemical properties of Mg alloys, primarily, through microstructural modifications.

I. Background

The composition of different Mg alloys is known to affect their current capacity, potential, and anode efficiency [1,2]. Many alloying elements have been used in attempts to improve the electrochemical properties of magnesium anodes. Significant improvements of electrochemical properties have been achieved by controlling the adverse effects of impurity elements such as Fe, Ni, and Cu with alloying elements [3]. Out of alloying elements, Ca is considered as a very effective element that can improve the electrochemical properties of Mg-alloys because of its relatively low potential in comparison with specified elements such as Mn, Al, Zn in high Mn alloys or AZ63 alloys with the effect of grain refining, and the extended solid solution at 516.5C as shown in phase diagram of Mg-Ca alloy [4]. In addition, since Ca has a low density (1.55g/cm^3), Mg-Ca alloys have the added advantage of preserving the low density of magnesium. Ca has recently been used as a common inhibitor for the ignition of molten Mg alloys [5,6]. Despite the apparent potential for Mg sacrificial anodes, Mg-Ca based alloys have received little attention. It is the purpose of the present paper to report results of a preliminary electrochemical characterization of the as-cast Mg-Ca alloys. Electrochemical data will be correlated with chemical composition of impurities, and the microstructural change before and after Ca is added. This paper shows that small addition of Ca imparts beneficial effect in electrochemical properties of Mg alloys, primarily, through microstructural modifications.

II. Experimental method

In order to investigate the electrochemical properties of Mg alloys as Ca contents, *nominally pure (greater than* 99.9%) Chinese magnesium ingot of commercial grades and nominally pure (greater than 99.8%) calcium of type of granular was electric furnace melted in steel crucible under CO_2+ 0.1% SF_6 mixed gas. Samples are prepared separately by cooling a melt into steel molds preheated to 200℃. Chemical compositions of the obtained magnesium alloys are listed in Table I. Samples for chemical analysis is taken from the top and bottom of each ingot, and, cylinder anodes 12.7mm in diameter and 152mm high were machined from the center of produced Mg-Ca alloys without heat treatment. Evaluation of anode efficiency and open circuit potential were carried out according to ASTM G97-89 [7] and ASTM G5-94 [8], respectively, with the standard test method for underground applications of magnesium sacrificial anodes. For this purpose, a known direct current (0.039 mA/cm^2) is passed through a test cell connected in series. Each test cell consists of a pre weighed magnesium anode specimen, a pot container, and a known backfill electrolyte (75% gypsum + 20% bentonite + 5% Na_2SO_4). The specimens are measured several times during the 14 days, and, test one hour after the current is off. After the test, each specimen is cleaned and weighed. The ampere-hours obtained per unit mass of specimen lost are calculated. After assessment of current efficiency, HNO_3 etching solution of 25% composition was used to investigate the microstructure of Mg-Ca alloys. Microstructure and chemical composition of Mg-Ca alloys were observed under optical and transmission electron microscopy (TEM) to understand microsturctural change before and after adding Ca.

Table 1. Chemical composition of Mg-Ca alloys (wt%)

Spec. Comp.	Mn	Ca	Al	Zn	Fe	Ni	Si	Cu	Mg
Pure Mg	0.0022	0.0022	0.0027	0.0032	0.0017	0.0001	0.013	0.0013	Bal.
Mg-0.22Ca	0.0022	0.22	0.0059	0.0087	0.0022	0.0005	0.0181	0.0028	Bal.
Mg -0.56Ca	0.0022	0.56	0.0077	0.0085	0.0027	0.0005	0.0175	0.0028	Bal.
Mg -1.31Ca	0.0022	1.31	0.0069	0.0085	0.0025	0.0005	0.0178	0.0028	Bal.

III. Result and Discussion

Figure 1 shows the values of open circuit potential (OCP) of magnesium alloys containing calcium and pure the pure magnesium. The OCP of pure magnesium was measured to be 1.62V. Addition of calcium of 0.22% to the pure magnesium resulted in lowering the OCP by 0.16V, i.e., -1.78V. Its OCP is equal or lower than that of the Mg-1.1%Mn alloy (-1.75V), which has been known to give the highest driving force for cathodic protection until now. However, further addition of the calcium up to 1.3% increased the OCP of Mg-Ca alloys up to 1.63V. It would be attributed to the change of microstructures of as-cast Mg-Ca alloys with the variation of calcium contents (Figure 2).

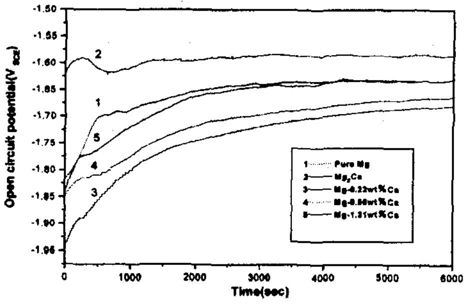

Fig 1. Open-Circuit Potential after 14day galvanostatic test of Mg-Ca alloy

As seen in Figure 2, the grain size decreased and grain boundaries were thickened with increasing the calcium content in Mg-Ca alloys. The transmission electron micrograph of the grain boundary region of Figure 3 shows the lamellar structure between grains. From the EPMA analysis with an electron beam of 10㎛, it was found that the calcium content at the regions with lamellar structure was 4.71% (Table II). Such a segregation of calcium is due to the eutectic reaction originated from the non-equilibrium solidification of Mg-Ca alloys. As shown in a step-scanned X-ray diffraction for Mg-1.3%Ca alloy of Figure 4, the observation of a second phase of Mg_2Ca is an evidence for the eutectic reaction. Under the condition of non-equilibrium solidification, the portions of the eutectic regions in Mg-Ca alloys and the Mg_2Ca with the eutectic regions increase with increasing calcium content in Mg-Ca alloys as shown in Figure 2. Thus, as-cast Mg-Ca alloys considered in this study consist of the solid solution and the Mg_2Ca phase. In order to predict the OCP of as-cast Mg-Ca alloys, OCP data for the solution and Mg_2Ca are required, because the OCP of an alloy composed of two different phases depends on the area ratio of the two phases. For this purpose, the Mg_2Ca sample was prepared by melting the mixture of calcium and magnesium granules in an electric furnace under argon atmosphere and its phase was checked by XRD (Figure 5). The OCP of Mg_2Ca phase is 1.58V, whereas that of the solid solution is not clear. The OCP of the solid solution with a maximum solid solubility in as-cast Mg-Ca alloys might be similar to that of Mg-0.22%Ca alloy, -1.78V, because the amount of Mg_2Ca phase in as-cast Mg-0.22%Ca alloy is very small as seen in Figure 2(b). This means that the Mg_2Ca phase is noble than the solid solution. Considering that the area ratio of the nobler Mg_2Ca phase to the solid solution increase with increasing the calcium content, the OCP of as-cast Mg-(0.22~1.33%)Ca alloys increase with increasing its calcium content. Figure 6 shows anode efficiencies of three kinds of as-cast Mg-Ca alloys and the pure magnesium. Addition of small amounts of calcium of 0.22% raises the anode efficiency from 50.4% to 62.1%, but further addition of calcium up to 1.3% decrease up to 50.4%. It is difficult to explain

Table 2. Chemical composition analysis of Mg-Ca alloy

Alloy comp. element	Mg	Ca
Mg-0.22Ca		
Matrix	99.785	0.215
Grainboundary	99.430	0.570
Mg-0.56Ca		
Matrix	99.673	0.327
Grainboundary	96.502	3.498
Mg-1.31Ca		
Matrix	99.883	0.117
Grain boundary	95.285	4.715

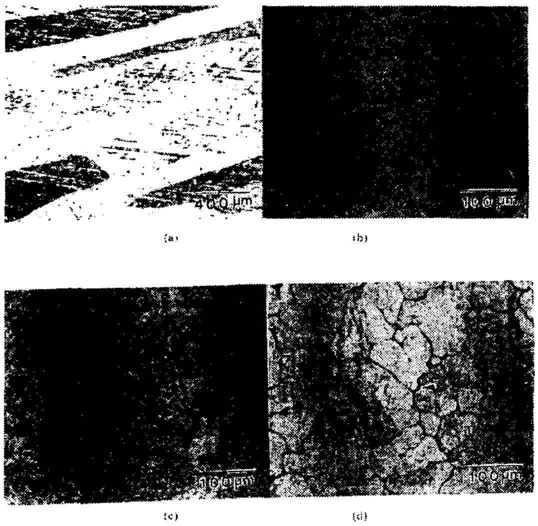

Fig 2. Optical micrographs of Mg alloys with Ca contents.
(a) pure Mg (b) Mg-0.22wt%Ca (c) Mg-0.56wt%Ca
(d) Mg-1.31wt%Ca

Fig 3. TEM micrograph of Mg-1.31wt%Ca alloy with Mg_2Ca compounds at grain boundary, indicating by an arrow in figure 2 (d)

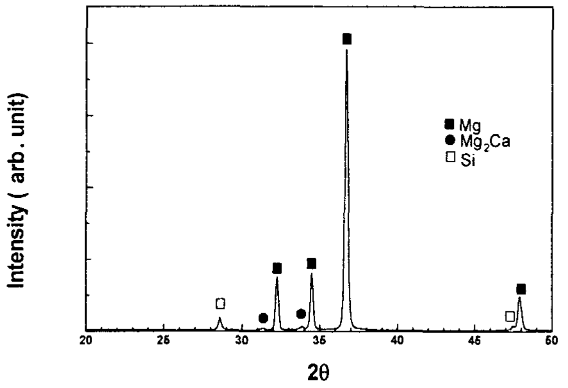

Fig 4. A step-scanned X-ray diffraction pattern for Mg-1.3%Ca alloy.

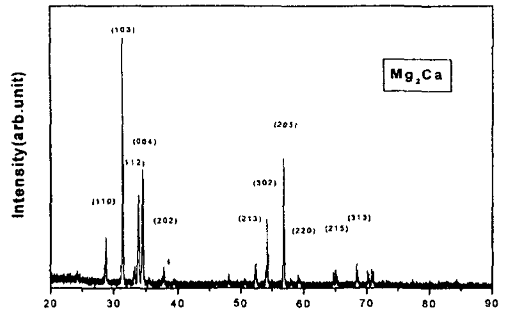

Fig 5. XRD spectrum of Mg-Ca alloy produced by a mole of 2:1, which shows only the pattern of Mg_2Ca compound.

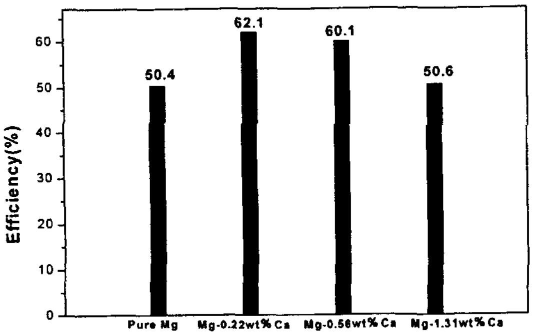

Fig 6. Anode efficiencies of three kinds of as-cast Mg-Ca alloys and the pure magnesium after 14day galvanostatic test

the reason for the former phenomenon. It may be attributed to the grain refinement and the modification of secondary phases by addition of calcium. The latter phenomenon, however, is easily understood. Since the Mg_2Ca phase is nobler than the solid solution, a galvanic cell is formed between the two phases, i.e., the Mg_2Ca phase and the solid solution take roles of a cathode and a anode, respectively. The area ratio of the cathode to anode increased with increasing the calcium content, so that the anode efficiency of as-cast Mg-(0.22~1.3%Ca) alloys decreased with the calcium content. Surface morphologies of as-cast Mg-0.22Ca and Mg-1.3%Ca alloys are shown in Fig 7. Photographs are taken from samples after electrochemical tests. The Mg-1.3%Ca alloy is severely attacked and exhibits large extended pits, while the Mg-0.22Ca alloy exhibits relatively uniform corrosion and small pit sizes. This means that increment of the area ratio of cathode to anode accelerates the local corrosion in eutectic regions and hence decreases the anode efficiency.

In summary, small addition of calcium in the range between 0.2% and 0.5% to the pure magnesium improves the anode the anode efficiency up to 62% and decreases the OCP up to 1.73V. For this reason, as-cast Mg-(0.2~0.5%)Ca alloys will be applicable to cathodic protection of buried steel structure, even though electrochemical properties of soils is fluctuated.

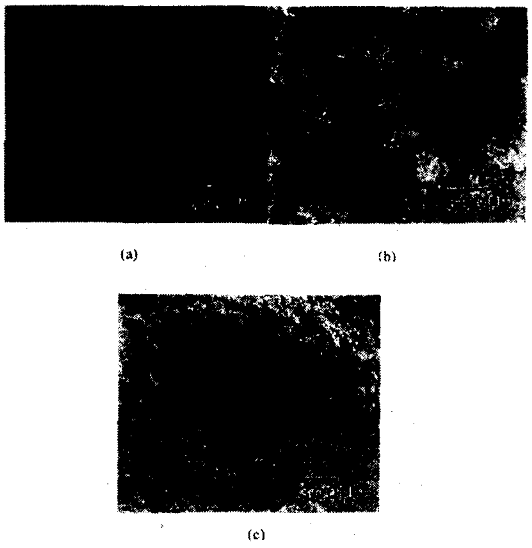

Fig 7. Surface morphology of Mg alloys after corrosion test. (a) commercially pure Mg, (b) Mg-0.22wt%Ca, (c) Mg-1.31wt%Ca

IV. Conclusion

The development of eutectic compound, Mg_2Ca phase into binary Mg-based alloys is not desirable to the control of electrochemical properties. However, small addition of calcium, below solubility limit, in magnesium alloy imparts beneficial effect in electrochemical properties of presented Mg-based alloys, primarily through microstructural modification.

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