Source of Calcium – CaO & $CaCl_2$ Addition and its Recovery Effect into Pure Mg

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Abstract

Over the past few years, numbers of researchers work on the Mg-Ca system. The reason behind this area is due to its very good high specific strength and stiffness, elasticity, low density, and biocompatibility. All most, all researchers use sources of calcium in its master alloy form. The readily available master alloy contains 11 to 45 wt.% of calcium. Present research work selects two sources of calcium, like calcium oxide and calcium chloride. In both, the source of calcium, the amount of addition is fixed, and it is 3.5 wt.%. The result shows that recovery of calcium from calcium chloride is approximately 50% more compare to calcium oxide. Tensile strength, hardness, electrical conductivity, and corrosion rate measurement of developed Mg-Ca alloy were studied using the tensometer, Brinell hardness test, electrical conductivity meter, and immersion test. Results show that recovery of calcium from calcium chloride is more compare to calcium oxide. The presence of calcium increases the hardness, tensile strength, and corrosion resistance behavior. It decreases the electrical conductivity of calcium-containing alloy.

Keywords: Mg-$CaCl_2$, Mg-CaO, Tensile strength, Hardness, Corrosion rate

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1. Introduction

Mg and its alloys are very useful in automotive, aircraft, electronics, and sports industries due to high strength to weight ratio, lower density, higher damping capacity, good stiffness, and easily die-cast property. [1-5] It has the potential to be used as biodegradable implants in the human body for load-bearing and bone repairing applications. However, the use of this alloy is restricted in some areas due to the highly corrosive nature of chloride and the physiological environment. By alloy addition and surface treatment, this limitation can be overcome and the corrosion rate of magnesium can be enhanced. [6-11]

Calcium plays an important role as an alloying element in pure magnesium and its alloys. It can refine the grain and improve corrosion resistance, mechanical and thermal properties, and creep resistance. As per Mg-Ca binary diagram, the solubility of calcium in magnesium is 1.34 wt. % at 516.5°C. [6,12-14] Zijian Li et. al. [14] and Yuncang Li [15] reported that a higher amount of calcium causes brittleness in Mg-Ca alloy. An ultimate strain of Mg-Ca alloy decreased with increasing calcium content. So, the ideal calcium content for magnesium alloys is less than 1 wt.% preferred. [15, 16] On the other hand, calcium addition is also effective during the melting of magnesium alloys to prevent them from ignition and oxidation. At present, ignition-proof and non-combustible Mg-Ca alloys are used in the aerospace, rail, and construction area. [16,17]

In most of the studies, to develop Mg-Ca alloy, calcium is added as Mg-Ca master alloy (Mg-20%Ca, Mg-30%Ca). [18] But, in this study calcium was added in the form of calcium oxide and calcium chloride form to check its recovery in commercially pure magnesium. The effect of Ca on the tensile strength, hardness, electrical conductivity, and corrosion rate of magnesium were examined in detail.

2. Experimental Procedure

2.1. Casting

Commercial pure magnesium ingot (97.19%), calcium oxide, and calcium chloride were used to developed Mg-Ca alloys. Pure Mg ingot and calcium sources were procured from a local supplier of Vadodara. A resistance heating furnace was used to prepare the alloy inside the inert-graphite crucible. In a molten state, magnesium has a highly oxidized nature. Thus, to protect molten Mg from oxidation and burning flux 220 was used as a cover flux. Maximum 720 °C temp. was maintained on the furnace. 3.5 wt.%

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CaO was added in molten Mg at this temperature and held for 15 minutes. After that, it was stirred and poured into a preheated metallic die after degassing defluxing. By a similar process, Mg-Ca alloy was prepared from $CaCl_2$ addition.

2.2. Compositional evaluation of prepared alloys

The compositional analysis of developed magnesium alloys was checked by EDS analysis with ± 0.01% accuracy. (JSM-5610LV). The results of developed alloys are listed in Table 1.

Table 1. Compositional analysis pure Mg and developed alloys

Pure Mg & Developed Alloys	Ca	O	Mg
Pure Mg	-	2.81	Bal.
Alloy 1: Mg-Ca alloy (CaO addition)	0.52	4.68	Bal.
Alloy 2: Mg-Ca alloy ($CaCl_2$ addition)	1.16	3.64	Bal.

2.3. Mechanical and electrical properties

Room temperature ultimate tensile strength of pure magnesium and Mg-Ca alloys were measured using Monsanto-20 machine. The cross-head speed of the machine was set at 0.05 mm/min. Dimensions of the tensile specimen are shown in fig. 1. The hardness was measured by the Brinell hardness tester at 31.25 kg load. Electrical conductivity was measured on a conductivity meter (% IACS) which is based on the eddy current principle. An average of 3 measurements was taken for all alloys.

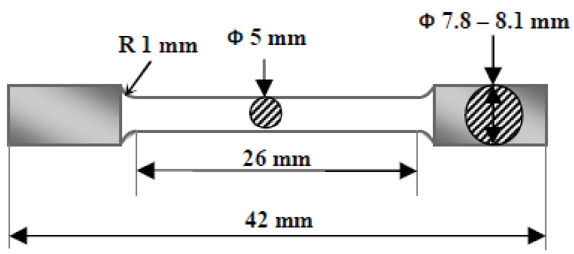

Fig. 1. Tensile Test Specimen

2.4. Immersion test

The corrosion rate of pure magnesium and both alloys was measured by immersion test (ASTM G31-71). [20] Three specimens of pure Mg and each alloy were taken. The dimensions and weight of all specimens were measured before the test. After those specimens were immersed in 3.5 weight % NaCl solution at room temperature for 24 hrs. Once the test was complete, the specimens were collected and dip in CrO_3, $AgNO_3$, Ba $(NO_3)_2$, and reagent water solution for 1 minute. [21] Specimens were dried in hot air and then weighed again.

3. Results and Discussion

3.1. Calcium recovery in magnesium

As per Haughton and Vossklihler, 1.8 % and 0.78 % Ca were soluble at 516°C respectively. [22] To develop Mg-Ca alloy, generally, Mg-Ca master alloy is added as calcium source but in this study, calcium was added in the form of calcium oxide and calcium chloride at 750 ºC. The melting point of $CaCl_2$ and CaO is around 780 ºC and 2572 ºC respectively. Due to the high melting point, calcium recovery from calcium oxide is very less i.e., 0.52 wt.%. Among both sources, maximum calcium was soluble from calcium chloride form.

3.2. Characterization of developed alloys

3.2.1 Hardness, UTS, and Electrical conductivity

Above mentioned properties are presented in fig. 2. As per result, the presence of a very small quantity of calcium increases hardness and UTS of pure Mg in a very remarkable way due to solid solution phenomena. Maximum hardness and UTS were achieved in alloy 2 - 52 BHN and 172 MPa respectively. However, the presence of calcium and Mg_2Ca precipitates obstruct the movements of electrons and decrease the electrical conductivity of pure Mg. [23]

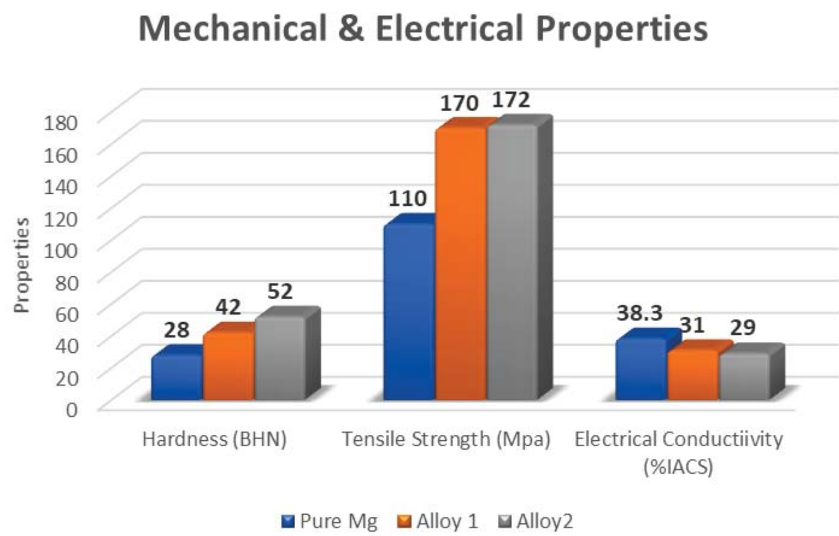

Fig. 2. Mechanical and Electrical Properties of all systems

3.3. Corrosion rate measurement

The corrosion rate of pure magnesium and developed alloys was measured by equation 1. [24]

$$mpy = \frac{534\,W}{D\,A\,T} \qquad (1)$$

To measure the density of pure magnesium and developed alloys water displacement method was used. The density of pure magnesium, Alloy 1, and alloy 2 is 1.738 gm/cc, 1.793 gm/cc, and 1.802 gm/cc respectively. Weight loss of all specimens was measured which is shown in table 2. The result shows that the corrosion rate of 0.5 wt.% calcium containing alloy is high compare to pure magnesium. However, more than 1 wt.% calcium containing alloy shows less corrosion rate compare to magnesium which shows in fig. 3.

Table 2. Weight loss in immersion test

Sr. No.	Pure Mg & Developed Alloys	Initial weight of Specimens (gm)	Final weight of Specimens (gm)	Total weight loss (gm)
1	Pure Mg	5.70	5.68	0.02
2	Alloy 1: Mg-Ca alloy (CaO addition)	5.68	5.65	0.03
3	Alloy 2: Mg-Ca alloy ($CaCl_2$ addition)	9.37	9.35	0.02

Macroscopic examination of all samples was carried out before and after the corrosion test. As shown in fig. 4 after 24 hrs. dipping in 3.5 % NaCl solution, very small pits were observed in pure magnesium sample. In Alloy 1, more pits were observed which are bigger than the pure magnesium sample. More amount of calcium decreases the corrosion rate. Here, Small and fewer pits were observed in alloy 2.

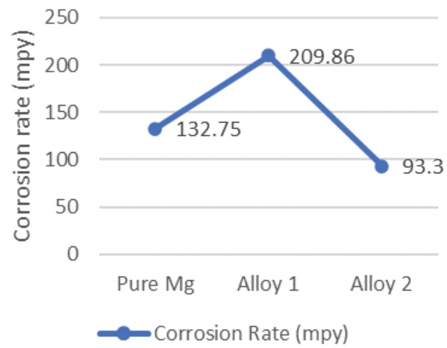

Fig.3. The corrosion rate of pure Mg and developed alloys

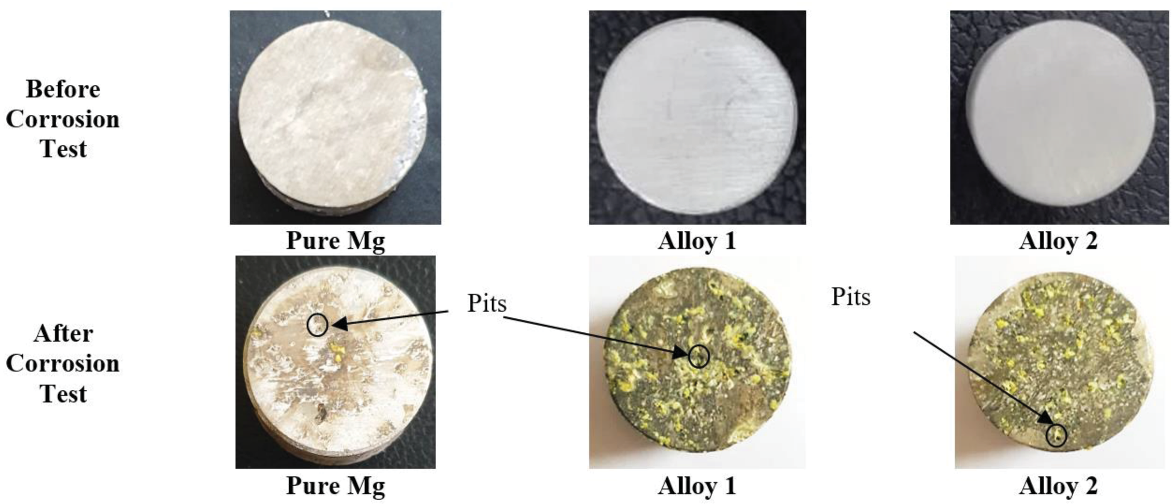

Fig.4. Sample before and after corrosion test

4. Conclusions

- Calcium chloride should also be used to develop Mg-Ca alloys. Calcium recovery from calcium chloride is more compare to calcium oxide.
- Compare to pure magnesium, the addition of 1 wt.% calcium increases hardness value from 28 BHN to 52 BHN and tensile strength from 110 MPa to 172 MPa.
- The presence of calcium in magnesium decreases electrical conductivity from 38.3 to 29 % IACS.
- The presence of calcium improves the corrosion resistance of commercially pure Mg in the case of a source of calcium from $CaCl_2$.
- In the case of the addition of calcium oxide, instead of reducing the corrosion rate, it accelerates it compare to commercially pure magnesium.
- Compare to the source of CaO and $CaCl_{2,}$ $CaCl_2$ addition offers higher hardness, tensile strength, and even corrosion resistance value.

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