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Original Research Paper

Quantitative evaluation of initial galvanic corrosion behavior of CNTs reinforced Mg–Al alloy

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ABSTRACT

The macroscopic corrosion phenomenon of the CNTs reinforced Mg composites remarkably occurred in the moist environment, due to a large potential of the galvanic cells formed between α-Mg matrix and CNTs. Therefore, it is necessary to reduce the potential difference at their interfaces in order to obstruct the galvanic corrosion phenomenon. In this study, AZ61B alloy composites reinforced with CNTs (CNT/AZ61B) were fabricated by powder metallurgy method, and their potential differences between CNTs and the α-Mg matrix were reduced by concentration of Al atoms around CNTs via heat treatment. The potential distribution around CNTs was measured by using scanning Kelvin probe force microscopy (SKPFM). Heat treatment of CNT/AZ61B composites at 823 K for 10 h caused the obvious concentration of Al atoms around CNTs, and resulted in the remarkable decrease of the potential difference at the interface between the α-Mg matrix and CNTs. Additionally, the salt water immersion test results indicated that the corrosion rate of CNTs/AZ61B composite materials after heat treatment was obviously reduced to less than about 30% of the non-treated composite material. Thus, the changes of α-Mg matrix potential by concentrating Al atoms around CNTs was effective to improve initial galvanic corrosion resistance of CNTs reinforced Mg composites.

1. Introduction

Magnesium (Mg) alloys, due to their low density of 1.738 g/cm^3 have applications in various structural and mechanical components. It is widely recognized that replacing the conventional structural materials such as steels or aluminum alloys with Mg alloys can significantly reduce the fuel consumption of the transportation vehicles [1]. However, some disadvantages such as poor corrosion resistance, low mechanical properties, and low formability have limited their applications. One method to improve the mechanical properties of Mg alloys is utilizing of effective reinforcements, that is, Mg based metal matrix composites (Mg-MMCs). Carbon nanotubes (CNTs) [2] have been considered as one of the superior reinforcement materials of Mg-MMCs because of their exceptional mechanical properties such as high Young's modulus of 4 TPa [3] compared with 44 GPa for pure Mg [4]. Thus, many efforts have been made to produce Mg-MMCs with CNTs to improve the mechanical properties [5–10]. In spite of the segregation of CNTs bundles caused by its own van der Waals force, some recent studies succeeded to improve mechanical properties of Mg alloys with CNTs [5,6,10].

However, according to the previous studies [11], carbon element is electrically much nobler than Mg. Therefore, the local galvanic cell was formed between the α-Mg matrix and CNTs of the composite, and resulted in a poor corrosion resistance of the Mg–CNT composites compared to the monolithic Mg material. Thus, it is necessary to reduce the potential difference at their interfaces in order to obstruct the galvanic corrosion phenomenon. Solid solution of Al is significantly effective to improve corrosion resistance of Mg by increasing the standard hydrogen electrode (SHE) of the α-Mg matrix [12]. Therefore, the concentration of solid-soluted Al atoms around CNTs is expected to improve corrosion resistance of Mg–CNT composites by reducing the potential difference between the α-Mg and CNTs. In this study, AZ61B alloy composites reinforced with CNTs were fabricated by powder metallurgy method. Heat treatment (HT) was served to the composites at 823 K for 10 h under Ar gas atmosphere to concentrate Al elements at the interface. SKPFM analysis was carried out to quantitatively measure the potential difference at the interface of the composites. In addition, the corrosion performance of the composites was evaluated with the immersion tests in 3 mass% sodium chloride (NaCl) aqueous solution.

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2. Experimental

2.1. Fabrication of AZ61/CNT composites

Fig. 1 showed the raw materials used in this study; (a), (b) and (c) were AZ61 Mg alloy powders, multiwalled CNTs (MWCNT) NC7000, and vapor grown carbon fiber (VGCF), respectively. The chemical composition of the AZ61 Mg alloy powder is Al, 6.38; Zn, 0.68; Mn, 0.28; Si, 0.04 mass%. Dimensions of NC7000 and VGCF were 1.5 and 8 μm in mean length and 9.5 and 150 nm in mean diameter, respectively.

AZ61/CNT composite was fabricated through two steps: the CNT-coating step with the solution containing zwitterionic surfactant, which is the surface active agent having both negative and positive charges at the tip of its hydrophilic groups, and the consolidation step by spark plasma sintering (SPS) technique [13]. In the CNT-coating steps, CNT coating on the powder surface was conducted as the schematic illustration shown in Fig. 2. First, AZ61 raw powders were dipped into the aqueous solution containing the zwitterionic surfactant, 3-(*N,N*-dimethyl stearyl ammonio) propane sulfonate, with CNTs. Then, the paste-like composite powders were dried at 353 K for 3 h, and heated at 773 K for 1 h in argon (Ar) gas atmosphere to thermally decompose residual surfactants. After removing surfactant residues, the composite AZ61 powders coated with un-bundled CNTs were consolidated into columnar billets having 42 mm of diameter and about 25 mm of height, the consolidation was carried out at 823 K for 5.5 h with 30 MPa pressure in vacuum by SPS. Subsequently, in order to densify the billets, hot extrusion was applied to the SPSed billets at 623 K with extrusion ratio of 37 and speed of 0.3 mm/s. The extruded AZ61 alloy rods had 7 mm in diameter and about 1 m in length. With these extruded rods, carbon content of each sample was measured by inert gas fusion instruments carbon–sulfur determination (LECO Co., Ltd., CS-200). Since no other carbon source was included in these composites the measured C content could be regarded as CNT content of the composites. For convenience, fabricated samples were coded depending on their content of CNTs as indicated in Table 1.

2.2. Enrichment of aluminum in Magnesium–CNT interface

In this study, in order to avoid the direct contact of α-Mg matrix with CNT, and reduce the potential difference in the galvanic cell, Al was attempted to be concentrated in the interface between α-Mg matrix and CNT. Several literatures reported a formation of ternary carbides of Al_2MgC_2 [14–20] by using Mg alloys containing a few Al elements. Formation of Al_2MgC_2 compounds indicates that solid-soluted Al atoms concentrated around the CNTs by the above HT could improve SHE of the α-Mg matrix [12]. Thus, the solid-soluted Al concentration around CNT is expected to improve corrosion resistance by reducing potential difference between the Mg and CNTs. Furthermore, the formation of Al_2MgC_2 is also expected to improve the corrosion resistance of Mg alloy by preventing the direct contact of α-Mg matrix with CNTs. However, the previous studies reported that a needle-like Al_2MgC_2 never covered the entire CNT surface [14]. Besides, Al_2MgC_2 formation via solid-state reaction requires long-time HT at relatively high temperature [19,20]. That is, it is difficult to form a layer structured Al_2MgC_2 compounds at the interface between α-Mg matrix and CNTs. As a result, the formation of Al_2MgC_2 has few effects on the corrosion resistance of Mg because it never prevents the direct contact of α-Mg matrix with CNTs. Therefore, the solid-soluted Al concentration is more important than Al_2MgC_2 formation from a viewpoint of improvement corrosion resistance of AZ61B alloy. When solid-soluted Al is concentrated in the α-Mg matrix near CNTs due to the Al_2MgC_2 formation, the potential difference between the matrix and CNTs will be reduced by increasing SHE of α-Mg matrix around CNTs. As a result, the improvement of corrosion resistance of the composites reinforced with CNTs is expected. In this study, heat treatment was applied to the Mg–Al alloys with CNTs composites to form solid-soluted Al-rich area around CNTs in the Mg matrix via the formation of Al_2MgC_2 compounds. The HT at 823 K for 10 h under Ar gas atmosphere was employed to concentrate Al atoms in the matrix of the extruded CNT/AZ61B composites.

2.3. Evaluation of local corrosion behavior scanning Kelvin probe force microscopy (SKPFM)

Surface potential difference (SPD) between α-Mg matrix and CNTs was calculated by measuring surface potential between each phase and the tip of $PtIr_5$ cantilever attached to SKPFM [21]. SKPFM calculates, in short, surface potential between cantilever and sample surface by measuring electrostatic force between them. The previous studies [12,20,22] reported that a surface potential is proportional to both a SHE and a standard electrode potential (SEP). Therefore, the surface potential measurement provides the basic platform to understand how large driving force of the galvanic couples is. Thus, the measurements were mainly conducted between α-Mg matrix and CNTs in the present study. SPD between two phases at the specimen surface was defined as the below expression with the surface potential acquired by SKPFM measurements.

$$\begin{aligned} \mathrm{SPD} &= V_{SP,2} - V_{SP,1} \\ &= (\Phi_{ptIr5} - \Phi_2)/e - (\Phi_{ptIr5} - \Phi_1)/e \\ &= (\Phi_1 - \Phi_2)/e \end{aligned} \tag{1}$$

where $V_{SP,1}$, $V_{SP,2}$, Φ_1 and Φ_2 are surface potential of phase 1, surface potential of phase 2, work function of phase 1 and work function of phase 2, respectively. Work function is the required energy to accelerate an electron from Fermi level, where electrons can possess the highest energy in the material, to vacuum level, which is the energy level enough far from the sample surface. For SKPFM scanning, specimens of 10 × 10 mm were ground with #600, #2000 and #4000 SiC abrasive papers, and subsequently polished with 0.25 μm diamond pastes. Then, the specimen surface was immediately cleaned in ethanol by using ultrasonic vibration. Though thickness of surface MgO films on specimen surface might affect experimental results due to the sensitiveness of surface potential

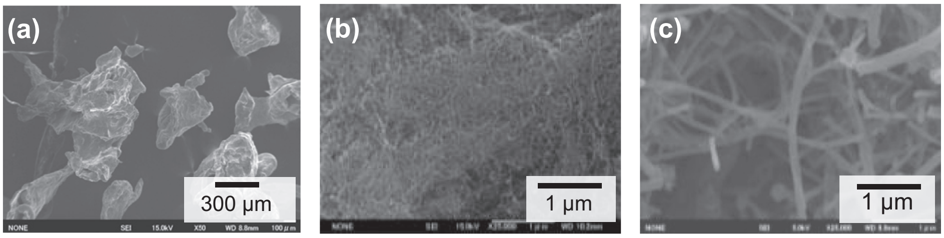

Fig. 1. FE-SEM observation on AZ61 powders (a), NC7000 (b), and VGCF (c).