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Review

Superhydrophobic surface of Mg alloys: A review

M. Yeganeh*, N. Mohammadi

Department of Materials Science and Engineering, Faculty of Engineering, Shahid Chamran University of Ahvaz, Ahvaz, Iran

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Abstract

In the present review, the formation of superhydrophobic (SHP) structures on the surface of Mg alloys was investigated. Different methods including hydrothermal technique, chemical and electrochemical deposition, conversion and polymer coating, and etching routes were discussed. The superhydrophobicity could form on the surface of Mg alloys by the application of different chemical, electrochemical, and physical methods followed by the immersion of these alloys in the solution containing modifying agents including fatty acids or long-chain molecules. The formed morphology, composition, and contact angle were reported and the effect of synthesis route on these characteristics was reviewed.

Keywords: Mg alloys; Superhydrophobic surfaces; Chemical deposition; Electrochemical coating; Conversion coating; Polymer coating; Etching.

Contents

1. Introduction

As one of the lightest engineering materials, magnesium alloys have exhibited quite special properties including high specific strength, low density, high thermal conductivity, electromagnetic shielding, excellent machinability, good vibration and shock absorption, high damping capacity, fine electromagnetic interference shielding properties, good weldability under the controlled ambient, excellent castability, and recyclability which lead to the specific applications such as automotive, aerospace, communication, electronics, medical, and other industries [1–6]. However, the inherent poor corrosion resistance of Mg alloys due to their low standard electrode potential is the major shortcoming regarding their applications in the aqueous or atmospheric media [7,8]. Besides, magnesium endures high chemical activity and the formed oxide film of magnesium alloy under the natural conditions

* Corresponding author.
E-mail address: m.yeganeh@scu.ac.ir (M. Yeganeh).

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is porous and non-protective [9]. Another problem is that the chemical activity of industrial magnesium alloys is typically inhomogeneous. For instance, AZ91D alloy which has been extensively used in the automobile industries is made of two phases including α (Mg) and β ($Mg_{17}Al_{12}$) phase [10]. Various surface treatment methods have been applied to reduce the chemical and electrochemical activity of magnesium including physical vapor deposition (PVD) [11–19], electroless plating [16–20], plasma electrolytic oxidation (PEO) [21–27], chemical conversion treatments [28–34], sol–gel coatings [35–39], calcium phosphate coatings [40–44], hydroxyapatite coatings [45–49], and polymer coatings [50–55]. One of the recent interesting strategies to improve the corrosion resistance of Mg alloys is the development of superhydrophobicity at the surface of these alloys [10,56–59]. Superhydrophobic surfaces are generally defined as the surfaces which water contact angles (θ) show the greater values than 150° and the sliding angles are smaller than 5° [60,61]. It could exhibit self-cleaning, anti-icing, anti-bacterial, anti-reflection, fluidic drag reduction, anti-corrosion, and anti-fogging behavior of surfaces if the superhydrophobic properties are created in the textiles, glasses, polymers, and metals [62–68]. If the direct contact of surface regarding magnesium alloy with the reactive environment reduces, the chemical activity of magnesium alloy decreases sufficiently. Thus, synthesis of a superhydrophobic layer/surface would be an attractive approach to improve the corrosion resistance of magnesium alloy, and therefore it could expect more potential applications for these interesting alloys [69].

Surface modification of Mg alloys due to their high activity and inhomogeneity is difficult [10]. Moreover, the formation of the corrosion products is quite complicated and not well understood yet. For example, when AZ91 Mg alloy is dipped in the aqueous solutions, the formed film on the surface of the α phase consists of three layers including an exterior layer of $Mg(OH)_2$, a middle layer of MgO, and an interior layer of Al_2O_3. The surface film on the β phase is different from that on α phase which leads to the inhomogeneity of surface chemistry [15,18,19]. Consequently, it is a great challenge to control the formation of corrosion products under the laboratory conditions [70–73].

In recent years, the fabrication of superhydrophobic surfaces has become an interesting area of active research-ing. In general, the main techniques which are applied for manufacturing of micro- and nanostructured layers, such as lithography, etching, chemical and electrochemical deposition, casting, plasma treatment, and replication have been used for the synthesis of superhydrophobic surfaces [74]. There are two significant requirements to fabricate a superhydrophobic surface including the roughening of the surface and the development of low surface energy. These two requirements lead to two major routes of producing superhydrophobic surfaces. The first route is to make a rough surface from an intrinsic hydrophobic material, and the second one is to modify an initially rough surface by changing the surface chemistry or applying a hydrophobic component layer [63,74,75].

In this review, the procedures and the routes of superhydrophobic surfaces (SHPSs) which were fabricated on the Mg alloys were summarized. It must be mentioned that most of these procedures require a distinct method of surface treatments (immersion, coating and roughening processes) with the various modification processes to decrease the surface energy. The main idea of categorization in this review relies on the synthesis processes before the modification stages. In this review, all processes categorize on the basis of chemical, electrochemical or physical surface treatment including hydrothermal technique, chemical and electrochemical deposition, conversion and polymer coating, and etching processes. Besides, it must be noted that before the processes, the Mg surfaces were polished, cleaned by alkaline or acidic solutions, and deoxidized by mixing of acidic and/or basic solutions [76].

2. Superhydrophobic processes

As mentioned earlier, SHPSs could be developed by chemical, electrochemical, and physical surface treatment. These methods could facilitate the formation of coatings or surface roughening on Mg alloys. Chemical routes are useful methods to fabricate SHPSs. In this regard, chemical processes are one of the most widespread methods for development of superhydrophobic structures. The most conventional methods to create superhydrophobicity on the surface of Mg alloy by chemical routes include hydrothermal treatment, conversion coating, chemical deposition treatments, and etching. In these processes, the surface is mainly treated by chemical substances which could react with the surface or deposit on it. One of the other reliable routes to obtain this goal is electrochemical techniques. These techniques are powerful methods to manipulate the surface of the electrodes in the electrolytic media by applying suitable electrical power. Changing the surface morphology or composition by electrochemical techniques including electrodeposition, anodizing, plasma electrolytic oxidation (PEO), and etc. could help to form superhydrophobic structures. The other processes including polymer coating could belong to the chemical or physical routes according to the technical procedures of surface treatment.

2.1. Hydrothermal process

SHPSs which are fabricated by hydrothermal process, obtained by the application of heating during the immersion of Mg plates into a Teflon-lined autoclave in the appropriate solutions including H_2O, H_2O_2, urea, and NaOH followed by cooling, drying, and surface modification using fluoroalkyl silane (FAS), stearic acid (SA) or silanes [77–85]. FAS molecules are extensively used as a hydrophobic modifying agent since those are well-known organic substances with an extremely low free energy surface due to C–F groups [63]. However, it is widely accepted that such fluorinated chemical substances are expensive and could result in potential risks to human health and environment [69]. Generally, the modifying substances could react with the surface of Mg to