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Fabrication of superhydrophobic layered double hydroxides films with different metal cations on anodized aluminum 2198 alloy

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ABSTRACT

Layered double hydroxide (LDH) films with different metal cations, such as Mg^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, were fabricated on anodized aluminum 2198 alloy. The structure, morphology and composition of the LDH films were investigated. The results showed that different metal cations greatly influenced the growth and crystallization procedure of the LDH nanocrystals, which led to different morphologies of the LDH films. After surface treatment with 1H,1H,2H,2H-Perfluorodecyltrimethoxysilane (PFDTMS) solution, all of the four types of LDH films showed excellent superhydrophobic property.

1. Introduction

In recent years, superhydrophobic surfaces with water contact angle (CA) larger than 150° have aroused great interest because of their significant potential for practical applications such as photoresponsive devices [1], microchemical sensors [2], chemical microreactors [3] and biosensors [4]. Different methods, including polymerization [5], sol–gel processing [6], chemical etching [7] and anodic oxidation [8], have been employed in the fabrication of superhydrophobic materials. Very recently, synthesis of layered double hydroxides (LDHs) as superhydrophobic surfaces has received increasing attention. LDHs are a class of synthetic anionic clays that consist of positively charged layers containing alternatively distributed divalent and trivalent cations in the sheets and charge balancing anions between the layers [9]. Generally, structure of LDHs can be represented by the generic formula $[M'_{1-x}M''_x(OH)_2]^{X+}A^{n-}_{x/n}\cdot mH_2O$, where M′ is a divalent metal cation such as Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ga^{2+}; M″ is a trivalent metal cation such as Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+} and La^{3+}; and A^{n-} represents an m-valence interlayer anion such as CO_3^{2-}, OH^-, NO_3^-, SO_4^{2-} and ClO_4^- [10]. As a result, a large family of isostructural materials with varied physicochemical properties can be obtained by changing the identity of the metal cations of M' and M″ as well as the interlayered anions of A^{n-}. Zhao et al. [11] prepared hybrid Mg–Al LDH nanoplatelet for rendering cotton fabrics with dual factions of superhydrophobic and UV-blocking. Duttaand Pramanik [12] synthesized a cone-shaped Ca–Al LDH intercalated with dodecyl sulfate and the measured contact angle was 140°.

In comparison with LDH films arranged in a random fashion, the oriented LDH films always show better superhydrophobic behavior. An oriented structure can dramatically decrease the area of contact between the liquid and solid, which reduces the adhesion of a liquid droplet to the solid surface and sliding angle. Duan [13] fabricated oriented Ni–Al LDH film on PAO/Al substrate, and the contact angle reached 163°after hydrophobic treatment with a sodium laurate solution. Li et al.[14] prepared Zn–Al LDH nanowalls on aluminum substrates in situ with contact angle as high as 167.3°. However, few works use the practical aluminum alloy as substrate. In the present work, M–Al LDH (M=Mg, Co, Ni and Zn) films were prepared in situ on anodized aluminum 2198 alloy and modified with 1H,1H,2H,2H-Perfluorodecyltrimethoxysilane (PFDTMS). The aim of this work is to investigate influence of different anions on the structure, morphology and surperhydrophobic property of the LDH films.

2. Experimental

Aluminum 2198 alloy plates (major elements, wt%: Cu 2.9–3.5, Li 0.8–1.1, Zn 0.35, Mg 0.25–0.8, Mn 0.50, Fe 0.10, Ti 0.10, Zr 0.04–0.18, Si 0.08, and Cr 0.05) were anodized in a sulfuric acid electrolyte for 30 min with applied voltage of 15 V. The M–Al LDH layers were fabricated by immersion of the anodized samples in 0.05 M $M(NO_3)_2$ salt (M=Mg, Co, Ni and Zn) and 0.3 M NH_4NO_3 mixture solution with a pH in the neutral range by adding diluted ammonia. The synthesis was carried out at 45 °C for several hours. After the reaction, the filmed samples were washed with deionized water

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and dried at room temperature. Then, the as-prepared films were immersed vertically in the mixed solvents (60 mL deionized water and 40 mL methanol) with the addition of 0.6 g PFDTMS (n-$CF_3(CF_2)_7CH_2CH_2Si(OC_2H_5)_3$) for 2 h, followed by washing with deionized water and drying in an oven at 60 °C for 2 h.

3. Result and discussion

The glancing angle X-ray diffraction (GAXRD) patterns of the samples obtained at a glancing angle of 1° are depicted in Fig. 1. In these samples, well-resolved reflections of typical LDH phases are observed along with the reflections intrinsic to the aluminum. For Mg–Al LDH sample, positions of the characteristic LDH reflections of (003) and (006) are clearly found and the (111) and (200) reflections are associated with pure aluminum. For Co-, Ni- and Zn–Al LDH films, the diffraction peaks show a decreased (003) reflection intensity and the peak of (006) plane almost extinguishes. Generally, intensity of the (003) reflection is contributed by diffraction from both M–Al–OH layers constituting the LDH 'host' structure and the 'guest' anions layer. All of the fabricated LDHs have the same 'guest' interlayer of NO_3^- anions. Hence, the observed lower intensity of the (003) reflection certainly results from a higher atomic scattering factor for the M–Al–hydroxide (M=Co, Ni and Zn) 'host' layer, probably originated from the loss of crystallinity [15]. Meanwhile, the broadening reflection of (003) observed for Zn–Al LDH film may arise for the same reason.

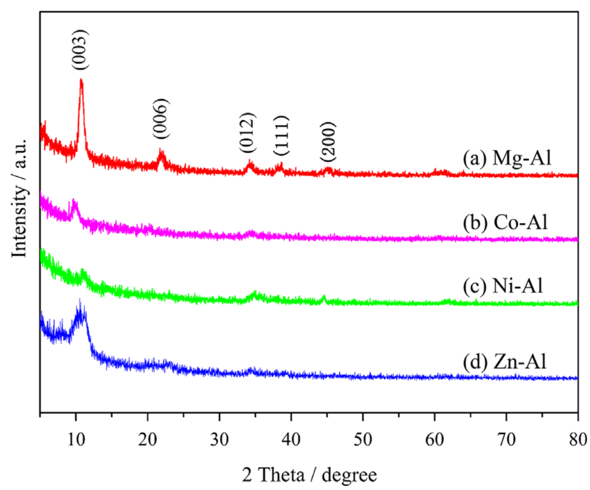

Fig. 1. GAXRD patterns of (a) Mg–Al, (b) Co–Al, (c) Ni–Al and (d) Zn–Al LDH films fabricated on aluminum 2198 alloy.

Fig. 2 gives the photographs and scanning electron microscope (SEM) images combined with energy dispersive spectrum (EDS) analysis of the LDH samples. The photographs show that the filmed samples obtained with Mg^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} display various colors of white, pink, light green and gray, respectively. The SEM images indicate that the types of metal cations greatly influence the morphology of the samples. For Mg–Al LDH, a flower-like structure is observed on the top layer and each 'flower' consists of nano-flake petals. For Co–Al LDH, most LDH microcrystals have an obvious blade-like morphology. The flakes are preferentially oriented perpendicular to the substrate, which is correlated with the faster crystal growth rate in the direction of bulk solution. The Ni–Al LDH exhibits flat area and the layer is much more compact with fine flakes. Meanwhile, several clusters observed above the compact layer, probably due to the presence of intermetallics of the substrate alloy [16]. The EDS images show that the Mg–Al LDH displays the highest Mg/Al ratio and this is related to the relatively high crystallinity mentioned in the GAXRD analysis.

The adhesion strength of the films between the LDH and the anodic aluminum oxide (AAO) layer could be determined by a stretch test. A radial stress was imposed along the filmed samples and the different elastic moduli of the separate layer led to generation of different strains. It is shown in Fig. 3 that for Mg- and Co–Al LDH, an obvious delamination is observed on the site even though the AAO layers underneath only exhibit minor cracks. This indicates that the parallel bonding strength within LDH layer is stronger than the vertical bonding strength between LDH layer and AAO layer. In contrast, Ni- and Zn–Al LDH display tight adhesion with the AAO layer. The LDH layer ruptured with the AAO film, and from the fracture, the layered structure of LDH–AAO–Al alloy is clearly observed. Then, it is assumed that the bonding strength of Ni- and Zn–Al LDH with the AAO substrate is stronger than Mg- and Co–Al LDH.

The variation of morphology and adhesion strength of LDH layer with different metal cations could be rationalized as follows. Compared with Mg^{2+} and Co^{2+} cations, Ni^{2+} and Zn^{2+} cations

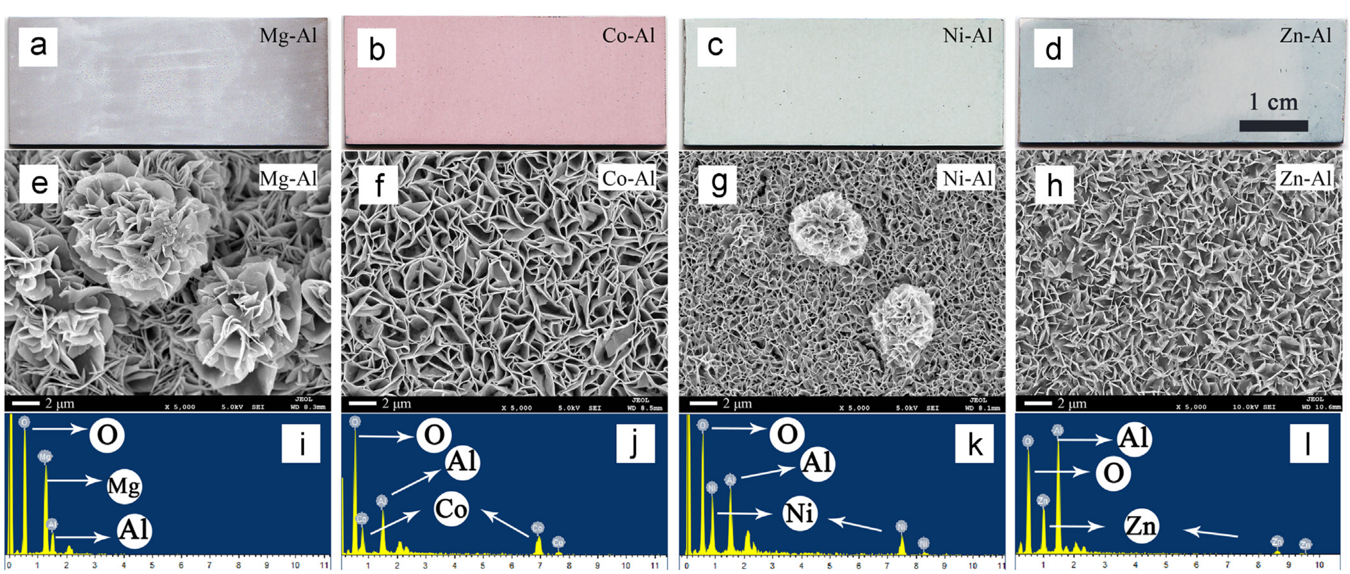

Fig. 2. Photographs of (a) Mg–Al, (b) Co–Al, (c) Ni–Al, and (d) Zn–Al LDH films and corresponding SEM morphologies of (e)–(h) with EDS analysis of (i)–(l). (For interpretation of the references to color in this figure ,the reader is referred to the web version of this article)