Self-assembled growth of MgO nanosheet arrays via a micro-arc oxidation technique

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Abstract

Unique magnesia (MgO) nanosheet arrays were fabricated via a promising micro-arc oxidation (MAO) technique on the surface of magnesium alloy. The non-uniform patterning of oxygen evolution on the sample surface and trapping of gas bubbles in the growing film are associated with the formations of the sheet and flower-like structures. These MgO structures may be useful in reinforcing composite materials or in further modifying other nanostructures.

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1. Introduction

In the past years, magnesia (MgO) has attracted considerable attention due to its applications in the insulating and buffer layers of multilayer electronic/photonic devices owing to its very large band gap, excellent thermal stability, electrical insulating properties, and the tendency to form films with highly MgO (1 0 0)-oriented textured microstructures [1–3]. Importantly, nanocrystalline MgO is a very important scientific and commercial material. Nanosized MgO powder has widely been used as catalyst in chemical industries [4–6]. In addition, experiments have shown that MgO, reduced to one-dimensional nanostructure, demonstrates distinctive capability to pin the magnetic flux lines within a high-temperature superconductor, so as to greatly improve the performance of high-temperature superconductors at elevated temperatures or in intensive magnetic fields [7]. And also Ga-filled MgO nanotubes were used as wide-temperature range nanothermometer [8]. Very recently, Fang et al. demonstrated that MgO nanostructures have a much higher relative dielectric constant as compared with MgO powders with microcrystals, especially at low frequencies at room temperature [9]. Therefore, it is worthy to focus a great deal of the current research effort on the preparation of such MgO nanomaterials for future technological applications.

To date various MgO morphologies have been synthesized. For instance, sol–gel routes were used to prepare MgO fibers [10]. MgO fishbone or fernlike nanostructures were generated by selective Co-catalyzed growth [11,12]. MgO nanowires were synthesized by oxide-assisted catalytic growth [13], a vapor-phase precursor method using MgB\textsubscript{2} powders [14], and the annealing treatment of Au-coated substrates prior to the MgO deposition process which affects the morphology of the final MgO structures [15]. MgO nanobelts were fabricated with many methods such as simple chemical vapor deposition process using infrared irradiation [16], the evaporation of Mg\textsubscript{2}N\textsubscript{2} precursor [17], and the heating of Mg in an Ar/O\textsubscript{2} flow [18]. MgO nanoflowers composed of fibers were synthesized with the conventional evaporation method using Mg and distilled water [9,19,20]. MgO nanosheets were generated by calcination of its precursors which were formed in the hydrothermal process [21]. MgO and Ga-filled MgO nanotubes were produced by a thermal treatment [8].
In this work, we present a relatively simple method of fabricating aligned MgO sheet-like nanostructures on the surface of magnesium alloys via a promising micro-arc oxidation (MAO) technology. This type of MgO nanostructures has not been reported before. The formation mechanism is explained by considering the non-uniform patterning of oxygen evolution on the sample surface and trapping of gas bubbles in the growing film.

2. Samples and experiments

MAO, a promising surface treatment method, is based on conventional anodic oxidation technology in a suitable electrolyte by increasing the anodic voltage to a high stage, usually accompanied by intensive gas evolution and sparking phenomenon at the anode surface [22–24]. The detailed sample fabrication procedures are described as follows. Rectangular coupons (20 mm × 10 mm × 3 mm) of a Mg alloy AZ91D were employed as substrates and mechanically polished with waterproof abrasive paper up to 800 grits prior to MAO. An aqueous solution of electrolytes was prepared using sodium silicate with addition of sodium hydroxide. The output of the power supply was connected to the bath, and another one to the samples immersed in the electrolyte. The apparatus is schematically shown in Fig. 1. An average current density of 4 A/cm² was maintained on the surface by controlling the direct current/voltage varying in the range of 120–195 V. The oxidation process lasted for 20 min and the electrolyte temperature was less than 50 °C. After the treatment, the samples were rinsed thoroughly with water and dried in warm air.

The morphology and chemical composition of the samples were characterized with a FEG JSM6335 field-emission scanning electron microscope (SEM), equipped with an EDAX PV7715/89 ME energy dispersive X-ray spectrometer (EDX). The phase composition of the fresh and MAO treated Mg alloys was investigated by means of X-ray powder diffraction (XRD) (Rigaku D/Max-Data; Cu Kα, 40.0 kV, 30.0 mA). All the measurements were performed at room temperature.

3. Results and discussions

The typical SEM images are depicted in Fig. 2. SEM observations reveal that many sheet-like structures form on the substrate surface. The nanosheets are slightly curved and approximately 300–400 nm in width and tens of nanometers in thickness. Most of them stick together to form nanosheet arrays. A large quantity of flower-like branched structures was also observed on the substrate. Fig. 3 shows these unique structures. These structures exhibit so-called flower morphology, which was named previously for silicon oxide nanostructures and ZnO nanostructures [25,26]. The flowers are approximately of several micrometers in size, and composed of hundreds of thin petals. The petals are obviously of the same morphology with aforementioned nanosheets. The flower-like structures reported here are similar to MoS₂ nanoflowers formed via connection of nanosheets [8] and nestlike Mg₅(CO₃)₄(OH)₂·4H₂O spheres formed by a self-assembly of nanosheets in the hydrothermal process [21]. Therefore, we can infer that the current flower-like structures are built from small one-dimensional nanosheets in a highly close-packed assembly. These nanosheets are aligned with one another perpendicularly to the surface.

We used XRD to probe the phase composition of the fresh and MAO treated Mg alloys. Fig. 4 shows the corresponding XRD spectra. The fresh Mg alloy consists of Mg solid solution (α) phase and an intermetallic compound phase (β, Mg₁₇Al₁₂). The reaction product formed after MAO is MgO with a cubic structure (f) which has a lattice parameter of 4.21 Å (JCPDS 78-0430). It should be noted that the location of MgO (1 1 1) peak at 2θ of 36.932° is very close to the strongest peak for Mg at 2θ of 36.603°, which results in an enhanced peak. The corresponding EDX spectrum from the sheet-like products shown in the inset of Fig. 4 gives additional proof, where Mg
and O are the main elements and their atom ratio is approximately equal to unity.

The detailed formation mechanism for the MgO nanosheets can be understood on the influence of oxygen bubbles release combined with internal stress and non-uniform oxygen evolution arising with the film growth during the complex MAO process. Fig. 5 gives a schematic diagram of their formation process. The substrate is firstly dissolved and loses metal brightness, but this process only lasts for a few seconds. With the increasing of the cell voltage, a thin dielectrical passive film with numerous cracks and channels is subsequently formed on the anode surface, which is immediately enshrouded by a continuous oxygen gas envelope [27]. The oxygen gas is formed by oxidation of water molecules or hydroxyl ions at the film/electrolyte interface according to the following reactions [27]: 

\[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \]

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e} \]

Another possible route for oxygen formation at the film/electrolyte interface during MAO is thermal decomposition of water, which occurs via the following path [28]:

\[ 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH} \]

\[ 2\text{HO} \rightarrow \text{H}_2\text{O} + (1/2)\text{O}_2 \]

All the reactions are conducted through the whole stage, and the oxygen gas is released mostly from the anode surface. On the other hand, an alternative source of oxygen formation is the oxidation of O\(^{2-}\) within the film according to the reaction [29]:

\[ 2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e} \]

When a large numbers of oxygen bubbles are present in the film, cracks and channels formed by micro-arc discharge may connect bubbles to each other, and some oxygen may also be contained as isolated atoms or molecules within the film [30]. Cations and anions have to migrate around bubbles in order to form new film materials at the film/electrolyte and metal/film interfaces, which results in numerous sheet-like structures.

It should be noted that a number of small-size separate sparks were observed during the MAO process. Once sparks are found on the anode surface, the MAO is always accompanied by intensive oxygen evolution. Thus, non-uniform oxygen evolution on the sample surface is thought to be the main reason leading to unique flower-like structures with lots of nanosheets.

4. Conclusions

A relatively simple method of fabricating MgO nanosheet arrays has been described on the basis of MAO technique. The non-uniform patterning of oxygen evolution on the sample surface and trapping of gas bubbles in the growing film contribute to the unique sheet and flower-like structures. These MgO structures may be useful in reinforcing composite materials or in further modifying other nanostructures.
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