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Impurity-induced discharges in plasma electrolysis

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ABSTRACT

The mechanism of impurity-induced discharges in plasma electrolysis (PE) was elucidated on the basis of a novel microstructural interpretation. We identified the presence of impurity compounds decorating the rim of the micro-pores, which were 'fingerprint' of plasma discharge activities. The formation mechanism of inorganic layer by PE was suggested based on the distribution of impurities and a transient diffusion pattern accompanying plasma discharges.

1. Introduction

Plasma state acquired a ubiquitous role in the advances of cutting-edge technologies such as chemical synthesis and materials engineering [1,2]. Recently, plasma electrolysis (PE) was developed to fabricate a conformal layer of inorganic materials in aqueous medium by utilizing a high-voltage. This method was able to convert the surface of metals into a thick and adhesive inorganic layer with excellent structural and functional properties [3–5].

PE utilized myriads of short-lived plasma discharges causing a paradoxical effect. As positive consequence, they triggered the occurrence of the condensed structure with excellent growth rate. On the other hand, their excessive temperature and pressure inevitably caused the micro-defects. To understand this complex processes, various studies had been conducted based on voltage-time responses [5,6], growth direction [7], optical emission [8], and defect analysis [9]. Although a number of discharge mechanisms were available, local breakdown of dielectric solid might be the most plausible considering an excellent agreement with the microstructural evolution of inorganic layer [5,8]. A lack of attention, however, was paid towards the impurities derived from the incorporation of electrolyte components, despite the fact that the multicomponent electrolytes were favored. One of the most profound theories relating to impurities was established by Albella et al., which postulated that the incorporation of the electrolyte components provided impurity centers triggering an avalanche of electrons relating to dielectric breakdown [10]. Impurity ionization became an integral part of recent advances in plasma discharge mechanics [11]. Nevertheless, the roles of impurities remained unresolved in microstructural aspect.

The main source of impurities in PE was the electrolyte containing oxygen-rich substances such as silicates. These substances would facilitate the formation of plasma discharges accompanying incorporation phenomena with ease [1,12]. The present work demonstrated through microstructural analysis that the plasma discharges nucleated at specific sites where the electrolyte components were incorporated. We found that the rim of the micro-pores was rich of Si from the silicate-based electrolyte. This suggested the occurrence of impurity-induced discharges which was explained by the electronic behavior around Si-compounds. The formation of inorganic layer was discussed based on the influence of impurity-induced discharges on the microstructural evolution.

2. Experimental procedure

As a case study, AZ91 Mg alloy was used for the substrate. Details of the apparatus set were documented elsewhere [13]. The specimen was treated for 250 s under alternating current condition at 50 mA cm^{-2} utilizing an electrolyte formulated from 0.08 M KOH and 0.05 M Na_2SiO_3. The morphologies of inorganic layer were observed using field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800). Constitutive compounds of the oxide layer were determined based on X-ray diffraction pattern (XRD, Rigaku D/MAX-2500) with Cu Kα radiation source. Field-emission transmission electron microscope (FE-TEM, Technai F20) operating at 200 kV was utilized to perform detailed observation on inorganic layer and to obtain the selected area electron diffraction (SAED) patterns. The specimen for TEM observation was fabricated using focused ion beam (FIB, Helios Nanolab 600).

3. Results and discussion

Fig. 1 displays the microstructure and composition of inorganic layer via PE in silicate electrolyte. Fig. 1a shows that a number of

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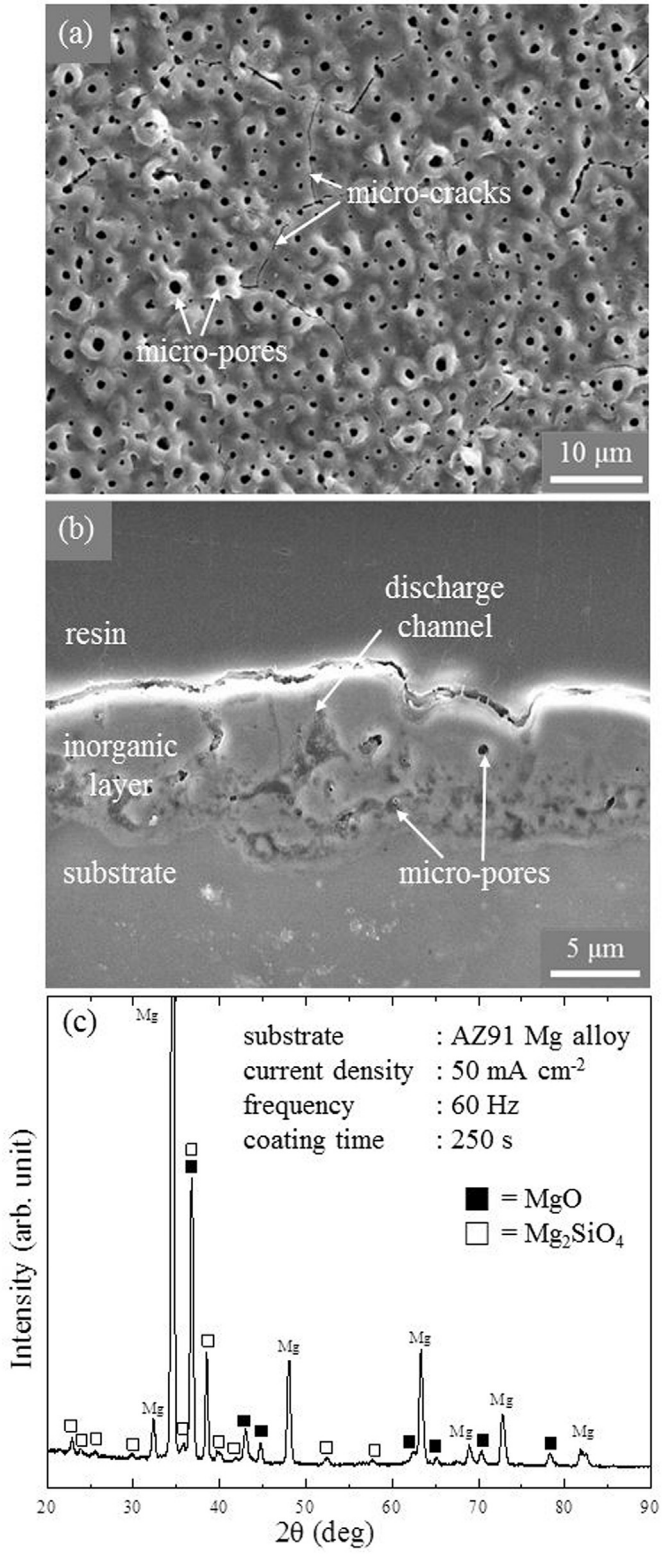

Fig. 1. Microstructure of inorganic layer formed on AZ91 Mg alloy via PE in silicate electrolyte taken from (a) surface and (b) cross-section areas. (c) XRD pattern of inorganic layer. The peaks associated with metallic Mg were attributed to the Mg alloy substrate.

circular-shaped micro-pores having average size of ~0.7 μm were distributed uniformly throughout the surface of inorganic layer. These micro-pores were remnants of plasma discharges located close to inorganic layer-electrolyte interface. A number of strong discharges appeared, providing short-circuit path to eject molten materials outward. This defective structure was denoted commonly as discharge channel, which was identified in Fig. 1b. Parts of these structural defects might be covered by the subsequent growth of inorganic layer, where shallow pores remained at the surface.

EDS analysis showed that inorganic layer comprised a larger amount of Si at the surface (~13 at.%) than the depths (~5 at.%). XRD analysis in Fig. 1c showed that MgO and Mg_2SiO_4 were the main constitutive compounds. Mg_2SiO_4 was stable under high temperature (up to T_m) and pressure (up to ~14 GPa) [14,15]. Thus, the phase transformation of Mg_2SiO_4 during PE was unlikely. By utilizing reference intensity ratio [16], the relative fraction between MgO and Mg_2SiO_4 was calculated to be 1:3. This was striking because a low crystallization temperature of MgO, i.e., T_c ~700 K, would favor the formation of crystalline of MgO as compared to Mg_2SiO_4 (T_c ~1173 K) [17,18]. Such phenomena might be attributed to local heating by plasma discharges affecting the evolution of Mg_2SiO_4.

Fig. 2 shows TEM observation of inorganic layer from cross-sectional area. As Fig. 2a pointed out, two different layers were identified by the defect characteristics in nature. The outer layer exhibited large micro-pores with irregular shape due to overlapping plasma discharges [2,19] while the inner layer had compact structure with few nano-sized pores. Detailed inspection of the outer layer (Fig. 2b) revealed a combination of an amorphous region and another region containing nano-crystalline grains with an average size of ~20 nm appeared as dark-shaded particles. Fig. 2c suggested that crystallinity of the inner layer was more developed than the outer layer, which was in a good agreement with the diffraction rings in selected area electron diffraction (SAED) pattern shown as the insets. Simulations of SAED patterns (Figs. 2d and e) showed the coexistence of MgO and Mg_2SiO_4.

In PE, electrochemical, thermal, and plasma reactions took place simultaneously [1–5,20]. Due to the non-equilibrium nature of the plasma in liquid system, the decoupling of these reactions was still incomplete. Therefore, the discussions in reaction mechanics of PE [5,8,13] emphasized on the electrochemical reactions assisted by plasma discharges having temperature and pressure of ~3500 K and ~2.5 bar, respectively [21,22]. In such condition, the surface of Mg alloy substrate was oxidized upon contact with electrolyte, viz.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \quad \Delta G = -320.86 \text{ kJ mol}^{-1} \tag{1}$$

A variety of other molecules or ions, such as OH^-, were also able to oxidize Mg in place of H_2O. Subsequently, $Mg(OH)_2$ was converted to MgO by thermal dehydration.

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad \Delta G = -172.05 \text{ kJ mol}^{-1} \tag{2}$$

This endothermic step took place instantaneously under the intense heating by plasma discharges. Hence, $Mg(OH)_2$ was unlikely to be retained in spite of the high pH level. Simultaneously, Na_2SiO_3 from the electrolyte was incorporated as SiO_2 in the inorganic layer,

$$Na_2SiO_3 + H_2O \rightarrow SiO_2 + 2NaOH \quad \Delta G = 385.91 \text{ kJ mol}^{-1} \tag{3}$$

which were more feasible to occur through anodic oxidation than thermal activation. Thereafter, SiO_2 combined with MgO to form Mg_2SiO_4 via solid-state reaction.

$$2MgO + SiO_2 \rightarrow Mg_2SiO_4 \quad \Delta G = -531.92 \text{ kJ mol}^{-1} \tag{4}$$

Thermodynamic data to calculate ΔG was taken from ref. [23]. The endergonic nature of Eq. (3) implied that it would be the limiting step in the formation of Mg_2SiO_4. In addition, SiO_2 might form via atomization of Si within the core of plasma, which was estimated to have a temperature of ~5500 K [8]. This was supported by spectral lines of Si from electrolyte shown in earlier studies on PE which indicated that Si was involved actively in plasma activities [24,25]. After Mg, O, and Si were atomized within plasma discharge, oxides of Mg and Si would form by quenching to form a combination of crystalline and amorphous structures whose mechanism remained unresolved to date because