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A New Method for Phosphorus Recovery Using Magnesium Alloy Electrode under Tensile Stress

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The electrochemical activity of a magnesium alloy (AZ91-Zn-In-Sn-MnS) was controlled by applying tensile stress in sludge concentrated in a gravitational precipitation tank for phosphorus recovery. Phosphorus was removed from the sludge through anodic deposition on an electrode and recovered as concentrated phosphate solutions through cathodic dissolution under a tensile stress of 10 MPa. The magnesium alloy is a more practical material for phosphorus recovery, since its electrochemical activity can be controlled under tensile stress conditions than conventional metals such as aluminum and cast iron, with which recovery of phosphorus in the form of concentrated phosphate solutions is difficult.

Keywords: Phosphorus recovery, Tensile stress, Electrodeposition, Sewage sludge

INTRODUCTION

Phosphorus in wastewater or sewage sludge is expected to be removed through so-called tertiary treatments in wastewater treatment facilities for the benefit of environment [1-3]. Recently, phosphorus has been considered one of the most important resources to recover because it is one of the world's exhaustible natural resources [4,5]. Phosphates are recovered in the forms of stable calcium phosphate (hydroxyapatite, HAP, $Ca_5(PO_4)_3OH$) and magnesium ammonium phosphate (MAP) from wastewater and slurries [6].

However, it will be necessary for phosphate recovery processes to be simpler and more economical. It is desirable for phosphate recovery processes to be simplified such that they use a single piece of equipment and to produce versatile concentrated phosphate solutions. Processes that generate hydroxyapatite and magnesium ammonium phosphate and other similar methods produce solid phosphate salts, whose usage is limited to fertilizers.

Electrodeposition of phosphate ions on conventional metal electrodes, such as those made of cast iron and aluminum, is another well-known method to remove phosphorus from wastewater and slurries. However, practical recovery of phosphorus in the form of phosphate ions using these metals is difficult and has low potential in industry, owing to their high affinities for phosphorus. Lead has favorable characteristics as the electrode material for free phosphoric acid recovery. However, lead dissolves slightly in the processing of slurries owing to the anodic polarization for electrodeposition of phosphorus. In addition, stainless steels are also problematic as materials for phosphate adsorption electrodes for phosphate recovery owing to the formation of an insulating phosphate layer on the surface of steel [7,8].

Magnesium alloys, such as AZ91 containing elements such as Zn, In, Sn, Mn, and S, have been found to be suitable electrode materials for the recovery of phosphate ions, which are deposited from the sludge and dissolve into concentrated solutions under tensile stress. In this study, the activity of a magnesium alloy surface was controlled by applying tensile stress. Magnesium alloys, which are strongly affected by tensile stress owing to their low yield strengths [9,10], are expected to be practical electrode materials for the recovery of phosphorus from various solutions or slurries; this includes phosphate ions through anodic deposition and subsequent cathodic dissolution on the alloy surface.

EXPERIMENTAL

The experimental system for the recovery of phosphorus from concentrated sewage sludge is shown in Fig. 1. A sheet of magnesium alloy electrodes [11,12] was placed in a small single cell and stretched using a tension tester (EZ-Test CE, Shimadzu Corp.). An electrochemical measurement system (HZ-7000, Hokuto Denko Co. Ltd.) and a potentiostat/galvanostat (HA-151, Hokuto Denko Co. Ltd.) were connected to the small single cell in order to obtain voltage-current curves and for cyclic voltammetric measurements. The sewage sludge was circulated in the cell by a tubing pump at 2-5 mL/min for phosphorus deposition.

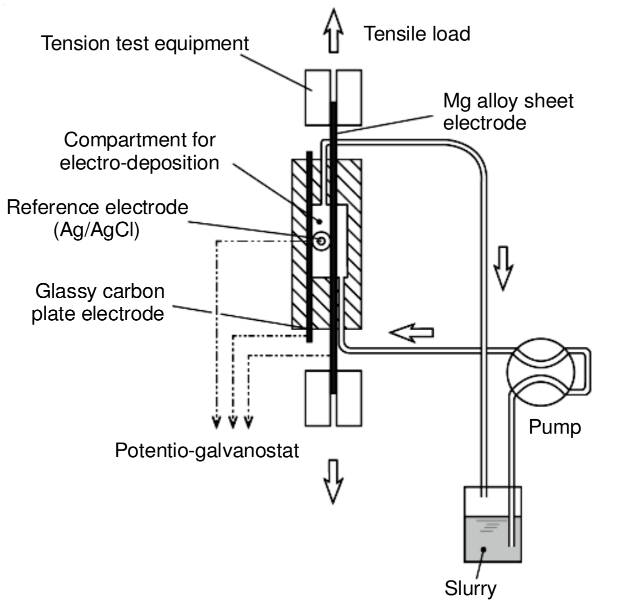

Fig. 1. Equipment for phosphorous recovery by the magnesium alloy electrode under tensile stress

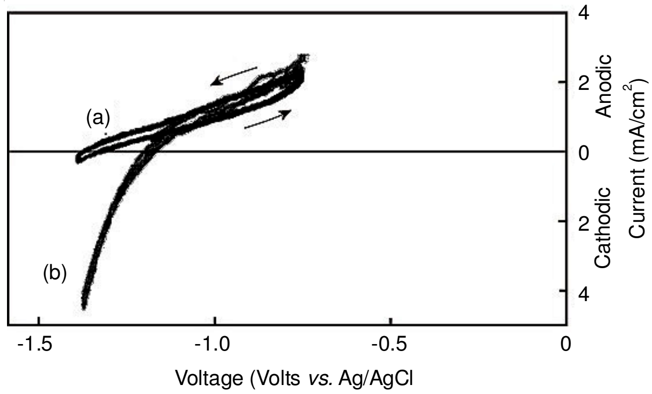

Fig. 2. (a) 0.1 M $NaHCO_3$; (b) 260 mg phosphorous in 1 M $NaHCO_3$; Current-Voltage curves of the magnesium alloy electrodes in 0.1 M $NaHCO_3$ including 260 mg phosphorous as K_2HPO_4 under 1 M Pa tensile stress.

The equipment for phosphorous recovery by magnesium alloy electrode under tension stress are shown in Table-1. Dipotassium phosphate (340 mg/L) (special grade, Wako Pure Chemical Industries Ltd.) was added to the sludge to adjust phosphorus concentration. After the deposition, sodium acetate/acetic acid solution with a concentration of 0.1 M and pH = 6 was circulated in the cell by a tubing pump at 2-5 mL/min. The electrode potential was controlled using a Ag/AgCl reference electrode. The phosphorus ion concentrations in the solution and sludge were determined using colorimeter and phosphorus deposited on the electrodes was observed using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) (JSM-5500LV, JEOL Ltd.).

RESULTS AND DISCUSSION

The activation of magnesium alloy was confirmed by proceeding test in CH_3COOH-CH_3COONa solution in the range of 0-10 MPa at -1.0 V *vs.* Ag/AgCl, as anodic current was increased from 2 MPa of the tensile stress [10].

Fig. 2 shows the cyclic voltage-current curves of magnesium alloy electrodes in 0.1 M $NaHCO_3$ (curve a) and 260 mg/L-K_2HPO_4 in 0.1 M $NaHCO_3$ (curve b). The point at which the current was 0 mA was shifted toward the anodic direction upon the addition of potassium hydrogen phosphate under a tensile stress of 10 MPa, attributable to the formation of basic phosphate compounds, such as magnesium phosphate tribasic salts. Magnesium hydroxides, hypothesized to be formed on the alloy surface in this study, have been able to adsorb phosphates effectively for the improvement of the water quality of entropic lakes [13].

After deposition of phosphorous under 10 MPa, 90 mg/L of phosphorous concentration was determined in the slurry. By dissolution of deposited phosphorous, 680 mg/L of concentrated phosphorous solution was obtained as shown in Table-1. The pH value of sludge was maintained between 6.7 and 7.0 during the deposition and dissolution.

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were employed for the investigation of the mechanism. Anodic oxidation of magnesium alloy electrodes proceeds at a relatively high current density in the presence of corrosive substances, such as chloride ions. However, some driving forces are required in the cases of treatments of solutions or slurries without such corrosive substances. Tensile stress application is an effective method to achieve anodic oxidation with phosphate ion adsorption. Phosphate ions adsorbed to basic magnesium compounds are dissolved again in the concentrated solutions owing to cathodic polarization, which separates basic magnesium compounds into phosphate ions and basic magnesium electrode surfaces. Fig. 2 shows an anodic shift in the current potential curve upon the addition of phosphate to the sludge. The compositions of phosphate-adsorbed magnesium compounds are under investigation using X-ray diffraction, XPS and micro-Raman spectroscopy.

Fig. 3 shows the SEM images and EDX spectra of the electrodes after 10 mA/cm^2 electrodeposition for 10 min under a tensile stress of 10 MPa (A), 10 mA/cm^2 electrodeposition for 10 min without tensile stress (B) and application of a constant potential of -1.8 V *vs.* Ag/AgCl for 10 min for phosphate electro-dissolution, followed by electrodeposition under a tensile stress of 10 MPa (C).

The ratios between the numbers of Mg and P atoms, Mg/P, were 1.5 for EDX spectrum (A), 3.9 for (B), and 4.6 for (C). The amount of phosphate after the anodic adsorption under a tensile stress of 10 MPa was larger than those after the other

TABLE-1
EQUIPMENT FOR PHOSPHOROUS RECOVERY BY THE MAGNESIUM ALLOY ELECTRODE UNDER TENSILE STRESS

Applied stresses for the electrode reactions	Phosphate ion concentration in the sludge	Dissolved phosphate ion concentration in solution
0 MPa tensile stress, deposition	340 mg dm^{-3}	No implementation
10 MPa tensile stress, deposition-dissolution	90 mg dm^{-3}	680 mg dm^{-3}
Remarks	After deposition at 10 mA for10 min	After dissolution at -1.8 V for 10 min succeeding the electro-deposition

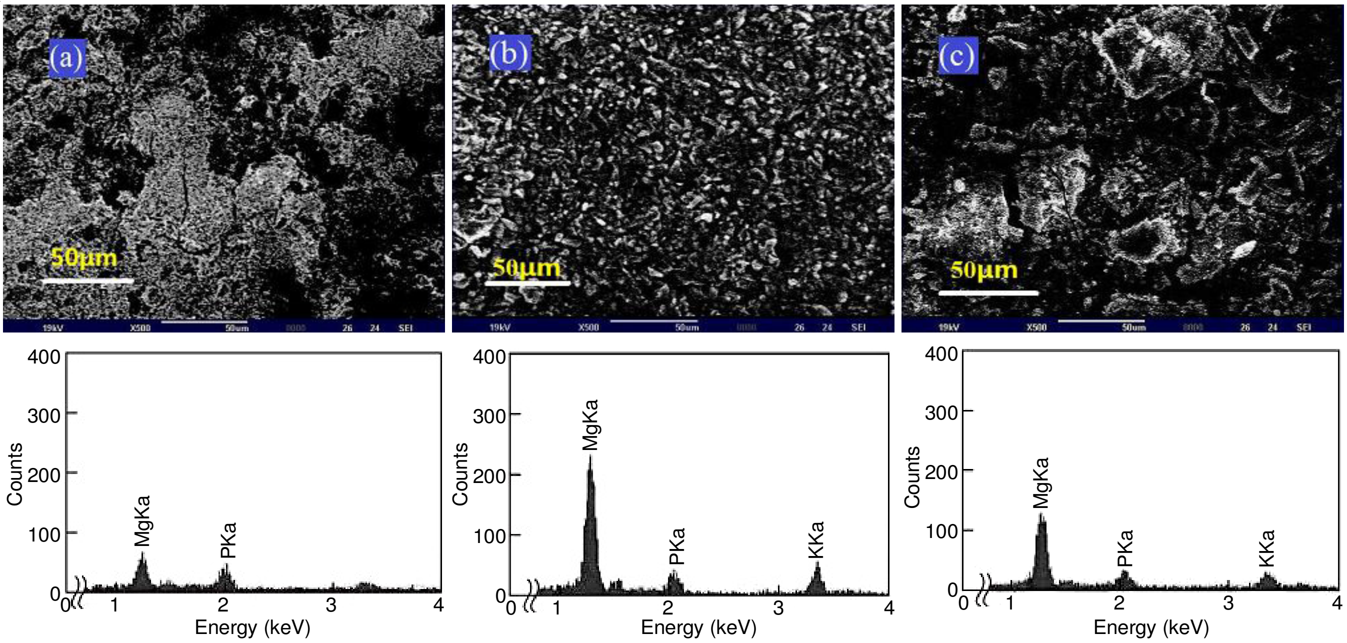

Fig. 3. SEM images and EDS spectra after 10 mA electro-deposition for 10 min under 10 MPa tensile stress (A), 10 mA electro-deposition for 10 min without tensile stress (B) and -1.8 V *vs.* Ag/Ag$^+$ and 10 min electro-dissolution under 10 MPa stress (C)

situations, (B) and (C). Anticorrosive composite films composed of amorphous or crystalline magnesium phosphate compounds and magnesium hydroxide may form on the surface of magnesium alloy [14]. The application of tensile stress was considered to be important for the activation of alloys utilizing stress corrosion. The similar phenomena are observed in magnesium alloys; magnesium alloys can be activated by applying tensile stress, for both charge and discharge stages. Impedance analyses showed that the total impedance depended on the extent of tensile stress application. Under a larger tensile stress, such as 10 MPa, the ratio of a charge transfer process become smaller in the total impedance. It was considered that mechanical control, such as through tensile stress application, is effective for restricting the passivation of magnesium alloys. In case of other metals, such as aluminum and iron, their plastic deformation characteristics under effective tensile stress conditions is a critical defect for this application. On the other hand, stainless steels with high Young's modulus require stronger tensile stresses, for example, of 20 GPa or higher and designing practical equipment to achieve these tensile stresses seems to be difficult. Magnesium alloys are expected to be among the most suitable electrode materials for the recovery of phosphates from sludge and solutions. A system for phosphate recovery that targets the treatment of rock phosphate residue is being designed.

Conclusion

A practical method for phosphorus resource recovery from wastes, such as wastewater or various forms of sludge, was studied. It was confirmed that magnesium alloy electrodes could remove phosphates from sludge and dissolve them through reverse polarization for phosphate resource recovery. Like with other materials, such as stainless steels, aluminum and cast iron, application of the magnesium alloy to practical phosphate recovery equipment was difficult owing to its mechanical characteristics.

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