

Preparation of New Corrosive Resistive Magnesium Coating Films

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고내식성의 신 마그네슘 코팅막 제작

이 명 훈

Key words : Magnesium coating film(마그네슘 코팅막), Corrosion-resistance(내식성), Ion plating(이온 플레이팅), Morphology(물포로지), Crystal orientation (결정배향성), Adsorption(흡착), Occlusion(흡장)

Abstract

The properties of the deposited film depend on the deposition condition and these, in turn depend critically on the morphology and crystal orientation of the films. Therefore, it is important to clarify the nucleation occurrence and growth stage of the morphology and orientation of the film affected by deposition parameters, e.g. the gas pressure and bias voltage etc.

In this work, magnesium thin films were prepared on cold-rolled steel substrates by a thermo-electron activation ion plating technique. The influence of nitrogen gas pressure and substrate bias voltage on their crystal orientation and morphology of the coated films were investigated by scanning electron microscopy (SEM) and X-ray diffraction, respectively. The diffraction peaks of magnesium film became less sharp and broadened with the increase of nitrogen gas pressure. With an increase in nitrogen gas pressure, film morphology changed from columnar to granular structure, and surface crystal grain-size decreased. The morphology of films depended not only on gas pressure but also on bias voltage, i.e., the effect of increasing bias voltage was similar to that of decreasing gas pressure. The effect of crystal orientation and morphology of magnesium films on corrosion behaviors was estimated by measuring anodic polarization curves in deaerated 3% NaCl solution. Magnesium, in general, has not a good corrosion resistance in all environments. However, these magnesium films prepared by changing nitrogen gas pressure showed good corrosion resistance. Among the films, magnesium films which exhibited granular structure had the highest corrosion resistance. The above phenomena can be explained by applying the effects of adsorption, occlusion and ion sputter of nitrogen gas.

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1. Introduction

Magnesium metal is 35% lighter than aluminum and has good vibration resistivity. However, magnesium has not been applied as much as aluminum because of its poor corrosion resistivity in all environments. Recent tendency in electronics and mechanical engineering fields aiming for high performance and energy savings requires material to be light weight more and more¹⁾. Furthermore, new materials usually meant new bulk materials in traditional materials development. In recent years, however, surface coated materials are, in a broad sense, considered to be new materials. The surface coating - modified materials gain new properties by the combination of the applied surface properties with the intrinsic ones of the substrate. If a new surface coating technique can be developed to improve its corrosion resistivity, magnesium metal will find new applications in various fields.

In general, light metal, particularly magnesium, is difficult to plate using conventional coating techniques such as chemical or electrochemical process. This is due to the presence of the easily formed oxide layer. In order to limit oxidization during coating, vacuum deposition techniques can be used as an alternative to conventional techniques operating in wet conditions or in air. It is well known that coated films, particularly those deposited from plasma - assisted vacuum coating technique, are usually quite different from the respective bulk material as to their structure and properties²⁾. For this reason, the use of plasma - assisted techniques, e. g., physical vapor deposition such as ion plating technique, has spread into various types of industrial applications^{3 - 4)}. However, few studies have been reported dealing with magnesium metal and using the new techniques^{5 - 6)}.

In this work, magnesium films were prepared onto the cold - rolled steel substrates by ion plating technique. Thus, I have found some interesting morphological and orientational effects and the corrosion resistance relation in magnesium films prepared by changing the nitrogen gas pressures and substrate bias voltages. Finally, it was shown that the corrosion resistance of magnesium films can be improved by controlling crystal orientation and morphology.

2. Experimental Details

2.1 Preparation of films

Fig. 1 is a schematic representation of the ion plating apparatus used in this study. The apparatus consists of three main parts, i.e. (1) a substrate holder, (2) an ionization system and (3) a crucible of metal evaporator. A resistance heating system was used to evaporate magnesium metal. The purity of magnesium used in this experiment was 99.99%. In order to enhance the ionization efficiency, a filament of 0.8mm tantalum wire in diameter was set a level of 2cm above the evaporator and negative bias voltage of 100V was supplied on the ionization

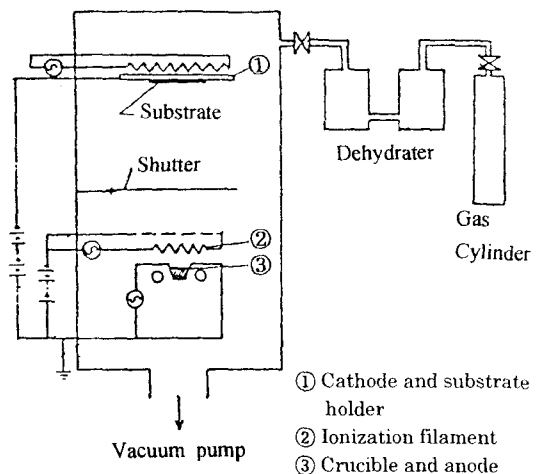


Fig. 1 Schematic diagram of the PVD ion - plating system

filament against evaporator. The current between the ionization filament and evaporator (called the ionization current) was controlled by adjusting the ionization filament current. The cold-rolled steel plates used as substrates were progressively polished to a final abrasive size of $0.05\mu\text{m Al}_2\text{O}_3$ and then ultrasonically cleaned in a bath of acetone for 30 minutes, prior to mounting in the vacuum chamber. The source-to-substrate distance was 13 cm.

Prior to the evaporation process, the system was initially evacuated to a pressure in the region of $3.5 \times 10^{-3}\text{Pa}$. The substrate was ion cleaned in an argon glow discharge at a pressure of 1.3 Pa with a bias voltage of -1.0kV for about 5 minutes to remove the residual oxides from the surface. As the surface was cleaned, the current was found to reach an equilibrium value. After the ion cleaning, the system was pumped down to a base pressure of $3.5 \times 10^{-3}\text{Pa}$ again. Nitrogen gas pressures of 10^{-3} , 10^{-2} and $10^{-1} \times 7.3\text{Pa}$ and bias voltages of 0, -0.2 , -0.5 and -1.0kV were used in ion-plating arrangement. Once the system reached stable condition, the evaporation started. The ion plating process lasted typically 20 minutes with the rates of about $0.6\mu\text{m} \cdot \text{min}^{-1}$ resulting in coatings of $10 \pm 5\mu\text{m}$ thickness. The purity of nitrogen gas used in this experiment was 99.9%. The substrate temperature was measured by a thermocouple attached to the back side of the substrate holder. The substrate temperature during deposition was below 115°C without any temperature control.

2.2 Characterization techniques

The top surface and cross section of the obtained films were examined by scanning electron microscopy (SEM). The composition of these films was determined by electron probe micro-analysis (EPMA). X-ray diffractome-

ter with $\text{Cu K}\alpha$ radiation was used to study the crystal structure and the preferred orientation of the films. Anodic polarization measurements of each specimen by masking all $0.25\text{cm}^2 (0.5 \times 0.5\text{cm}^2)$ area without polishing were carried out from the rest potential, at $2\text{mV}/\text{sec}$ in deaerated 3% NaCl solutions at room temperature. Before the anodic polarization measurements, each specimen was equilibrated with the solution for 30 minutes. Potentials were measured versus SCE (saturated calomel electrode).

3. Results

3.1 Crystal orientation and morphology of magnesium films

In order to investigate the influence of nitrogen gas pressure and bias voltage on the crystal orientation and morphology of magnesium films, the specimens were prepared by changing nitrogen gas pressure from 7.3×10^{-3} to $7.0 \times 10^{-1}\text{Pa}$ at bias voltage from 0 to -1.0kV respectively. The X-ray diffraction patterns as a function of nitrogen gas pressure at the different bias voltage for the deposited magnesium films are shown in Fig. 2. In Fig. 2, it can be seen that the crystal orientation of the films changed with the increase of nitrogen gas pressure and bias voltage. And the X-ray diffraction patterns of all the magnesium films coincided well with the value of American Society for Testing and Materials (ASTM) card. The X-ray diffraction patterns of the magnesium films deposited at the no bias voltage of 0 kV exhibited (002) preferred orientation as the nitrogen gas pressure increased to $7.3 \times 10^{-2}\text{Pa}$ from $7.3 \times 10^{-3}\text{Pa}$. Here, the diffraction peaks of the film deposited at high nitrogen gas pressure of $7.3 \times 10^{-1}\text{Pa}$ became less sharp and broadened. The crystal orientation of the films ion plated at the gas pressure

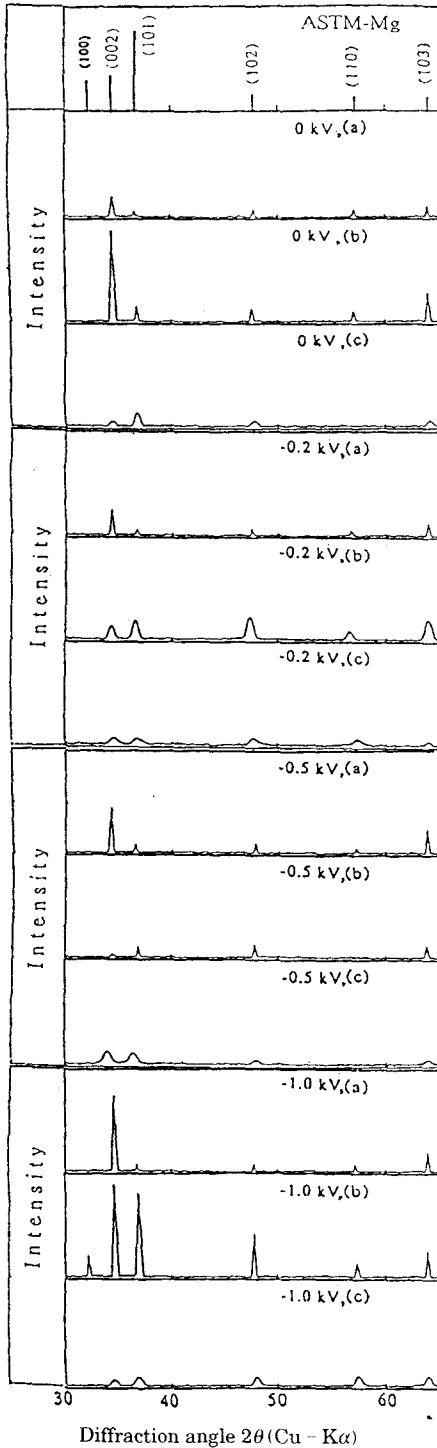


Fig. 2 X-ray diffraction patterns of magnesium films deposited at various N_2 gas pressures of (a) 7.3×10^{-3} Pa, (b) 7.3×10^{-2} Pa and (c) 7.3×10^{-1} Pa.

of 7.3×10^{-3} Pa had a (002) preferred orientation regardless of the negative bias voltages. From the bias voltages of -0.2 , -0.5 kV and -1.0 kV in Fig. 2, the X-ray diffraction peak of (002), however, decreased and the intensity of (101) peak increased slightly as the gas pressure increased up to 7.3×10^{-2} Pa. As shown in Fig. 2, the diffraction peaks became less sharp and broadened at the gas pressure of 7.3×10^{-1} Pa regardless of the bias voltages. And it can be seen that the crystal orientation of the films was influenced not only by nitrogen gas pressure but also substrate bias voltage.

The SEM photographs of top surface and cross section for deposited magnesium films as a function of nitrogen gas pressure at the different bias voltages are shown in Figs. 3(A), 3(B), 3(C) and 3(D). It can be seen that the surface and cross sectional morphology of these films varied with deposition conditions such as nitrogen gas pressure and substrate bias voltage. The magnesium films which were deposited by vacuum evaporation of no bias voltage exhibited from columnar to a granular structure with porosity and defects as the increase of nitrogen gas pressure. The morphology of the ion plated films deposited at the bias voltage of -0.2 kV changed from a granular structure (without defects or pinholes) with the increase of nitrogen gas pressure as shown Fig. 3(B). This related to the broadened diffraction peaks of the film shown in Fig. 2. From the bias voltages of -0.5 , -1.0 kV in Fig. 3(C) and 3(D), the film ion plated at low nitrogen gas pressure exhibited clearly columnar structures. However, column width of the films become smaller with the nitrogen gas pressure increased up to 7.3×10^{-1} Pa. From the results of Fig. 3(A), 3(B), 3(C) and 3(D), it can be seen clearly the effect of increasing bias voltage will be similar to that of decreasing nitrogen gas pressure.

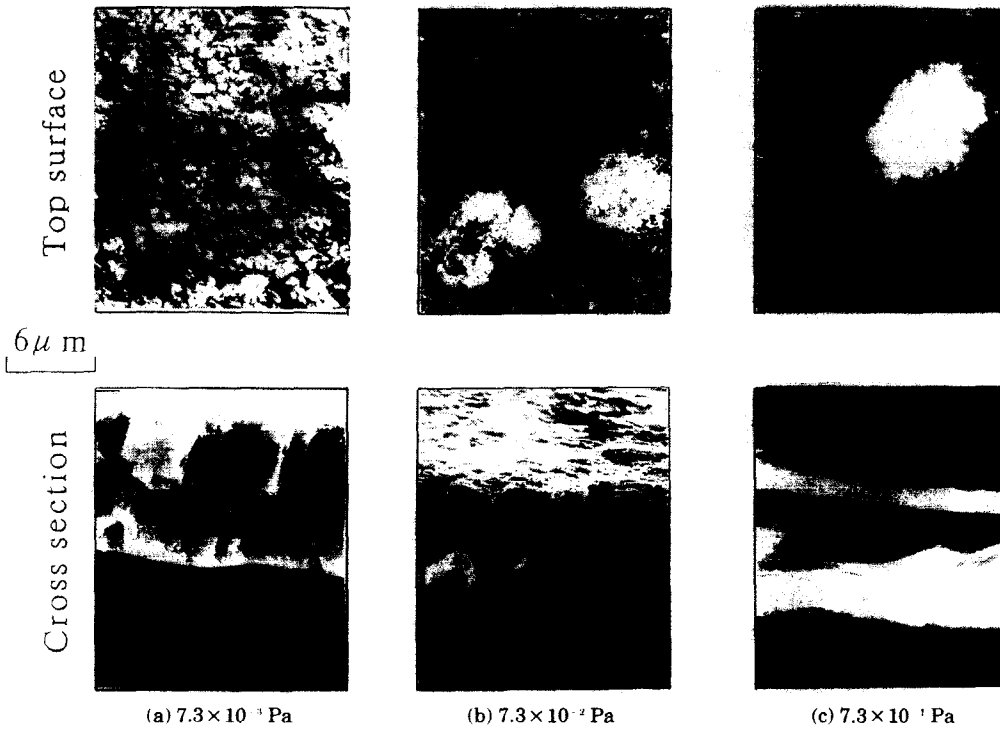


Fig. 3(A) SEM photographs of magnesium films deposited at different N_2 gas pressures (Bias Voltage ; 0 kV).

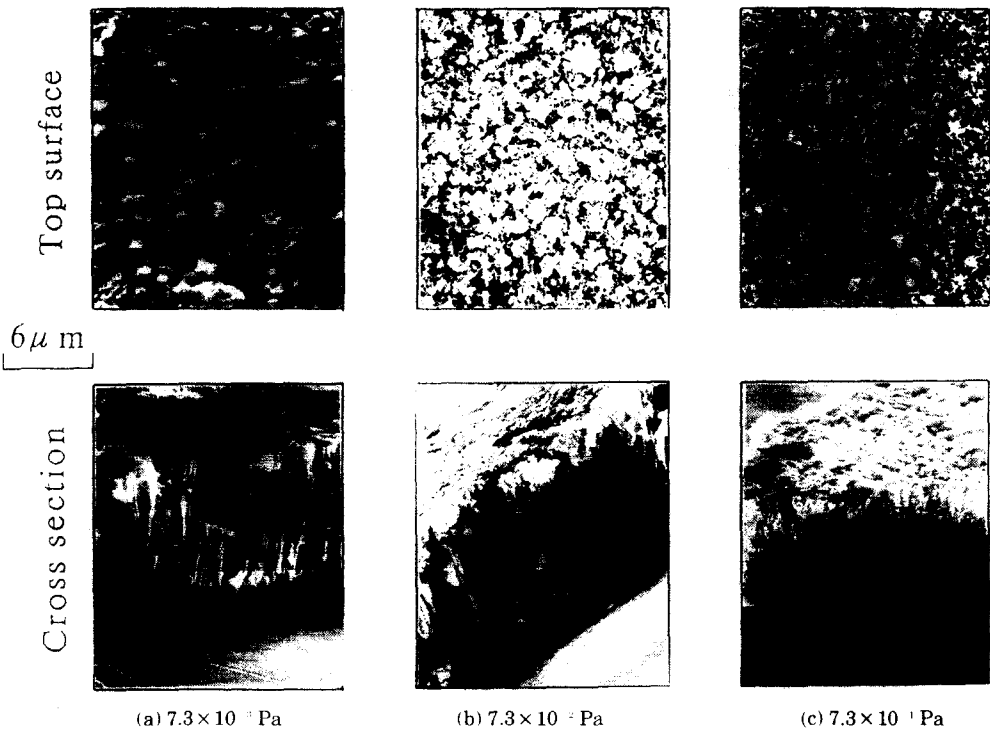


Fig. 3(B) SEM photographs of magnesium films deposited at different N_2 gas pressures (Bias Voltage ; -0.2 kV).

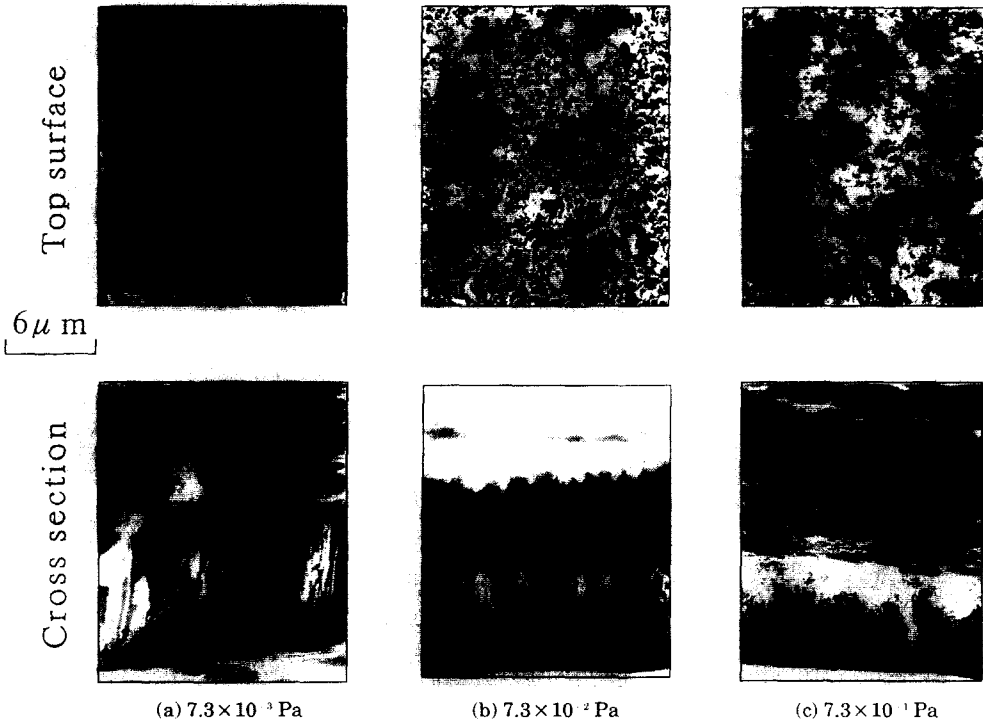


Fig. 3(C) SEM photographs of magnesium films deposited at different N₂ gas pressures(Bias Voltage ; - 0.5 kV)

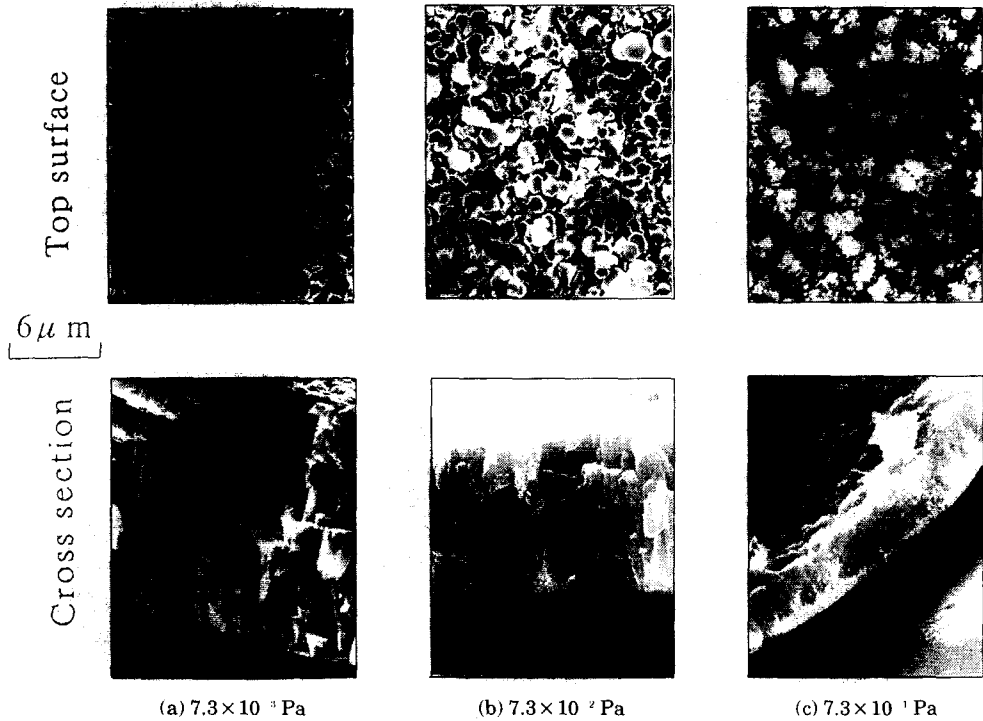


Fig. 3(D) SEM photographs of magnesium films deposited at different N₂ gas pressures(Bias Voltage ; - 1.0 kV)

3.2 Corrosion test of the deposited magnesium films

The result from corrosion test of the deposited magnesium films as a function of nitrogen gas pressure is shown in Fig. 4. It shows the anodic potentiodynamic polarization curves for the films measured in deaerated 3% NaCl solution. The pure magnesium of 99.99% used in evaporation metal were also measured the anodic potentiodynamic polarization curves to compare with the deposited magnesium films. All the deposited magnesium films appeared to show the active/passive polarization behaviors. When scanned from the rest potential, most of the films firstly became active and there was a substantial increase in corrosion current (critical

current density for passivation) as shown in Fig. 4(A), (B), (C) and (D). The deposited magnesium films nearly tend to show low corrosion current (passive current density) to compare with 99.99% magnesium ingot of the evaporation metal. The polarization behavior of these films changed with the gas pressure and bias voltage. Fig. 5 shows the anodic polarization curve (for reference purpose only) identifying potentials and current densities for the measured parameters : rest potential E_r , passive potential (the start potential of the passive region) E_p , pitting potential E_t , the difference between pitting potential and passive potential $E_t - E_p$ (the passive region) and passive current I_p . Fig. 6 (A) and 6(B) present the dependance of these

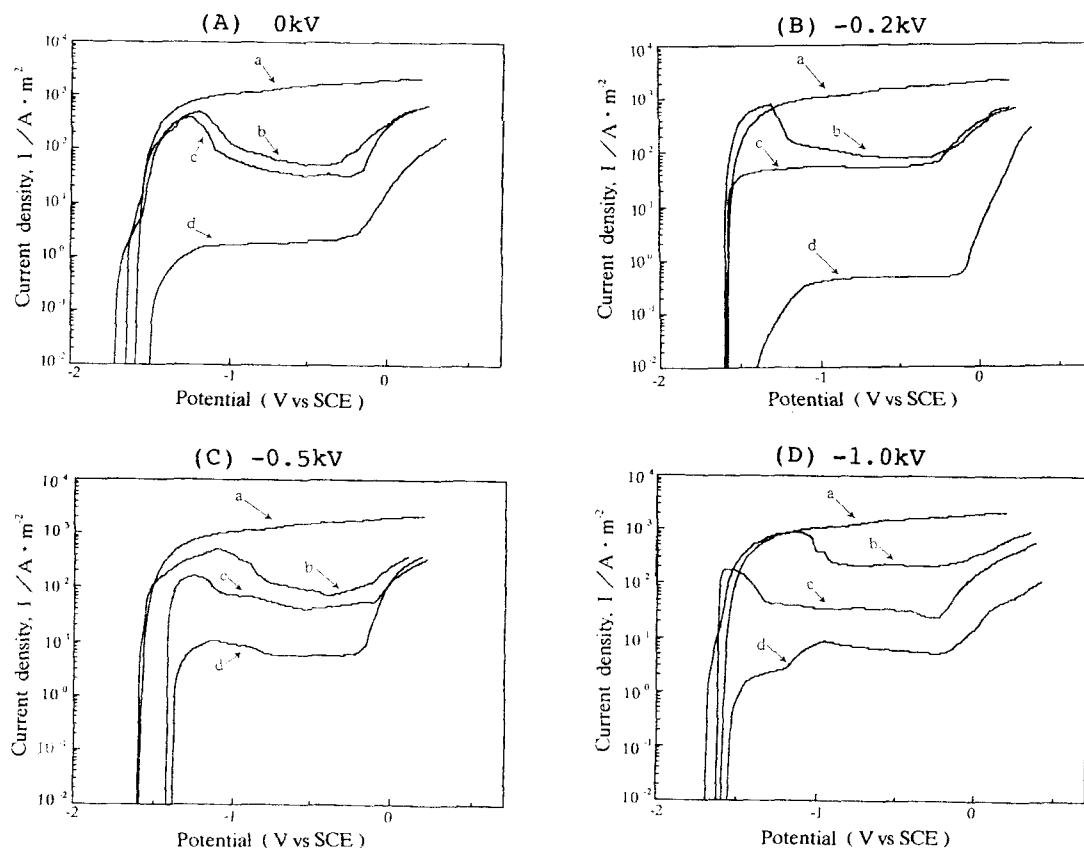


Fig. 4 Anodic polarization curves of magnesium films deposited at various N_2 gas pressures (7.3×10^{-3} Pa ; (b), 7.3×10^{-2} Pa ; (c), 7.3×10^{-1} Pa ; (d)) and 99.99% Mg - Ingot ; (a), measured in deaerated 3% NaCl solution.

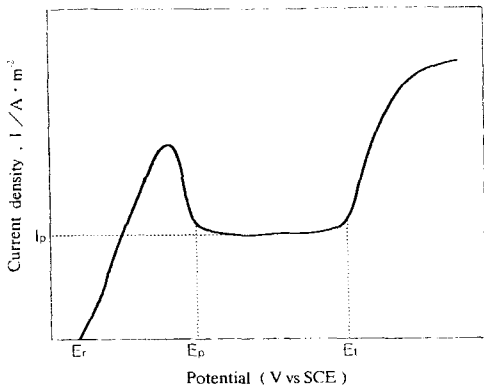


Fig. 5 Anodic polarization curve (for reference purpose only) identifying potentials and current densities (I_p ; Passive current, E_p ; Passive potential, E_t ; Pitting potential and $E_p - E_t$; Passive region).

several parameters by the variation for the polarization curves of magnesium films observed in Fig. 4. The passive current density (I_p) of all the deposited magnesium films tend to decrease with the increase of nitrogen gas pressure as shown in Fig. 6(A). From Fig. 6(B), it can be also seen that the passive region ($E_t - E_p$) of the films tend to increase with the increase of the gas pressure. Eventually, corrosion-resistance of the magnesium films obtained in this experiment exhibited at high nitrogen gas pressure of 7.3×10^{-1} Pa. That is, the magnesium films which had fine granular structure showed good corrosion resistance.

4. Discussion

The structure zone model has been used to provide an overview of the relationship between the microstructure of the films deposited by PVD and the most prominent deposition conditions⁷⁻⁹. B. A. Movchan and A. V. Demchishin⁹ have proposed it firstly such model. They concluded that the general features of the resulting structures could be correlated into three zones depending on T/T_m . Here T_m is the melting point of the co-

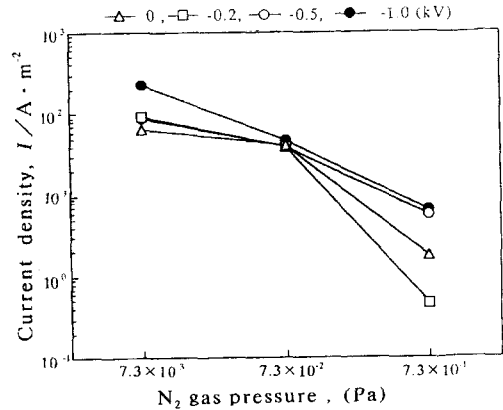


Fig. 6(A) Diagrams for corrosion tendency of magnesium films deposition at various N_2 gas pressures in deaerated 3% NaCl solution for passive current (I_p).

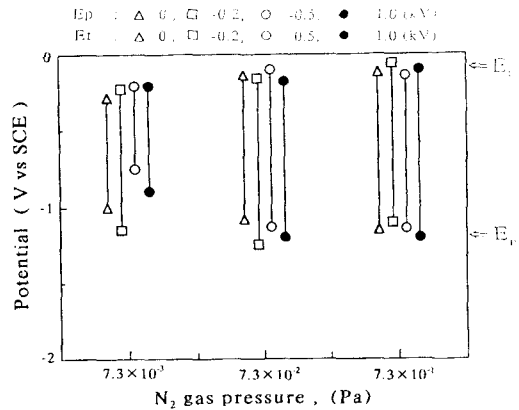


Fig. 6(B) Diagrams for corrosion tendency of magnesium films deposition at various N_2 gas pressures in deaerated 3% NaCl solution with passive potential(E_p), pitting potential(E_t), and passive region($E_p - E_t$).

ting material and T is the substrate temperature in kelvines. Zone 1 ($T/T_m < 0.3$) is dominated by tapered macrograins with domed tops, zone 2 ($0.3 < T/T_m < 0.45$) by columnar grains with denser boundaries and zone 3 ($T/T_m > 0.5$) by equiaxed grains formed by recrystallization. J. A. Thornton¹⁰⁻¹¹ has extended this model to include the effect of the sputtering gas pressure and found a fourth zone termed zone T (transition zone) consisting of a dense array of poorly defined

fibrous grains. R. Messier¹²⁻¹³ found that the zone I - T boundary (fourth zone of Thorton) varies in a fashion similar to the film bias potential as a function of gas pressure. Some current computer simulation studies¹⁴⁻¹⁵ have shown the mechanism of the formation and growth of columnar structure, and the change of microstructure, for example, from zone 1 to zone T. However, there has not nearly enough model for explaining the change in morphology with crystal orientation of the films¹⁶. The structure zone model only provide an information about the morphology of the deposited film. In general, the properties of the deposited films depend on the deposition condition and these, in turn depend critically on the crystal orientation and morphology of the films. Therefore, it is important to clarify that the nucleation occurrence and growth stage for the crystal orientation and morphology of the film affected by deposition conditions. In this experimental results, the crystal orientation and morphology of the magnesium film which showed good corrosion resistance tend to have granular structure with (002) preferred orientation or broadened peak. The morphology of magnesium films tend to change from columnar structure to a granular structure with the increase of nitrogen gas pressure, although the substrate temperature was constant. In this case, the preferred orientation of the films exhibited (002) and the diffraction peaks of the films became less sharp and broadened. From the results it is obvious that the nitrogen gas pressure plays a large part in affecting the formation of the crystal orientation and morphology of deposited films. We think that the adsorption or occlusion of nitrogen atoms on the growing film surface during the deposition may be play an important role in this case, because such gas adsorbates could also change the growth mechanism of nuclei.

Since the cold rolled steel plate of substrate

which was used in this work is polycrystal, the orientation of the nuclei would have been random at the early growth stages. Consequently the film orientation depends on the growth of the nuclei. Generally the differences of growth rate of different crystal planes are expected to be small at low substrate temperature. However, ion plating system is essentially a vapour deposition process in which the substrate surface is cathode of a glow discharge system. Therefore ion bombardment during the deposition will cause an increase in the bulk temperature and especially in the surface temperature of the growing film¹⁷⁻¹⁸. The adatom mobilities can be enhanced by such ion bombardment, although the substrate temperature may be relatively low. In this case, it is possible that the growth rate of different crystal planes become different. When the magnesium film was deposited by ion plating at high vacuum (low nitrogen gas pressure as there were little gas atoms adsorbed on the crystal face), the growth rate of (002) face which has the highest surface energy would be larger than (101) face. As a result, the area possession of (101) on film surface will increase. Therefore the film shows (101) orientation as shown in Fig. 7(A). When the nitrogen gas pressure increased, as the nitrogen atoms are easier to be adsorbed on the (002) surface than on the (101) surface the growth rate of (002) will become lower by the nitrogen adsorption. In this case, the area possession of (002) face on the film surface will be larger than the (101), as shown in Fig. 7(B). The film therefore will show (002) preferred orientation. When the magnesium film is deposited at high gas pressure, the crystal growth will be disturbed by nitrogen atoms adsorption as shown in Fig. 7(C). Eventually, the growth rate of all the crystal faces will decrease. The presence of occluded nitrogen atoms can also restrict atom

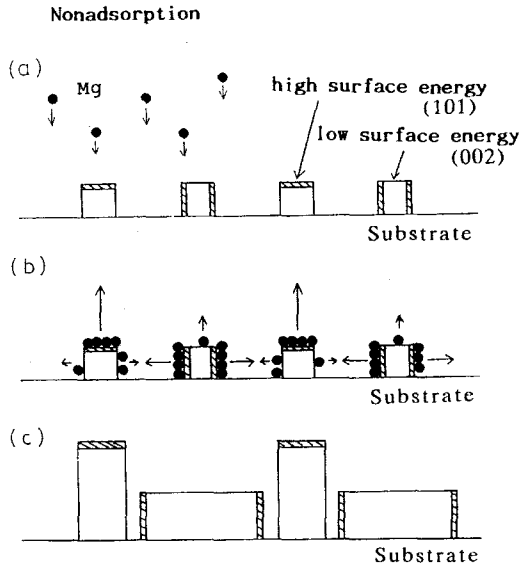


Fig. 7(A) Model of crystal growth of magnesium film under the nonadsorption.

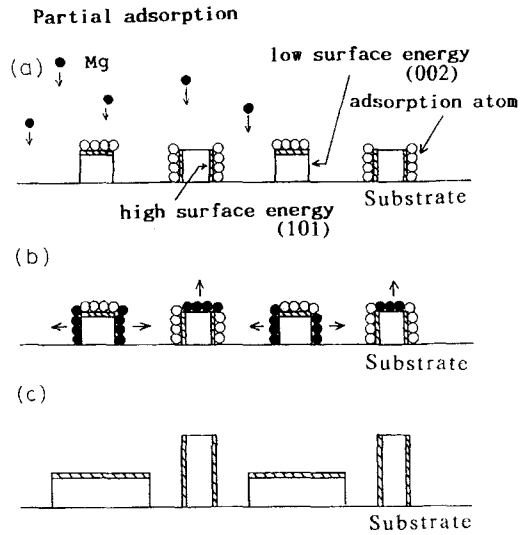


Fig. 7(B) Model of crystal growth of magnesium film under the partial adsorption.

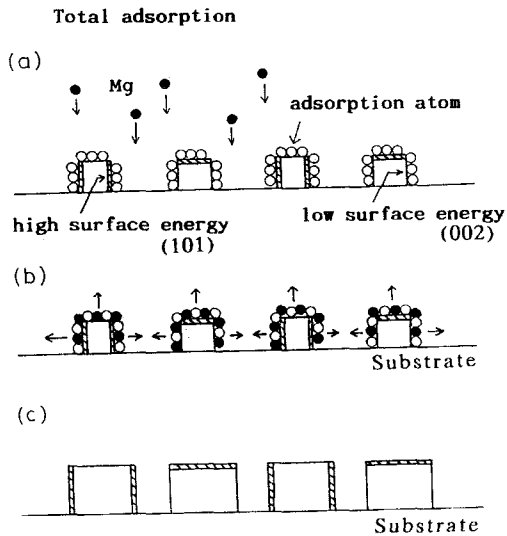


Fig. 7(C) Model of crystal growth of magnesium film under the total adsorption.

diffusion across grain boundaries, disturbing grain growth. It can be seen that the films which exhibited granular structure with (002) preferred orientation can be obtained by ion plating at relatively higher nitrogen gas pressure. Increasing bias voltage will enhance both adatom

diffusivities and ion bombardment. The ion bombardment will reduce the amount of adsorbed nitrogen atoms on the growing crystal surface. The enhanced adatom mobilities could also make it easy to create the nuclei orientation with low surface energy face. Consequently, the effect of increasing bias voltage will be similar to that of reducing nitrogen gas pressure. The nucleation and growth mechanism for granular structure of the deposited magnesium films are very complex in an ion plating technique because the morphology and orientation depend not only on the substrate temperature but also on the energy of deposition of the atoms or ions, the kinetic mechanism between metal atoms and nitrogen gas, and even on the presence of impurities. I recognize, by my empirical measurements, that the system is not fully characterized in film growth term but offers an understanding of film growth for reciprocal relation between crystal orientation and morphology of films with added explanation related to the effects of adsorption, occlusion and ion sputter of nitrogen gas.

5. Conclusion

The results of this investigation are summarized as follows :

1. All the deposited magnesium films showed obviously good corrosion resistance to compare with 99.99% magnesium ingot of the evaporation metal. And the magnesium film of fine granular structure which obtained at high nitrogen gas pressure of 7.3×10^{-1} Pa had the highest corrosion resistance.

2. The crystal orientation and morphology of the films depended not only on gas pressure but also on bias voltage. i.e., the effect of increasing bias voltage was similar to that of decreasing gas pressure.

3. The formation mechanism of crystal orientation and morphology can be explained by applying the effects of adsorption, occlusion and ion - sputter of nitrogen gas.

4. The properties of all the films can be improved greatly by controlling the crystal orientation and morphology with effective use of the plasma ion plating technique.

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