

Corrosion Resistance of Mg thin films by Ion plating according to gas (N₂) pressures and bias voltages

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Key words : Magnesium metal, Corrosion-resistance, Ion plating, Morphology, Crystal orientation, Adsorption, Occlusion

Abstract

Thin magnesium films were prepared on cold-rolled steel substrates by a thermo-electron activation ion plating technique. The influences 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 X-ray diffraction peaks of magnesium film became less sharpen and broadened with the increase of nitrogen gas pressure. With an increase in nitrogen gas pressure, film morphology was changed from columnar to granular

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The 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 ionization filament of 0.8mm tantalum wire in diameter was set at the level of 2cm above the evaporator and negative bias voltage of 100V was supplied on the ionization 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 surface roughness size of $0.05\mu\text{m}$ alumina powder and then ultrasonically cleaned in a bath of acetone for 30minutes prior to being mounted in the vacuum chamber. The source-to-substrate distance was 13cm.

Ahead of the evaporation process, the system was initially evacuated to the 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 1.3Pa with the bias voltage of -1.0 kV for about 5minutes to remove the residual oxides from the surface. 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 -1.0 kV were used in ion-plating arrangement. Once the system reached starting condition, the evaporation started. The ion plating process lasted typically 20minutes at 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 showed the value of 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 diffractometer 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 making all $0.25\text{cm}^2(0.5 \times 0.5\text{cm})$ 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

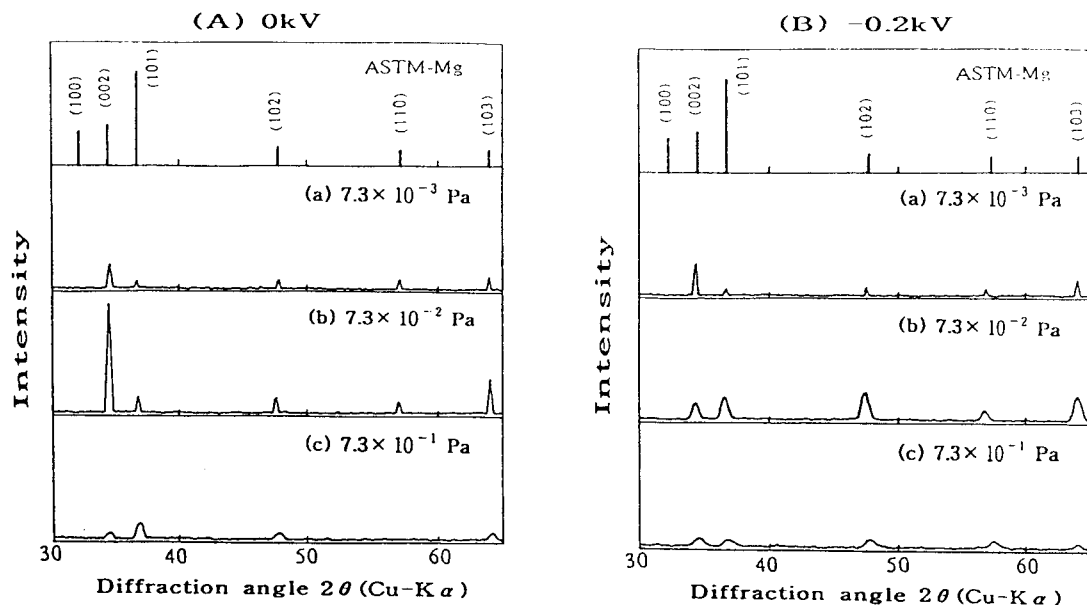
specimen was equilibrated with the solution for 30minutes. Potentials were measured versus SCE(saturated calomel electrode).

3. Results

3.1 Crystal orientation and morphology of deposited magnesium films

In order to investigate the influence of nitrogen gas pressure and bias voltage on the crystal orientation and morphology of deposited magnesium films, the specimens were prepared by changing nitrogen gas pressure from 7.3×10^{-3} to 7.0×10^{-1} Pa at bias voltage from 0 to -1.0 kV 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 diffraction intensity $[d(2\theta)]$ 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 (0 kV) was exhibited (002) preferred orientation as the nitrogen gas pressure



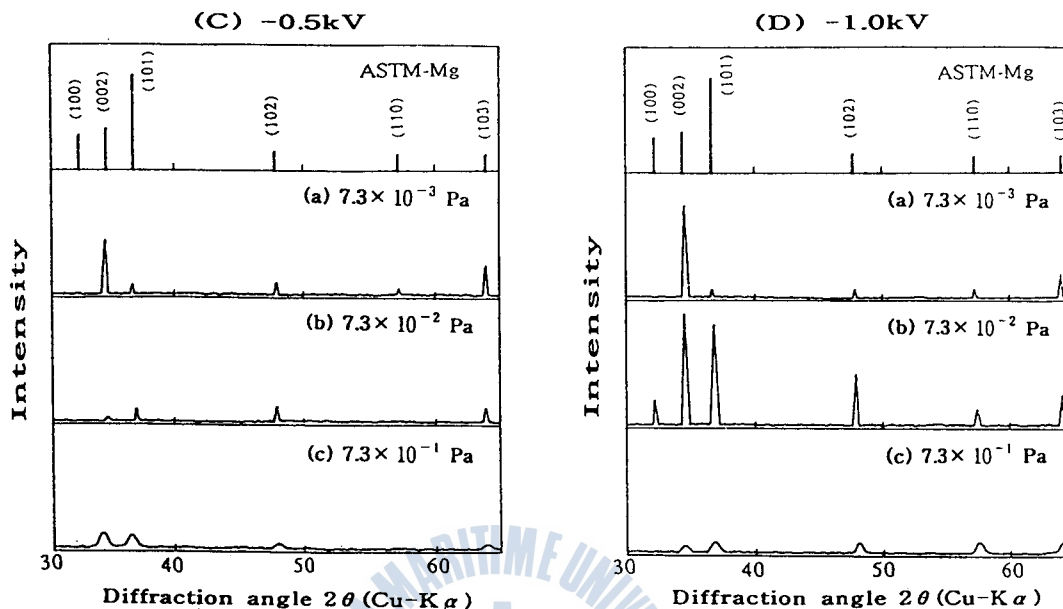


Fig.2 X-ray diffraction patterns of magnesium films deposited at various Bias Voltages and N_2 gas pressures of (a) 7.3×10^{-3} Pa, (b) 7.3×10^{-2} Pa and (c) 7.3×10^{-1} Pa.

increased to 7.3×10^{-2} Pa from 7.3×10^{-3} Pa. Here, the diffraction peaks of the film deposited at high nitrogen gas pressure of 7.3×10^{-1} Pa became less sharpen and broadened. The crystal orientation of the films ion plated at the gas pressure 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 Figs3(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.

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(A) 0 kV

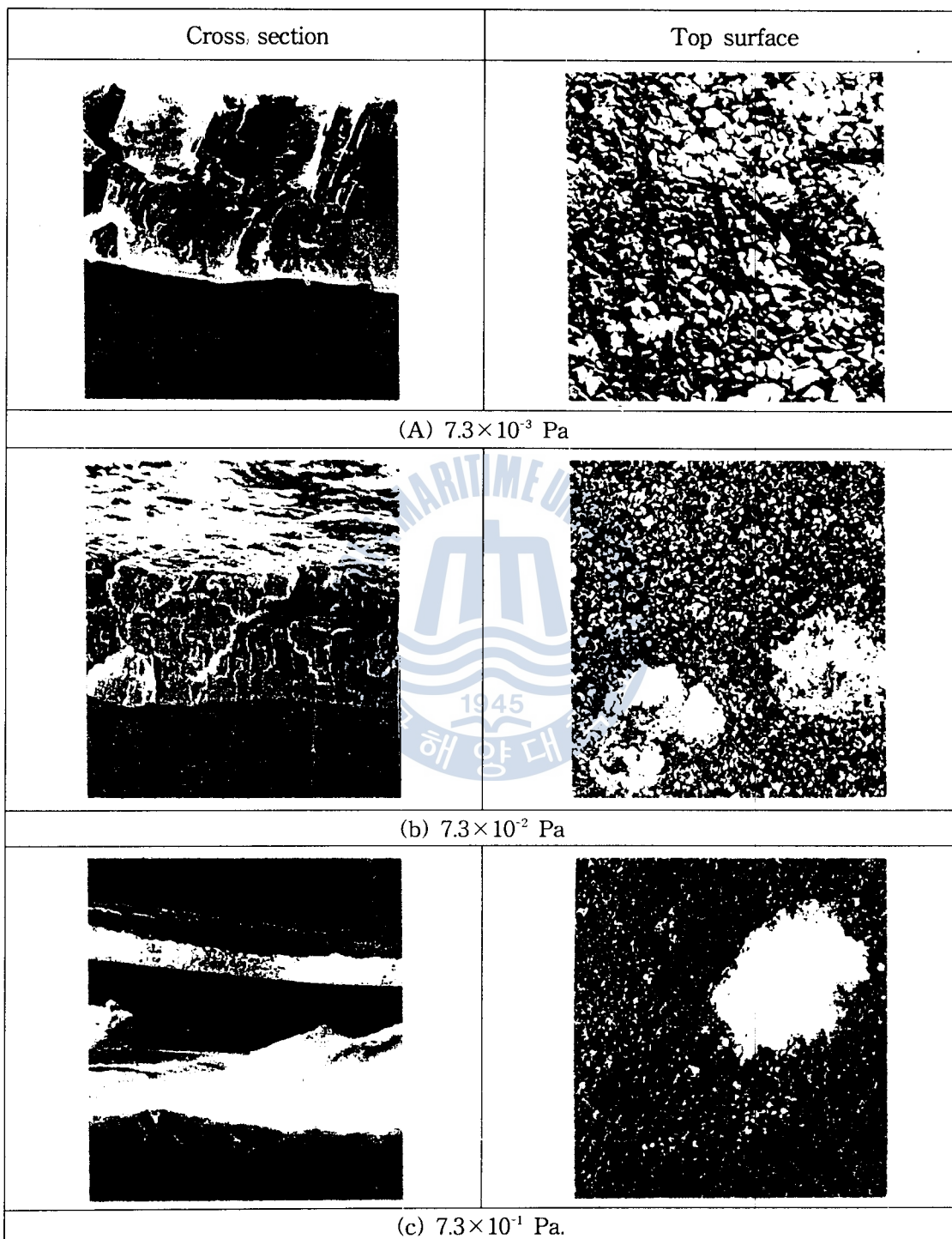


Fig.3(A) SEM photographs of magnesium films deposited at different N₂ gas pressures(Bias Voltage; 0 kV)

6 μm

(B) -0.2kV

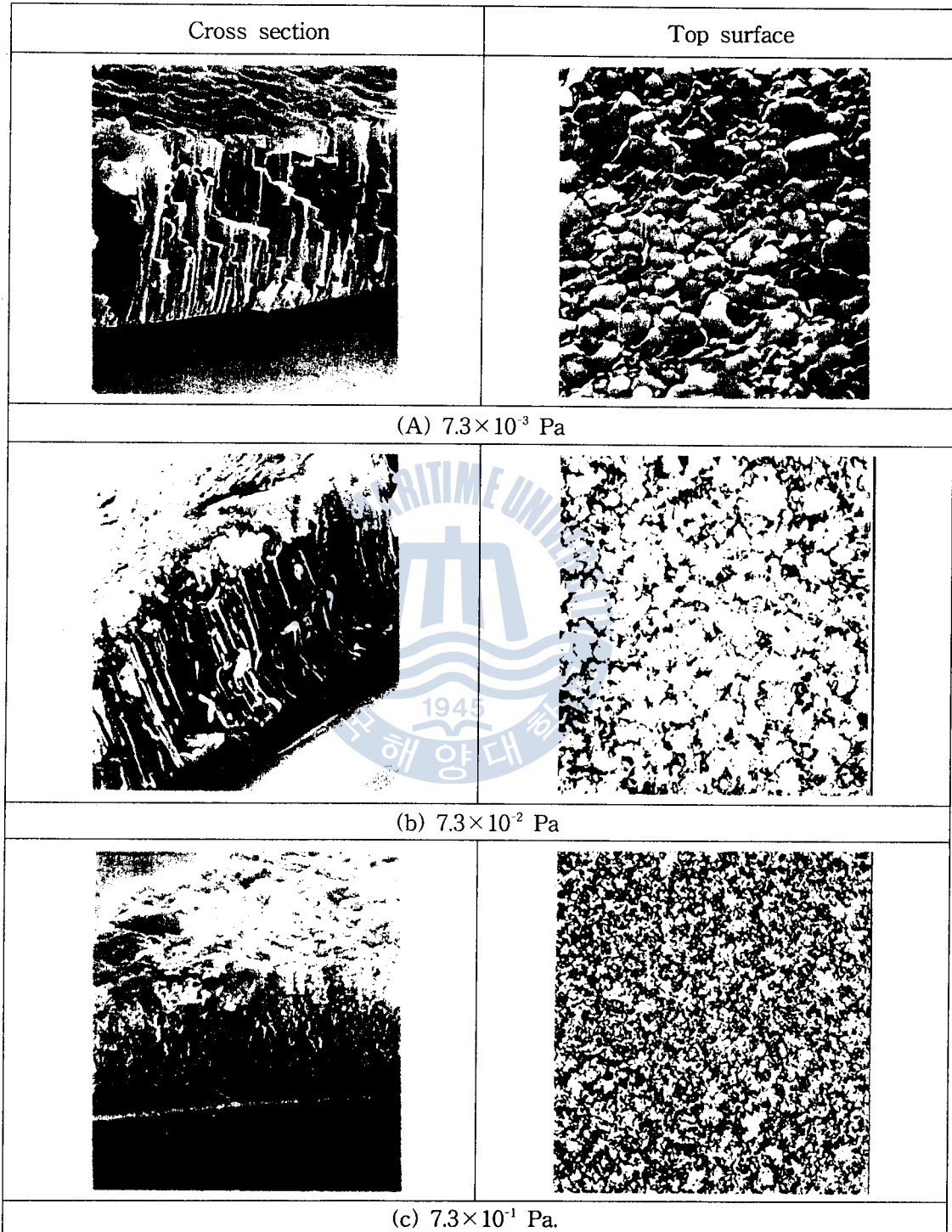


Fig.3(B) SEM photographs of magnesium films deposited at different N_2 gas pressures(Bias Voltage; -0.2 kV)

6 μm

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(C) -0.5kV

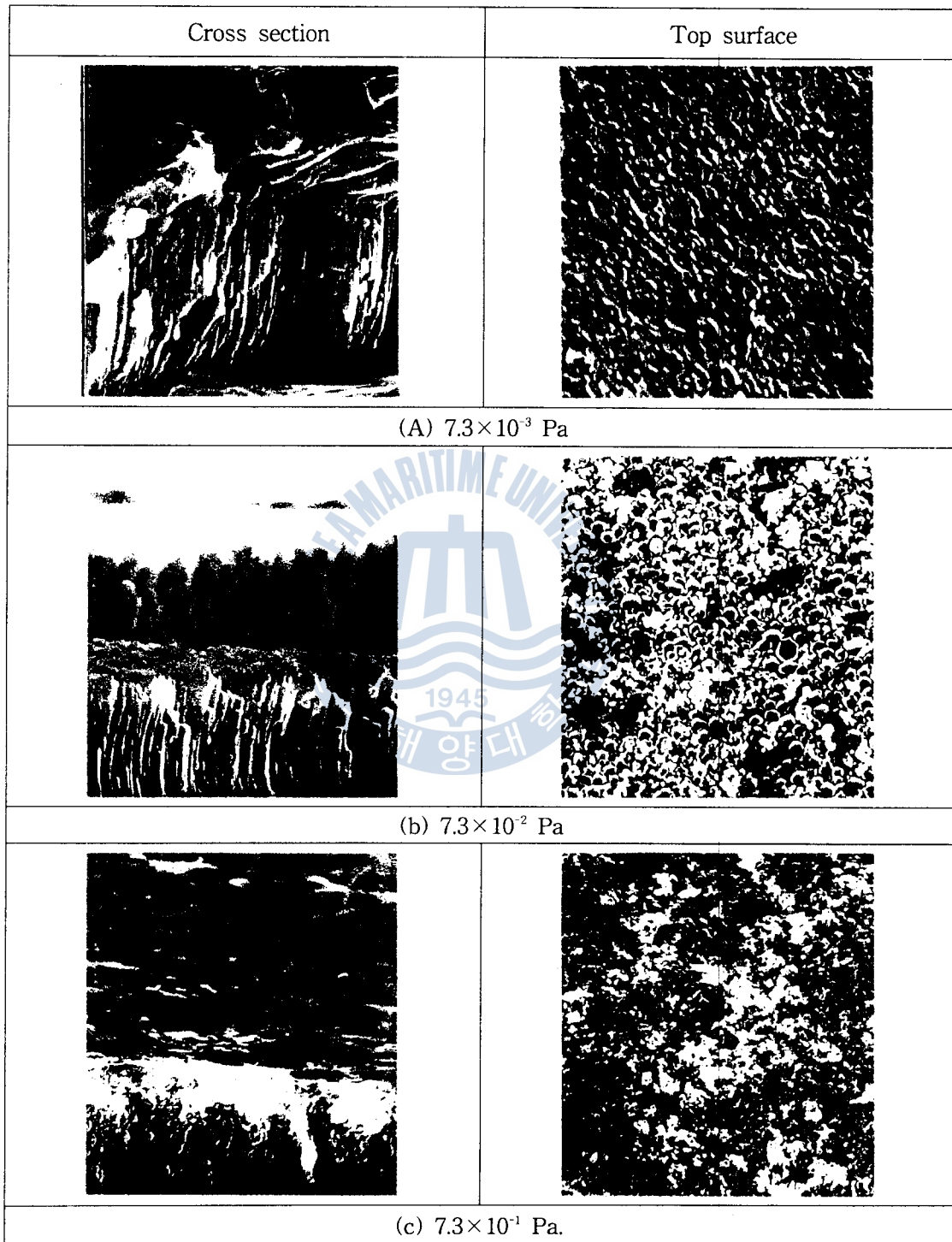
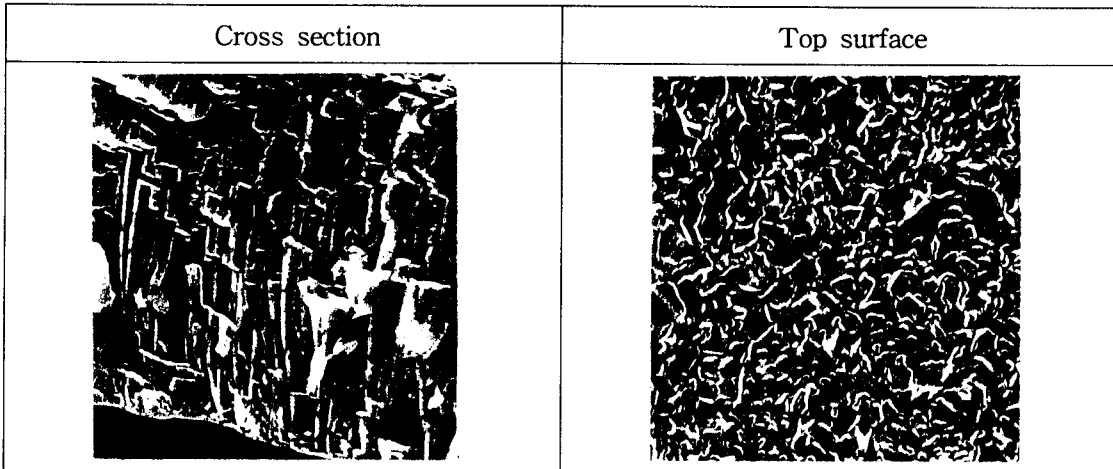


Fig.3(C) SEM photographs of magnesium films deposited at different N₂ gas pressures(Bias Voltage; -0.5 kV)

6 μm

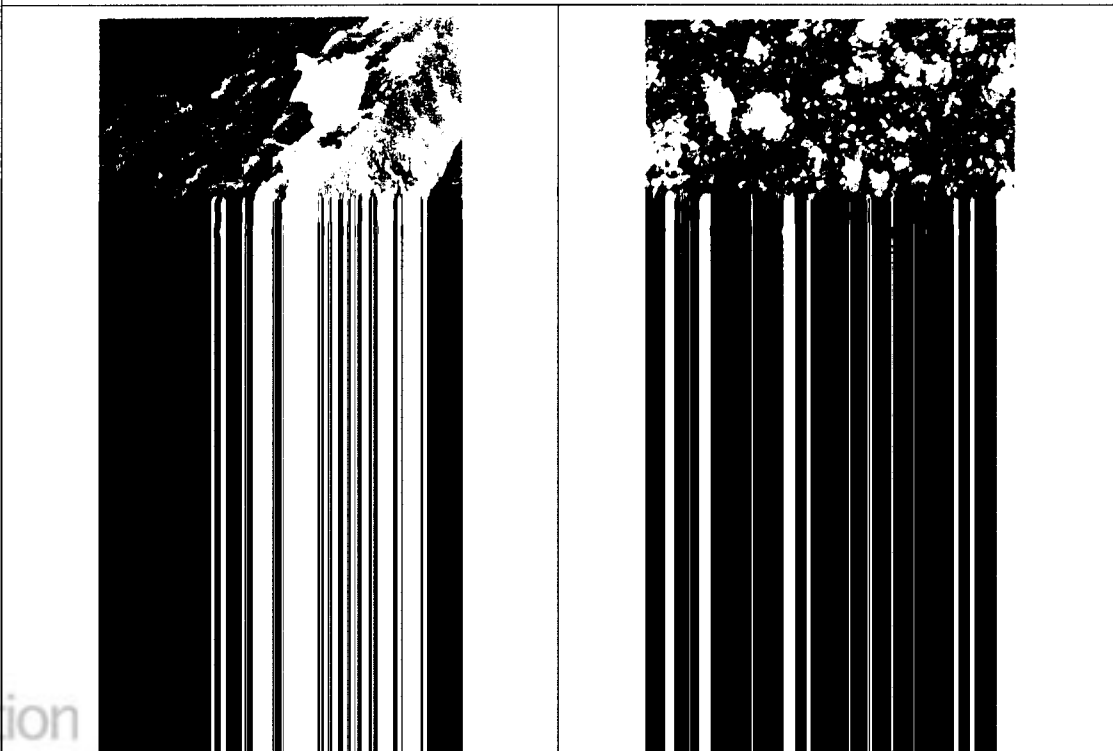
(D) -1kV



(A) 7.3×10^{-3} Pa



(b) 7.3×10^{-2} Pa



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(C) -0.5kV

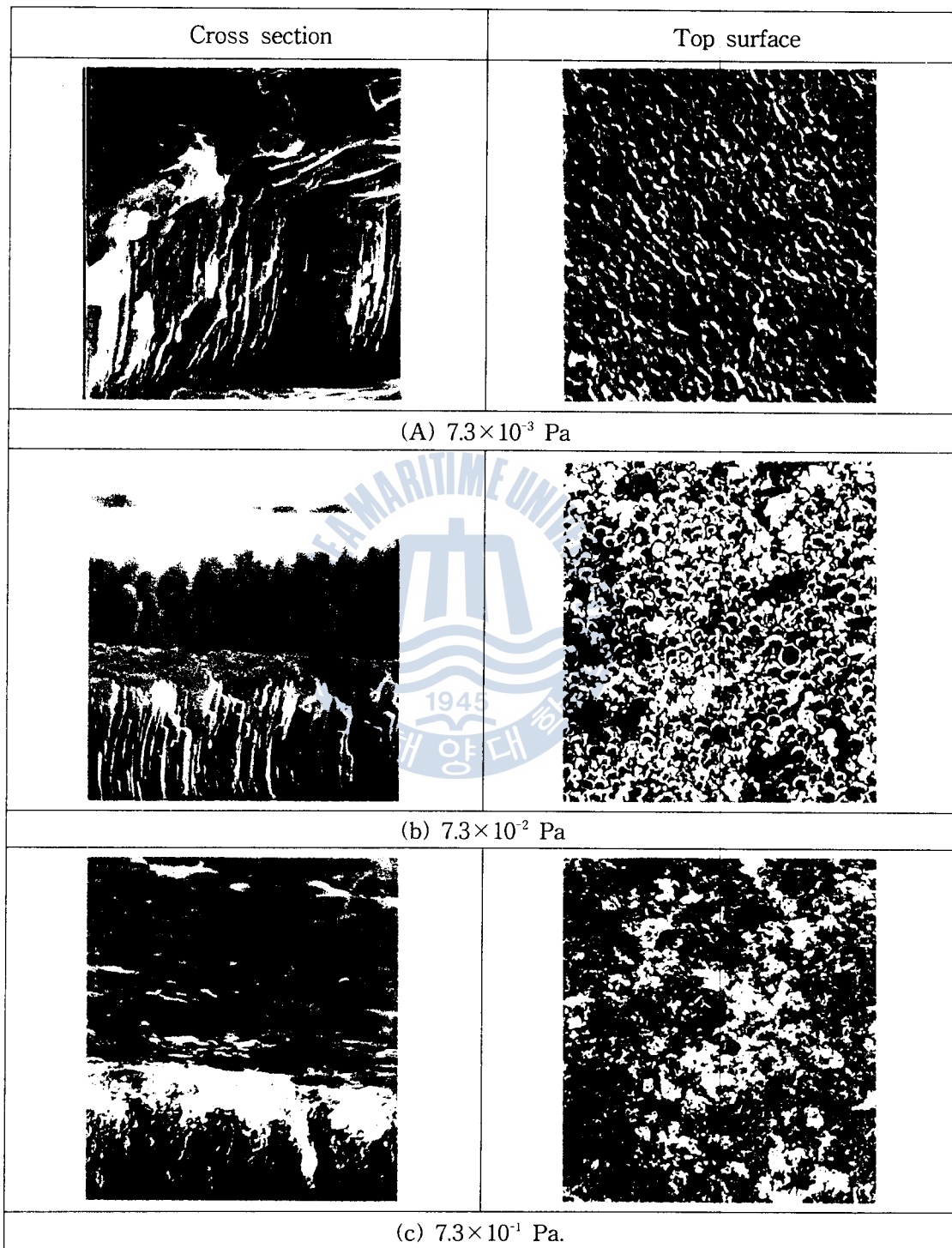


Fig.3(C) SEM photographs of magnesium films deposited at different N_2 gas pressures(Bias Voltage; -0.5 kV)

6 μm

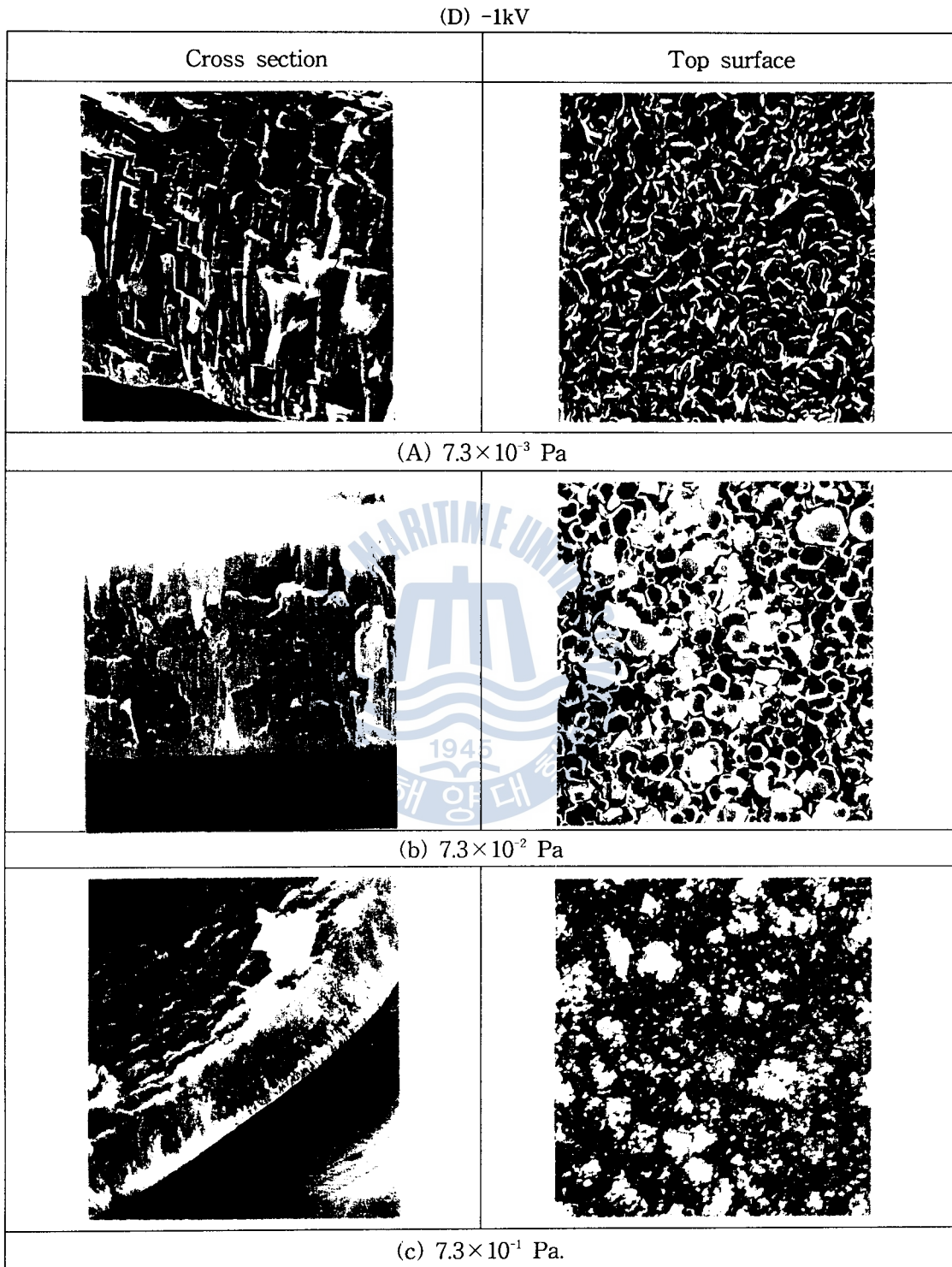


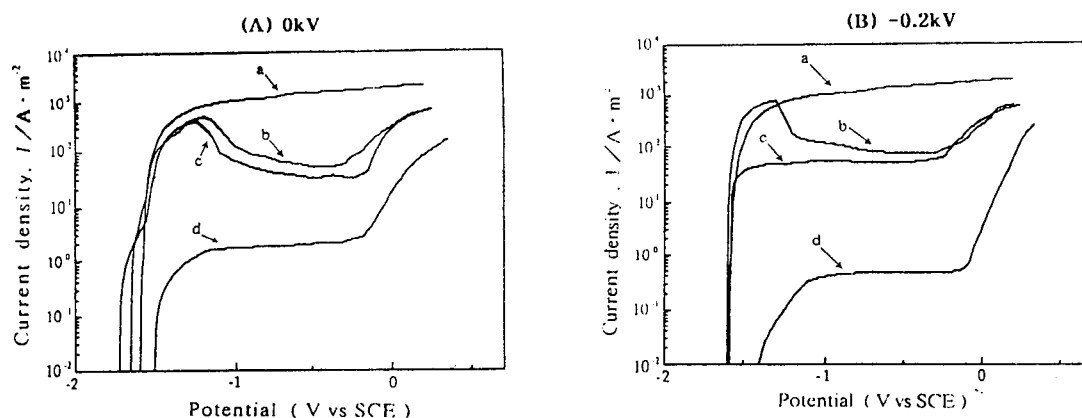
Fig.3(D) SEM photographs of magnesium films deposited at different N_2 gas pressures(Bias Voltage; -1.0 kV)

6 μm

The magnesium films which were deposited by vacuum evaporation of no bias voltage were exhibited from columnar to a granular structure with the increase of nitrogen gas pressure. The morphology of the ion plated films deposited at the bias voltage of -0.2kV was changed from a granular structure with the increase of nitrogen gas pressure as shown Fig. 3 (B). This is 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 became 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 that the effect of increasing bias voltage will be similar to that of decreasing nitrogen gas pressure.

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 in deaerated 3% NaCl solution. The anodic potentiodynamic polarization curves of the 99.99% pure magnesium used in evaporation metal was also measured to compare if 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).



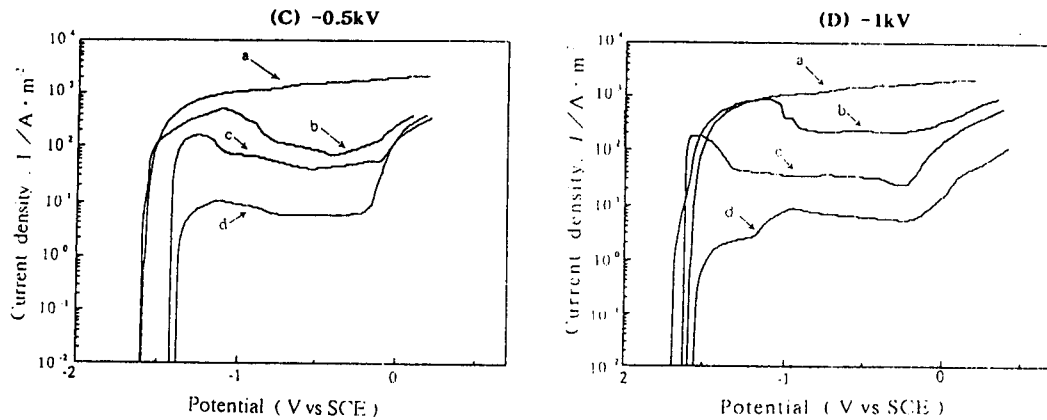


Fig4. Anodic polarization curves of magnesium films deposited at various N_2 gas pressures (7.3×10^{-3} Pa ; (b), 7.3×10^{-2} Pa ; (c), 7.3×10^{-1} Pa ; (d)) and 99.99% Mg-Ingot ; (a), measured in deaerated 3%NaCl solution.

The deposited magnesium films nearly tend to show low corrosion current (passive current density) compared 99.99% magnesium ingot for the evaporation metal. The polarization behavior of these films was changed according to 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 dependence of these 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), In addition it can be also seen that the passive region of the films tend to increase with the increase of the gas pressure. Eventually, the best corrosion-resistance of the magnesium films obtained in this experiment was 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.

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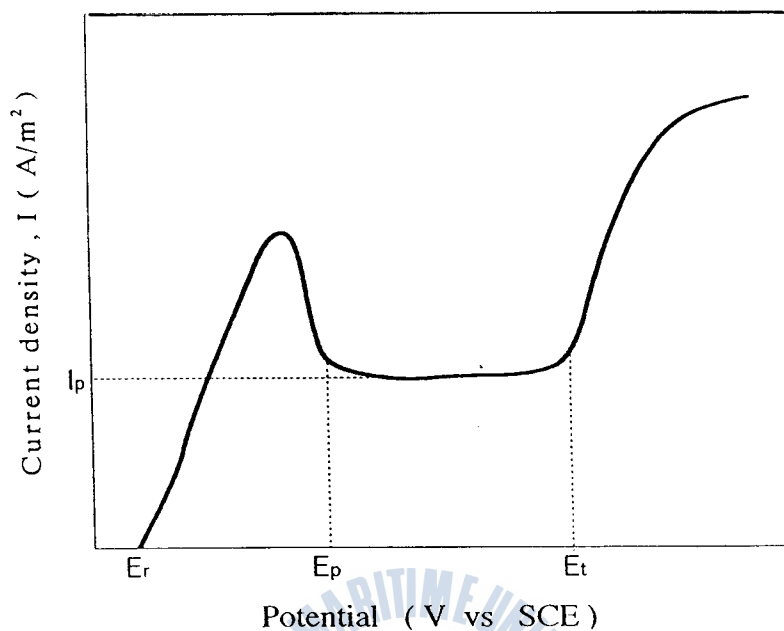


fig.5 Anodic polarization curve (for reference purpose only) identifying potentials and current densities (I_p ; Passive current, E_p ; Passive potential, E_t ; Pitting potential and E_p-E_t ; Passive region)

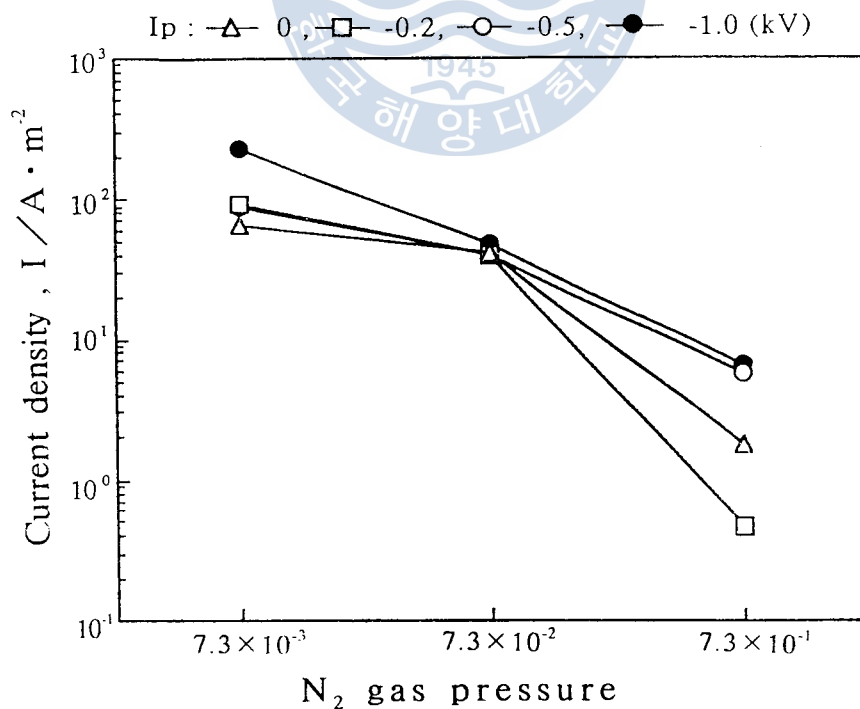


fig.6 (A) Diagrams for corrosion tendency of magnesium films deposition at various N_2 gas pressures in deaerated 3% NaCl solution for passive current(I_p)

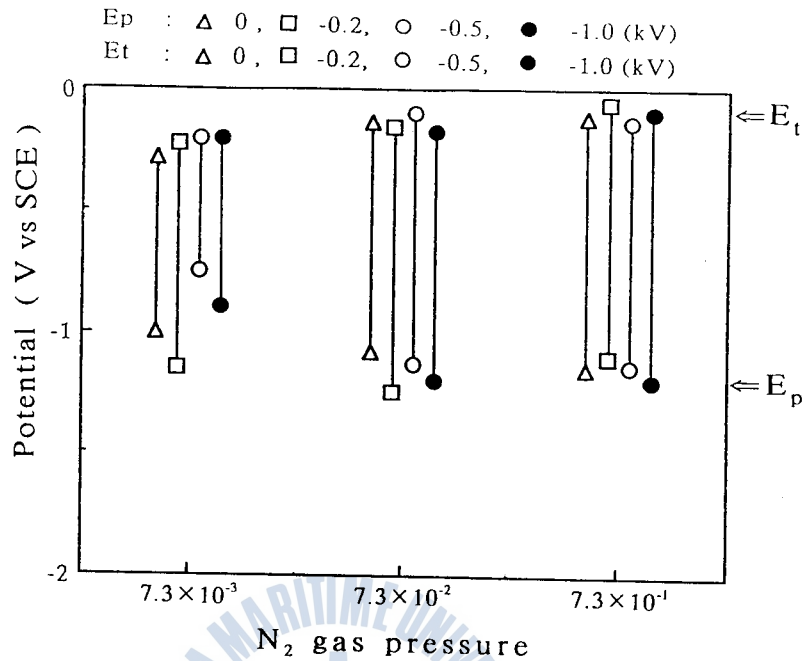


fig.(B) (A) Diagrams for corrosion tendency of magnesium films deposition at various N_2 gas pressures in deaerated 3% NaCl solution for passive current(I_p), Pitting potential(E_t), and passive region(E_t-E_p)

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 conditions⁷⁻⁸⁾. B.A.Movchan and A.V.Demchishin⁹⁾ have proposed firstly such a 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 coating 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 the 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 Thornton) 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 the growth of columnar structure, and the change of microstructure, for example, from zone 1 to zone T. However, there has not been nearly enough model to explaining the change in morphology with crystal orientation of the films¹⁶⁾ like this work. The structure zone model only provides an information about the morphology of the deposited film. In general, the properties of the deposited films depend on the deposition condition 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 are affected by deposition conditions. In these 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 was 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 great role in affecting the formation of the crystal orientation and morphology of deposited films.

The presence of occluded nitrogen atoms can also restrict atom diffusion across grain boundaries, disturbing grain growth. It can be seen that the films which exhibited granular and fine 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 the growth mechanism for granular and fine 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. It will be recognized, by these 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 compared 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 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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