

A Study on Preparation of Aluminum - Magnesium Alloy Coatings by Ion - Plating and Their Corrosion Resistance

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이온플레이팅법에 의한 Al-Mg 합금 코팅막의 제작과 내식성에 관한 연구

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Key words : Ion - plating(이온플레이팅), Aluminum - magnesium coating film(Al - Mg코팅막), Coating film with forced solid solution(강제고용체의 코팅막), Morphology(물포로지), Corrosion - resistance(내식성)

Abstract

알루미늄 코팅막은 부식환경으로부터 강판을 보호하는 데에 자주 사용된다. 그러나 이 코팅막은 때때로 사용조건에 따라 제한을 받는다. 아무리 강판상에 치밀한 良質膜을 코팅시켰다 할지라도, 사용중 이 피막이 손상을 받아서 강판이 일부라도 노출되는 경우는 강판과의 갈바닉(Galvanic) 작용으로 급격한 부식을 일으킨다.

본 연구는 내식성 개선을 목적으로 해서, 高密着性的의 코팅막을 제공하는 非平衡프라즈마 프로세스인 이온플레이팅법에 의해 냉간압연강판상에 Al-Mg합금 코팅막을 제작했다. 제작된 막들은 우선, EMPA측정에 의해 원소조성분석을 한 후, 相구조분석 및 表·斷面의 물포로지(Morphology)를 X선 회절 및 走査型 電子顯微鏡(SEM)에 의해 관찰했다. 또한, 이들막은 탈기시킨 3%NaCl 용액중 양극 분극 측정을 통해서 내식특성에 대한 평가를 행했다. 이들의 결과에 의하면, 알루미늄과 마그네슘의 組成比에 따라 柱狀, 微結晶 및 아몰포스(Amorphous)組織을 보이는 金屬間化合物이나 固溶體의 Al-Mg박막이 나타났다. 이들 Al-Mg합금 코팅막은 강판과의 갈바닉 부식작용에 대한 방지 및 부동태 피막의 형성을 촉진하는 등의 좋은 내식성을 나타냈다.

1. Introduction

Requirements for industrial materials are becoming more severe with the advance of sci-

ence and technology. However, since a single material can hardly satisfy all these requirements, materials of different properties are combined¹⁾. To reduce for weak points in single

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materials, there are some prevalent attempts to develop new functional coated materials by plasma assisted processes^{2,3}. Ion-plating, one of the plasma assisted processes offer a versatile method for producing dense highly adherent coating of controlled composition on substrate. Such characteristics are mainly due to the presence of ions in plasma assisted deposition process of non-equilibrium state, and these in turn depend critically on the structure and composition of the film and its substrate.

Aluminum coatings by a plasma assisted deposition process are often used to protect a substrate from corrosion caused by the environment. However, the aluminum coatings have occasionally some limitations which restrict its use in certain applications^{4,5}. Although undamaged aluminum coating on steel gives a good corrosion resistance, the protection is not so good because the corrosion can occur at an accelerated rate if the coatings are scratched or otherwise damaged. Thus coatings offering a better galvanic or sacrificial protection for steel are desirable than offering by pure aluminum. To this end, Al-Mg alloy coatings were studied.

In this paper we prepared Al-Mg coatings with columnar, microcrystalline or amorphous structure onto the cold-rolled steel substrate by ion-plating technique. The Al-Mg alloy coating, which will provide the galvanic protection of magnesium and/or the passivation improvement of aluminum, would be useful. Our results show that a good corrosion resistance can be obtained from passivated metal films because of an effective solid solution of the alloying elements.

2. Experimental details

2.1 Coating procedures

(100-x)Al-xMg alloy films (where $x=0.05, 3.5, 23.0, 46.0, 68.0, 88.0, 99.0$ at.% at Al) were ion-plated onto SPCC steel (cold-rolled steel). Fig. 1 is a schematic representation of the ion-plating apparatus used in this study. This apparatus consists of three main parts, i.e. (1) a substrate holder, (2) an ionization system and (3) a crucible for metal evaporation. The experimental apparatus of ion-plating was a thermo-electron activation type similar to the type described by ref.(2), but the evaporation source system is different. Electron beam source was used to evaporate the metal (Al-Mg alloy). Both purities of aluminum and magnesium used as the evaporation metal were 99.99%. In order to enhance the ionization efficiency, a tantalum filament as an ionization filament was set at a level of 2cm above the evaporator. A negative bias voltage of 120V was supplied on the ionization filament against the evaporator. The current between the ionization filament and the evaporator (called the ionization current) was controlled by adjusting the fila-

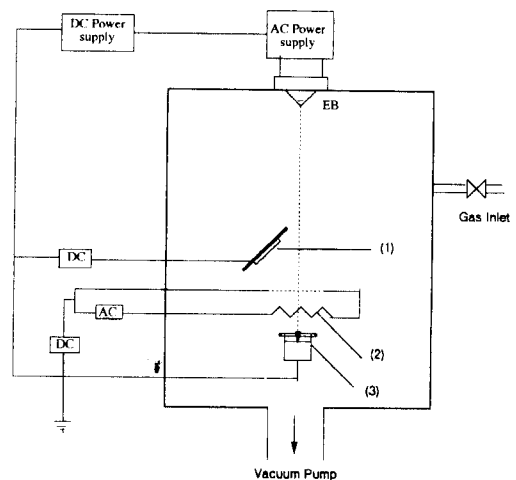


Fig. 1 Schematic Diagram of the Ion-plating System.

ment current. The cold - rolled steel plates used as substrates were progressively polished up 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 30min prior to mounting in the vacuum chamber. The substrate size was $2.5\text{cm} \times 4.0\text{cm}$ in width and 0.1cm in thickness.

Prior to the evaporation process, the system was initially evacuated to $4 \times 10^{-3}\text{Pa}$. The substrate was ion - cleaned for 10min in an argon glow discharge at 1.1Pa with a bias voltage of -1.0kV to remove an residual oxides from the surface. After the ion - cleaning, the system was pumped down to $4 \times 10^{-3}\text{Pa}$ again. The argon gas pressure and the bias voltage were adjusted to $4.6 \times 10^{-2}\text{Pa}$ and -0.5kV , respectively. Once the conditions became stable, the evaporation was started. The subatrate temperature was measured by a thermocouple attached to the back of substrate. The substrate temperature during deposition ranged from 130 to 170°C without any controll.

2.2 Characterization techniques

After ion - plating, samples for coating structure evaluation were immersed in liquid nitrogen and quickly fractured while the film remained brittle. Scanning electron microscopy (SEM) was used to observe the surface morphology and the cross - sectional structure of the coatings. The compositions of these films were determined by electron probe micro - analysis(EPMA) and their crystal structures were identified by the X - ray diffraction method with $\text{CuK}\alpha$ radiation. Anodic polarization curves by potentiodynamic measurements were carried out from the rest potential at $2\text{mV}/\text{sec}$ in deaerated 3% NaCl solutions at room temperature. The exposure area of each specimen was $0.25\text{cm}^2(0.5\text{cm} \times 0.5\text{cm})$ area without polishing. Before the anodic polariza-

tion measurements, each specimen was equilibrated with the 3% NaCl solution for 30min. Potentials were measured versus SCE(saturated calomel electrode).

3. Results

3.1. Structure and morphology of films

Fig. 2 shows the X - ray diffraction pattern of Al - Mg alloy films prepared at this experiment. The result of sturctural analysis by X - ray diffraction pattern is summarized in Table 1. This table shows that the crystal structure of the films changes with the composition ratio of aluminum and magnesium. Although the Al peaks in X - ray diffraction pattern could not be found in case of the 88.0 , 68.0 at.% Al films,

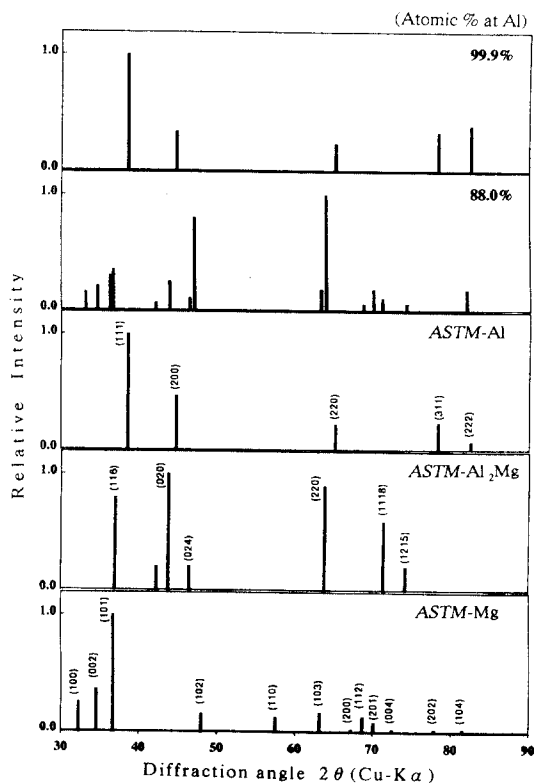


Fig. 2a X - ray Diffraction Patterns of Al - Mg Alloy Films Deposited at Different Compositions.

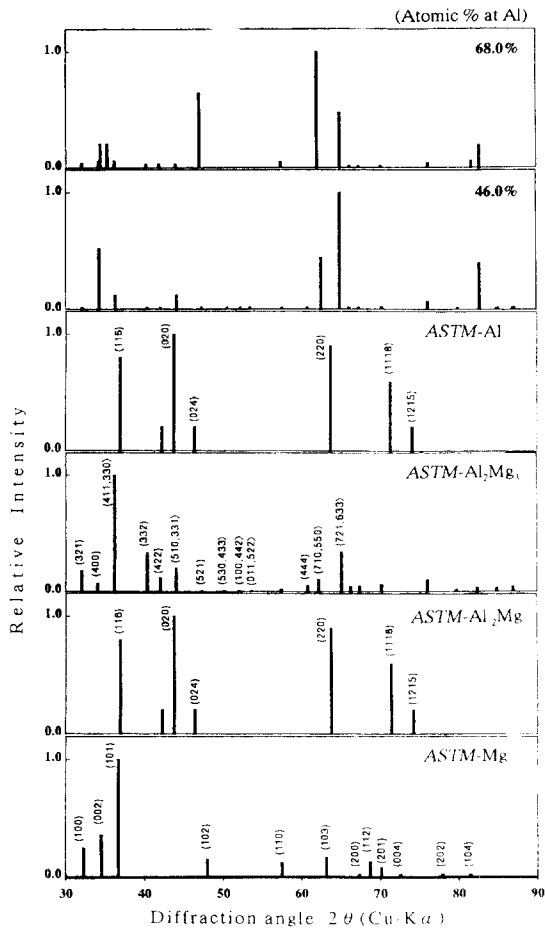


Fig. 2b X-ray Diffraction Patterns of Al-Mg Alloy Films Deposited at Different Compositions.

the deposit may have existed in amorphous or other form with intermetallic compounds (Al_2Mg or Al_2Mg_3) and magnesium. Mg X-ray peaks of the 23.0 and 3.5 at.% Al films constantly shift compared to the peak of ASTM (American Society for Testing and Materials) card (powder method). This fact are due to the formation of a solid solution containing aluminum in magnesium forcibly. Moreover, the measured interplanar spacings increased with aluminum content, indicating that the films were c. p. h. solid solutions and that they were in a state of tension. From the equilibrium

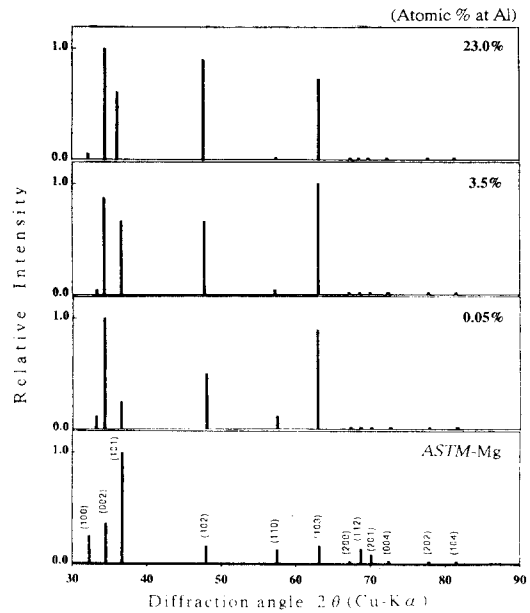


Fig. 2c X-ray Diffraction Patterns of Al-Mg Alloy Films Deposited at Different Compositions.

Table 1 Structural Analysis of X-ray Diffraction Patterns vs Al-Mg Film Compositions.

| Composition (at.% at Al) | Structural analysis of X-ray diffraction patterns | | | |
|--------------------------|---|----------|------------|-----|
| | Al | Al_2Mg | Al_2Mg_3 | Mg |
| 99.9% | ⊙ | | | |
| 88.0% | ☆ | ⊙ | | ⊙ |
| 68.0% | ☆ | | ⊙ | ⊙ |
| 46.0% | | | ⊙ | ⊙ |
| 23.0% | | | | ⊙ § |
| 3.5% | | | | ⊙ § |
| 0.05% | | | | ⊙ |

⊙ : Indicated as peaks.
 ☆ : Existed in amorphous-like.
 § : Existed in a solid solution

phase diagram of the Al-Mg system⁶⁾, the solid solution of aluminum in magnesium is limited to 11.8 at.%Al. Our film with 3.5 at.%Al were clearly c.p.h. magnesium solid solutions in accordance with the equilibrium phase diagram. However, 23.0 at.% Al film seemed to be super-saturated solid solution of aluminum in magnesium. Similar results have been occasionally reported⁷⁾, although permissible plasma assisted deposition process of non-equilib-

rium phase. Although not obserable in X - ray diffraction, domains of intermetallic compounds such as Al_2Mg_3 may exist in other form with magnesium solid solution. Therefore either the amount of the intermetallic compounds(e. g., Al_2Mg_3) was too low or the size of the intermetallic compounds domains was too small to be observed by X - ray diffraction. Small grain size and defects are known to broaden the diffraction peaks and to make it difficult to observe low intensity reflections⁸⁾. Thus the ion - plated 3.5 at.% Al - Mg film might be solid solution of aluminum in magnesium, whereas, 23.0 at.%Al film might contain a dispersion of an intermetallic compound(e. g., Al_2Mg_3) in c. p. h. magnesium solid solution. This ion - plated Al - Mg film is quite different from standard equilibrium diagram of the alloy system.

Fig. 1 shows the SEM photographs of the top surface and the cross sectional morphology of ion - plated Al - Mg films. Both the top surface

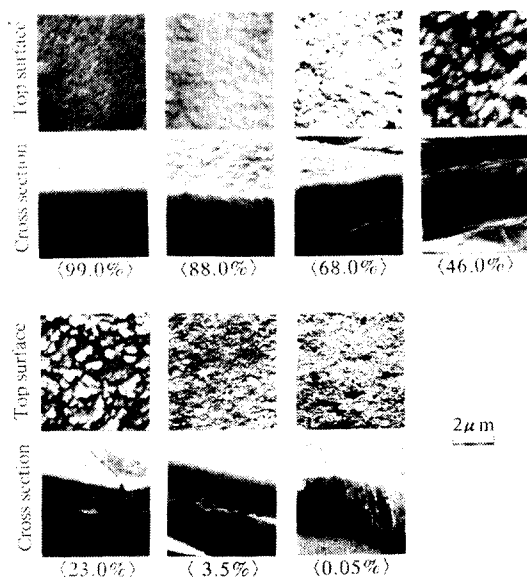


Fig. 3 SEM Photographs of Ion - plated Al - Mg Films as a Function of Composition Ratio of Al and Mg (at.% at Aluminum).

and cross section of these films look smooth without crack or pinhole, and vary with composition. As shown in Fig. 3, the structure of 0.05 at.% Al film is completely columnar. However, both the 3.5 and 23.0at.%Al films with the solid solution are completely noncolumnar structure with little voids in the film. Here, the structural grains of the 3.5% Al film are more densely packed than the ones of the 23.0 at.%Al film. The 46.0, 68.0 and 88.0 at.%Al films which coexist with intermetallic compounds with aluminum or magnesium have shown an amorphous - like or microcrystalline structure.

3.2. Corrosion test

The result from corrosion test of the ion - plated Al - Mg films as a function of aluminum content is shown in Fig.4 It shows the anodic potentiodynamic polarization curves for the ion - plated $(100 - x)Al - xMg$ films(where $x = 0.05, 3.5, 23.0, 46.0, 68.0, 88.0,$ and 99.0 at.% at Al), measured in 3% NaCl solution. The pure Al and Mg films on cold - rolled steel substrate were also measured the anodic potentiodynamic polarization curves to compare with the ion - plated alloy films. All the ion - plated

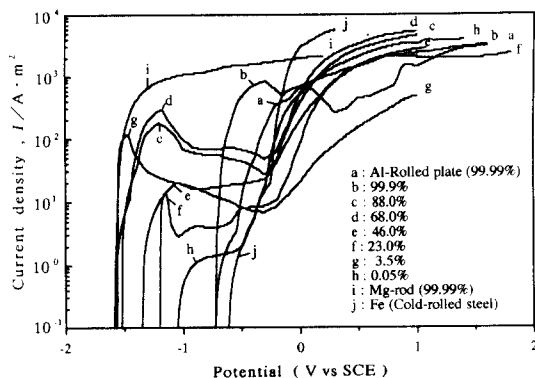


Fig. 4 Changes of Anodic Polarization Curves for Ion - plated Al - Mg Films as a Function of Composition Ratio of Al and Mg (at.% at Aluminum).

films, with the exception of 99.0 at.% Al film, appeared to show classical 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). The ion-plated Al-Mg films nearly tend to show low corrosion current (passive current density) to compare with the substrate and evaporation metals. The polarization behavior of these films changes with the composition ratio of aluminum and magnesium. Fig. 5 shows the anodic polarization curve (for reference purpose only) identifying potentials and current density for the measured parameters. Fig. 6 and 7 present the dependence of these several parameters by the variation of the polarization curves with the composition ratio of aluminum and magnesium observed in Fig. 4. These parameters are: rest potential E_r , passive potential (the potential at the start 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), passive current I_p , and critical current for passivation I_c . From Fig. 6, it can be

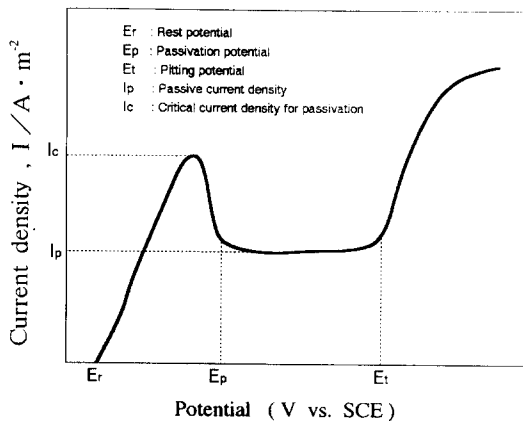


Fig. 5 Anodic Polarization Curve (for Reference Purpose only) Identifying Potentials and Current Densities.

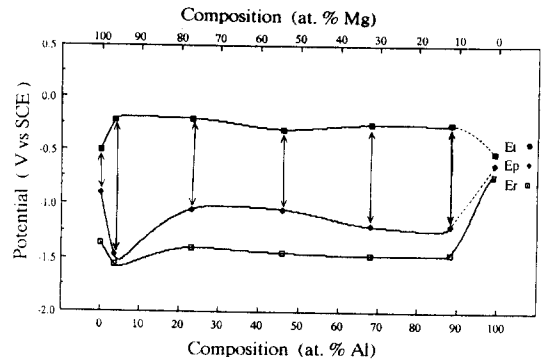


Fig. 6 Tendency of Rest(E_r), Passive(E_p), Pitting Potential(E_t) and Passive Regions($E_t - E_p$) for Ion-plated Al-Mg Films as a Function of Composition Ratio of Al and Mg.

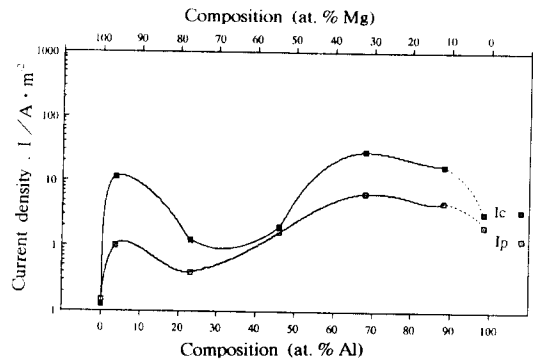


Fig. 7 Tendency of Critical Current for Passivation(I_c) and Passive Current(I_p) for Ion-plated Al-Mg Films as a Function of Composition Ratio of Al and Mg.

seen that the rest potential(E_r) tend to shift in the positive direction by the addition of aluminum. The maximum length for an passive region($E_t - E_p$) was obtained with the 3.5 at.% Al film. From Fig. 7, it can be seen that variation of passive current(I_p) exhibits relatively low value(1mA/cm²) at the 0.05, 3.5 and 23.0 at.% Al films.

4. Discussion

We have ion-plated Al-Mg films in the

hope of finding a passive metal that provide superior corrosion resistance for substrate. As can be observed from above table and figures, the structure and the morphology of ion - plated alloy films are nearly not to the same as the ones predicted by the equilibrium phase diagram and the structure zone model of Thornton (being used to provide an overview of the relationship between the microstructure of the coating deposited by PVD and the most prominent deposition conditions) respectively⁹⁻¹². Because of dissimilar vapour pressure of aluminum and magnesium which were used as evaporation metal in this study, magnesium of the higher vapour pressure at a faster deposition rate than aluminum of the lower vapour pressure resulting in a deposit of different composition than the original alloy. Also it is probably due to the distribution of the relatively changing different metal ion - energy in plasma, according to composition ratio of aluminum and magnesium. Through this plasma ion - plating, we can be obtained not only the presence of various Al - Mg alloy films but also the ones of films with forced solid solution such as 3.5 at.%Al. Such as those produced by ion - plating would be expected to offer corrosion resistance superior to that of conventionally processed alloys.

From Fig. 4, most of the ion - plated Al - Mg films tend to provide a good corrosion resistance. In alloy films containing aluminum and magnesium, the magnesium which is more active metal than aluminum, is expected to corrode preferentially prior to the corrosion of aluminum. But, the results of the anodic polarization curves shown in Fig. 4 reveals that the by - products of magnesium may contribute to the formation of passive layer. Among the ion - plated films, the 3.5 at.%Al film posses significantly lower corrosion rate with a pas-

sive region of 1.2V length and higher pitting potential than other films. Especially, the film had the highest resistance against pitting corrosion. The film with an effective forced solid solution of the alloying elements such as the 3.5 at.%Al film may produce a smaller and denser grain structure that can improve the formation of homogeneous passive layer in corrosion environment. Futhermore, the role of magnesium seem to facilitate the formation of passive layer and may contribute to the extensive passive region, although the effects of structure and composition on this passive layer were not fully understand. Therefore, it may also contribute to the sacrificial galvanic cell to protect substrate from corrosion environment such as penetrating blemishes. That is, the exceptional protection effect for substrate of the Al - Mg films fabricated in this study is attributed not only to the corrosion resistance of individual elements but also to the microstructure resulting from ion - plating onto SPCC steel substrate and to the role of magnesium in the formation of the passive layer. More sufficient datas will be needed for desirable evaluation of the relationship between the effects of magnesium concentration and film structure on corrosion resistance.

5. Conclusion

The results of this investigation are summarized as follows :

(1) The exceptional 3.5 at.%Al film with forced solid solution, fabricated in this study, is attributed not only to the microcrystallization of morphology but also to the improvement of corrosion resistance resulting from homogeneous passive film.

(2) The structure and properties of alloy film with an effective solid solution of the alloying

elements may be improved greatly by effective use of the plasma – ion plating technique.

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