

Mg₂Si Coating Technology on Magnesium Alloys to Improve Corrosion and Wear Resistance*

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Magnesium silicide (Mg₂Si) bulky materials are useful to improve the surface function of light metals such as magnesium or aluminum alloys, due to its superior corrosion resistance to the conventional stainless steel, and its high mechanical properties.

In this study, Mg₂Si thin film coated on AZ31 magnesium alloys by using a high frequency sputtering method, was examined. A neutral salt spray test to evaluate the corrosion resistance indicated that AZ31 substrate with Mg₂Si coating was hardly damaged after 240h. On the other hand, the non-treated one was corroded in only 1h. Concerning wear resistance under the oil lubricant test, a friction coefficient of the AZ31 alloy with Mg₂Si film is remarkably stable in employing S35C steel as a counter specimen. No sticking between both specimens was detected. In the combination of AZ31 alloy disc and S35C pin specimens, seizure and sticking phenomena occurred and the μ value suddenly increased. Accordingly, Mg₂Si coating technology is a suitable surface modification process to improve corrosion and wear resistance of magnesium alloys.

(Received October 25, 2005; Accepted December 16, 2005; Published April 15, 2006)

Keywords: magnesium silicide, thin coating film, sputtering, wear and corrosion resistance

1. Introduction

Magnesium (Mg) is the lightest metal of industrial materials (1.74 g/cm³). This metal is about 75% lighter compared with steel widely used as structural components. Recently magnesium alloys are used in various fields due to their high specific strength, high thermal conductivity, electromagnetic wave shielding effect, etc. Therefore, they are applied to the portable devices, in particular instrument housings for mobile computers, mobile phones, mini dhisc players and PDAs (Personal digital assistant).

When employing conventional magnesium alloys as industrial components, the improvement of corrosion resistance should be considered. This is because magnesium is easily and instantly corroded in underwater and in a wet environment. For example, the progress of bimetallic corrosion is dramatically quick by contact with magnesium and other metals. Therefore, the corrosion phenomena of magnesium alloys occurs remarkably fast.

Many efforts have been payed to the research of a corrosion protection of magnesium alloys. Song *et al.*¹⁾ discussed about the contact corrosion which occurred between magnesium alloy and other metals. It is also mentioned that magnesium alloys tend to cause contact corrosion. Yamamoto *et al.*²⁾ studied with interest to the corrosion phenomenon due to the electric potential difference caused by the impurity element of magnesium alloys. They developed the super-high-purity magnesium coating on the magnesium-alloys surface by using the vacuum deposition method. It showed the remarkable improvement of corrosion resistance. Takaya *et al.*³⁾ studied in detail the manganese system coating considered to have corrosion resistance equal to a chromium system coating.

Another problem in employing magnesium alloys as

components is that they have poor wear resistance due to their softness. Seizure phenomenon also easily occurs when magnesium alloys are contacted on other materials. Blau *et al.*⁴⁾ discussed on the tribological properties in using AZ91 alloys produced by various manufacturing methods, in particular the effect of their microstructures and mechanical properties on wear resistance. Both corrosion and wear resistance strongly depend on the surface characteristics of magnesium alloys. That is, the suitable surface treatment to improve them should be employed when applying magnesium alloys to industrial components.

In the previous works, the physical properties of magnesium compound Mg₂X (IVB group element, X = Si, Ge, Sn, Pb) were investigated. They were synthesized by the reaction of Mg and X element in solid-state *via* the powder metallurgy process. It was clarified that the intermetallic compounds Mg₂X have a high melting point, high hardnesses, and high Young's modulus. In particular, Mg₂Si shows a low density (1.99 g/cm³) and high micro-hardness of HV0.01 350–450, which is more than 5 times than conventional magnesium alloys (HV0.01 70–90). It is also reported that the magnesium composite alloys dispersed with fine Mg₂Si particles reveal high tensile strength and high hardness.^{5,6)} Moreover, Mg₂Si has superior corrosion resistance⁷⁾ to the conventional stainless steels in the neutral salt spray test specified in JIS Z 2371.⁸⁾

In this study, Mg₂Si thin film was deposited on the conventional magnesium alloys to improve the corrosion and wear resistance by sputtering process. In particular, the effect of microstructures of Mg–Si thin films on their properties was investigated in detail.

2. Procedure

2.1 Preparation of Mg₂Si sintering target material

In this study, the Mg₂Si sintering target material used in sputtering was made by the Spark-Plasma-Sintering (SPS)

*This Paper was Originally Published in Japanese in J. Jpn. Soc. Powder Metallurgy 52 (2005) 276–281.

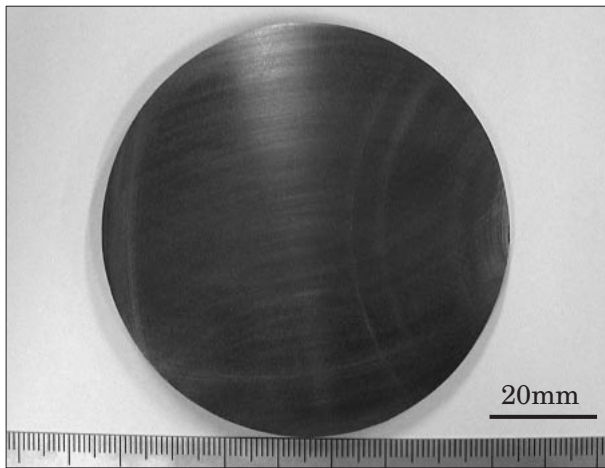


Fig. 1 Photograph of Mg₂Si target material consolidated by Spark Plasma Sintering.

method by using Mg–33.33 mol%Si mixed powder as a raw material. The pure Mg powder by Kojundo Chemical Laboratory Co., Ltd. (mean particle size; 127 μm, purity; 99.9%) and Si powder made from Toyo Metal Co., Ltd. (mean particle size; 21 μm, purity; 99.9%) were prepared as a starting material. Both powder was mixed at a rate of 2:1 by the mole ratio. The Mg₂Si sintered compact was made *via* the solid state reaction of a Mg–Si powder by applying the sintering temperature of 620°C and 5 MPa pressure for 10 min to the mixed Mg–Si powder in the carbon die in the about 5 Pa vacuum by using SPS system (Sumitomo Coal Mining Co., Ltd. SPS-1030 type). The sintered compact is shown in Fig. 1.

The Mg₂Si sintered compact was crushed and sieved to the diameter of grain of maximum size less than 125 μm. It was sintered using the SPS system (800°C, 15 MPa, 15 min), to from Mg₂Si target material with a diameter of 3 inches of 99.8% or more of relative density.

2.2 Preparation of thin film

Mg₂Si thin film was deposited by RF sputtering system, which is used in the mass production process in industries. Argon (99.999% or more) was used for sputtering gas. The AZ31 substrate is kept at about 60–90°C by watercooling. Structure analysis by X-ray diffraction, a Vickers hardness test, SEM observation, EDS analyses, etc., on the films were carried out.

2.3 Wet wear test by pin-on-disk method

A pin-on-disk type wear test machine (Takachiho Seiki, IIIT-2000 Type) was employed to evaluate the tribological properties under the lubricant. The hardness of the S35C steel pin specimen was adjusted to HRC40 (C scale). The top of pin type specimen has a spherical shape. Magnesium alloy AZ31 was used for the disc specimen. In the wear test, the pin specimen was fixed, and the disk one was rotated (Fig. 2). The pressing load of 100N and spinning-speed of 480 rpm (slide speed 1 m/s) were selected. Wear distance was set to 10,000 m. The test was carried out in the lubricant, using Toyota motor oil (10W-30). Changes in the friction coefficient and the damaged sliding surface were investigated.

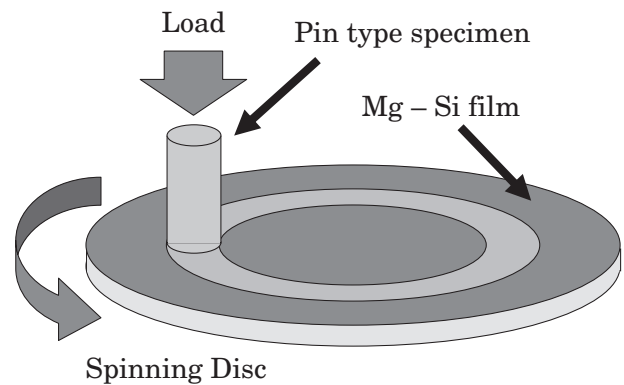


Fig. 2 Schematic illustration of Pin-on-disk type wear test.

Table 1 Conditions of neutral salt spray test (JIS Z 2371).

Item	Setting
Conc. of NaCl solution	50 g/L
pH	6.5
Compressed-air pressure	0.098 ± 0.01 MPa
Spray volume	1.5 mL/80 cm ² /h
Air saturation machine temp.	47 ± 2°C
Brackish water tank temp.	35 ± 2°C
Test tub temp.	35 ± 2°C

2.4 Corrosion resistance test by neutral salt spray test

Test conditions of neutral salt spray test method specified in JIS Z 2371 are shown in Table 1. Surface of specimens were washed by acetone just before the test. Corrosion resistance test was carried out in 24, 96, and 240 h. The Rating Number method, which quantitatively evaluate the corrosion area, was applied in this study. The relation between a rating number (*RN*) and the rate of corrosion area (*A*) is as a formula (1).

$$RN = 3(2 - \log 10A) \quad (1)$$

It becomes the following formula (2) when the Rating Number is between 9.3–9.8.

$$RN = 10 - A/0.1 \quad (2)$$

3. Results and Discussion

3.1 Preparation of sputtered thin film

The Mg–Si thin film was prepared on glass and copper substrate by using RF-sputtering system. Glass substrate was used for the thickness measurement and X-ray diffraction (XRD) of the film. Copper (Cu) substrate was for the observation on the film surface by scanning electron microscope (SEM), and component analysis by energy dispersive X-ray spectroscopy (EDS). The relation between thickness and sputtering time was shown in Fig. 3, when using various gas pressure conditions. The thickness of thin film was proportional to the sputtering time. On the other hand, the film forming velocity became slower when sputtering gas pressure became higher. This phenomenon is due to the increase of the density of vaporized magnesium in sputtering.

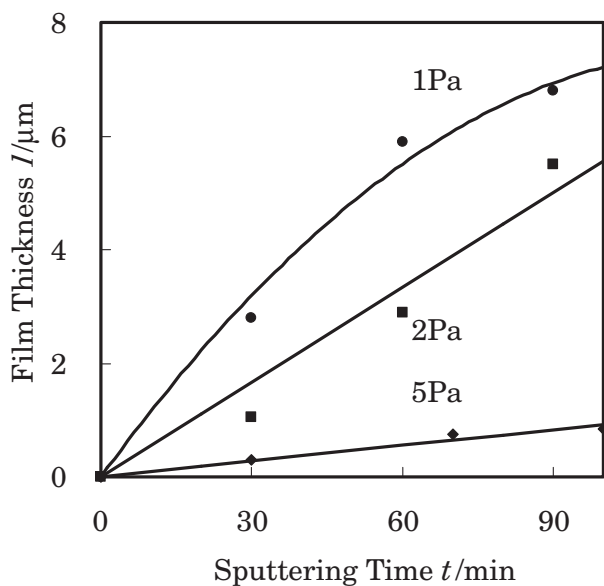


Fig. 3 Relation between film thickness and sputtering time under various sputtering gas pressures.

That is, when the vapor density was elevated, the collision probability of excited atoms and sputtering gas (Ar) are increased. Therefore, Mg and Si can not reach the substrate because they contact Ar atoms during sputtering.

The diffraction pattern of Mg–Si film which carried out the film forming process with a thickness of about 2 μm formed in a different sputtering gas pressure is shown in Fig. 4. The formation of the crystal structure of Mg–Si thin film is dependent on a sputtering gas pressure. For example, the clear diffraction peak of Mg_2Si is detected in employing the gas pressure of 1 and 2 Pa. On the other hand, when sputtering with a gas pressure of 4 Pa or more, the broad diffraction pattern is observed. It means the sputtered film has an amorphous structure. The SEM photographs of the gas pressure of 1 and 5 Pa Mg–Si-thin-film surface are shown in Fig. 5. The remarkable difference was not found in roughness of the thin film surface. The Mg/Si ratio in both films measured by EDS analyses in using ZAF method was about 2:1 (at%). However, the crystallized Mg_2Si thin film presented the color of dark blue, and the amorphous one showed silver black. The cross-sectional photograph of each thin film by SEM was shown in Fig. 6. In the case of 1 Pa gas pressure, it shows a columnar structure along a deposition direction. The crystal was growing in a film forming process clearly. On the other hand, in the case of 5 Pa gas pressure, it has uniform amorphous structure, not crystal one. Serikawa *et al.*⁹⁾ discussed the similar phenomenon of the crystallization mechanism in the Mg–Si coating by the ion beam spatter. By this report, the accumulation of the compressive stress inside a thin film was considered as the driving force of crystallization between Mg and Si atoms. It is thought that the crystal is generating by the same mechanism in the case of RF spatter used in this study. That is, when the gas pressure is low, the collision probability of excited atoms to the substrate increases. The internal stress is also accumulated for the reasons of Mg atom dissolving into supersaturation between deposited Si atoms. It was induced by this compression stress

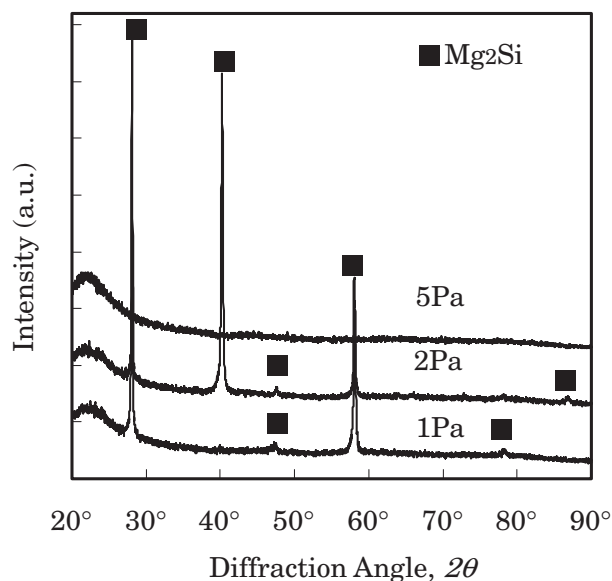


Fig. 4 X-ray diffraction patterns of thin films deposited under various sputtering gas pressures.

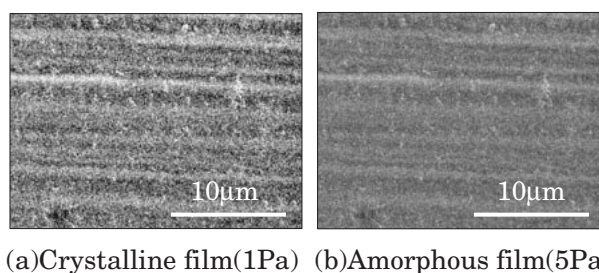


Fig. 5 Surface SEM images of crystalline Mg_2Si film (a) and amorphous Mg–Si film (b).

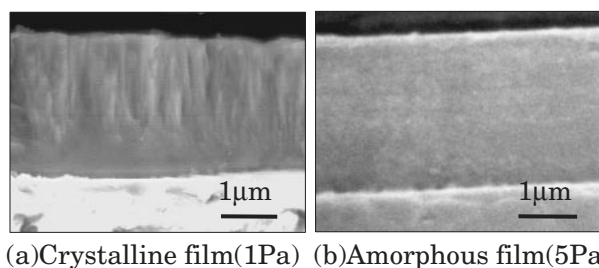


Fig. 6 Cross-sectional SEM image of Mg–Si thin films deposited under various sputtering gas pressures.

and the crystallization reaction occurred between Mg–Si atoms. On the other hand, when the gas pressure is high, the collision probability to the substrate becomes low. The relaxation of internal stress occurs according to the re-evaporation phenomenon of Mg which dissolved into supersaturation from the thin film surface. Therefore, it is thought that the coating of amorphous structure was formed. From these results, the crystal structure of Mg–Si thin film is controlled by adjusting the gas pressure, and the crystalline and amorphous Mg–Si thin film can be formed.

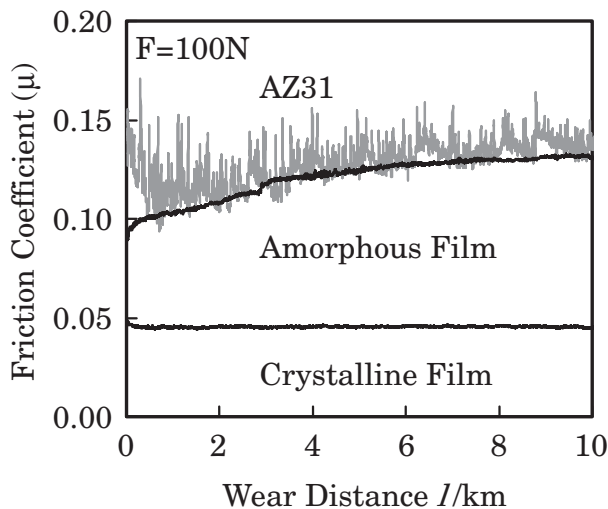


Fig. 7 Changes in friction coefficient under applied load of 100N in employing AZ31 alloy disk specimen with Mg–Si thin film or no coating.

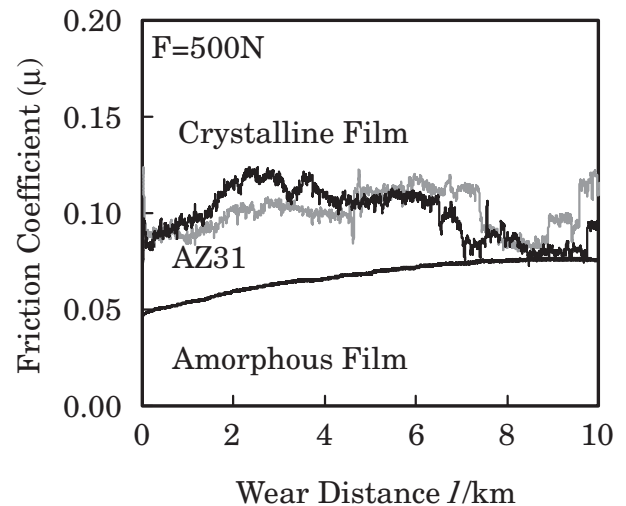


Fig. 8 Changes in friction coefficient under applied load of 500N in employing AZ31 alloy disk specimen with Mg–Si thin film or no coating.

3.2 Wear resistance of Mg–Si sputtered film

AZ31 alloy disk specimens with coated by crystalline or amorphous thin films, and without coating were used. Figure 7 shows a change in the friction coefficient when applying a lower load of 100N. In AZ31 raw material, it rapidly increased after about 100m sliding, and changed unstably. This phenomenon is due to that the abrasive wear by a hard pin specimen occurred on the disc surface from the observation of the sliding surface after a test. At this time, it is thought that friction coefficient (μ value) was changed by friction sliding with the stick-slip state in a test surface. On the other hand, when the Mg–Si coating which had crystalline or amorphous structure was formed on the disc surface, the friction coefficient was stabilized during the test. A crack and damage were not observed by the Mg–Si coating after 10,000m sliding. That is, this coating has a superior endurance. The friction test under higher load of 500N is shown in Fig. 8. In the crystallized Mg–Si coating, the friction coefficient increased because of the damage on the coating film in the initial stage. In the amorphous coating, however, it was stable during the last. In order to investigate the different results between them, the hardness of each thin film was measured by using the microhardness tester Akashi HM-100. The hardness of the crystallization film and an amorphous coating was about HV0.01 400 and about HV0.01 500, respectively. This result suggests that the higher hardness of the amorphous film causes a superior wear resistance to the crystallized one in applying a higher load of 500N. Generally, a crystallized film is considered to be harder than an amorphous one. In this result, however, it is in an opposite tendency as mentioned above. The crystallized thin film has the aggregate of a columnar crystal vertical to a substrate, as shown in Fig. 6, and not a single crystal. Therefore, the hardness is lower compared to the amorphous film.

3.3 Corrosion resistance of Mg–Si sputtered film

The neutral salt spray test (SST) specified to JIS Z 2371 was carried out on the specimens coated crystalline or amorphous Mg–Si film, and non-treated one. The appearance

of each specimen after SST was shown in Fig. 9. The white part in photograph means corrosion compounds. AZ31 non-treated specimen was remarkably corroded in 24h, and all surface was corroded in 96h. On the other hand, the coated surface with thin film was discolored. There was no difference in corrosion resistance by the crystal structure of thin films. In the surface (g) and (k), a specific types of corrosion was observed. This type of corrosion is called filiform corrosion.¹⁰⁾ Filiform corrosion is a kind of atmospheric corrosion. In this corrosion, the coated film is raised by the corrosion product, and proceeding in the shape of filament. Generally, this corrosion does not occur with pure magnesium. It is started under a coated film in many cases. It is considered that filiform corrosion was caused by the existence of Mg–Si thin films this time. In the case of this specimen, a pitting corrosion occurs at first, and the filiform corrosion was grew from pitting corrosion as the starting point. However, in general, the pitting corrosion can be inhibited by increasing the film thickness. This result was quantitatively evaluated by the Rating Number method, As shown in Fig. 10, the corrosion resistance of Mg–Si coating film has a superior corrosion resistance.

4. Conclusions

Mg–Si thin film coating process to the magnesium alloys was established by RF sputtering method in using Mg₂Si target made by SPS. The effect of the sputtering conditions on the crystal structure control of Mg–Si films and their wear resistance and corrosion resistance were investigated. The following results were obtained.

- (1) The solid state synthesis of Mg₂Si bulky materials by using SPS system was applied to prepare the sputtering target with no defect and crack.
- (2) The crystal structure of Mg–Si thin film is controlled by the gas pressure adjustment in sputtering, and a crystalline and amorphous thin film can be formed selectively.
- (3) In wear test, the durability of magnesium alloy AZ31

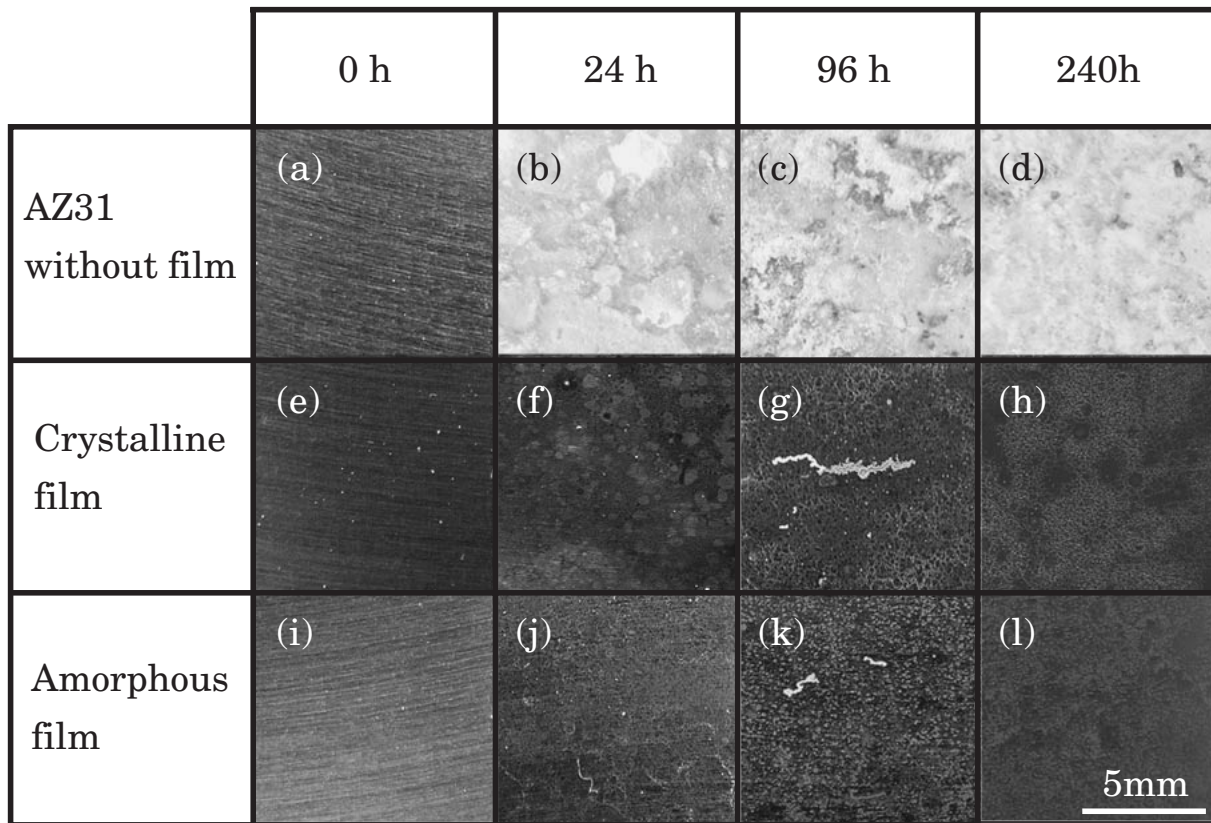


Fig. 9 Neutral salt spray test results; (a)–(d) AZ31 non-treated specimens, (e)–(h) those coated by crystalline Mg₂Si thin film and (i)–(l) those with amorphous Mg–Si thin film.

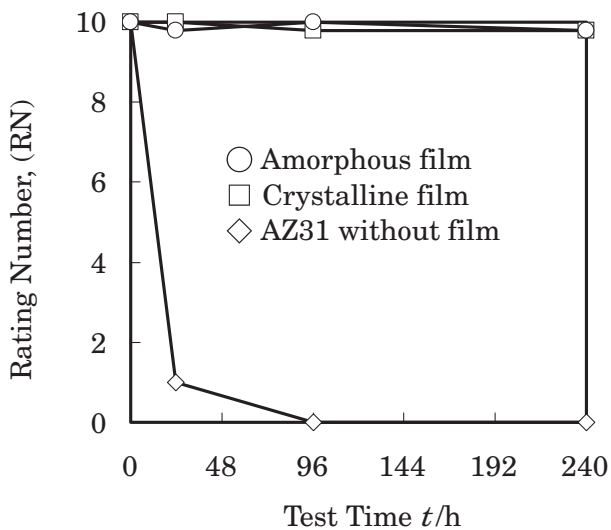


Fig. 10 Evaluation results of corrosion phenomena of each specimen by Rating Number method.

was improved by Mg–Si thin film coating. In particular, the friction coefficient of amorphous film was stable, and showed a higher endurance when high load conditions.

(4) As a result of neutral salt spray test, the corrosion

resistance of magnesium alloys were improved dramatically by Mg–Si thin film coating.

Acknowledgements

This work is financially supported by MEXT (Ministry of Education, Culture, Sports, Science and Technology). Many thanks of much effort to Dr. Yoshisada Michiura and Mr. Kimio Nakamura, Kurimoto Co. in the preparation of specimens and discussions.

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