Corrosion Protection of Mg-Li Alloy by Plasma Thermal Spraying of Aluminum

Masato Tsujikawa,* Shin-ichiro Adachi, Yukiko Abe, Sachio Oki, Kazuhiro Nakata, Masaichiro Kamita

Magnesium alloys containing lithium over 10 mass-% have good cold workability and high specific strength. However, the poor corrosion resistance of these alloys hinders their application. In this experiment, the effect on corrosion resistance of plasma thermal sprayed pure aluminum coating to Mg-Li alloy plates was investigated. Low-pressure plasma sprayings of pure aluminum were carried out after grit blasting. The corrosion resistance, which is evaluated by salt water spraying test, of plasma sprayed plates was improved. Furthermore, slightly cold-rolled surface after thermal spraying showed excellent corrosion resistance, due to closing of micro channels from surface to substrate.

Introduction

Studies of higher specific-strength alloys are performed widely. Magnesium alloys are the lightest of all practical metallic alloys for structures. They possess excellent mechanical properties including high specific strength and high specific rigidity. They are remarkable as materials for future generation aircraft. Notwithstanding, the specific strength of practical magnesium alloys has not attained that of high-strength aluminum alloy. It is important for expansion of magnesium usage that the specific strength of magnesium alloy exceeds the value of high-strength aluminum alloys.

M. Tsujikawa
Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho, Sakai 599-8531, Japan
Fax: (+81) 72 254 9317; E-mail: masato@mtr.osakafu-u.c.jp
S.-i. Adachi
Technical Research Institute of Osaka Prefecture, Ayumino, Izumi-shi 594-1147, Japan
Y. Abe
Graduate Student Osaka Prefecture University, Osaka, Japan
Present address: TOSTEM Co. Ltd., Nakazato 3000, Noda, Chiba, Japan
S. Oki
Kinki University, Kowakae, Higashi-osaka-shi 577-8502, Japan
K. Nakata
Joining and Welding Research Institute Osaka University, Mihogaoka, Ibaraki-shi 567-0047, Japan
M. Kamita
Yamani Co. Ltd., Uchi-awaji machi, Chuoh-ku, Osaka 540-0038, Japan

Two main ways exist to increase the specific strength of magnesium alloys. One way is the pursuit of high strength through addition of hardening elements such as yttrium and zinc, which usually increases the alloy's density. The other way is addition of an element lighter than magnesium, e.g. lithium (Li). First, the addition of Li decreases the density of alloy. Secondly, additional Li changes the crystal structure from close-packed hexagonal (CPH) to body centered cubic (BCC), Figure 1(a), thereby allowing cold-working. Using cold-working, work hardening, which is impossible for ordinary CPH magnesium alloys, is expected.

An alloy LA14 includes 14 mass-% Li and 1 mass-% Al is an Mg-Li alloy. With density 1.326 $g \cdot cm^{-3}$. The ultimate tensile strength of the cold-worked LA141 is 194–294 MPa, depending on the reduction ratio. Its specific strength is 175–223 $MPa \cdot (g \cdot cm^{-3})^{-1}$. These values are greater than the value of 125 of heat-treated aluminum alloy A6061-T6, and 150 of conventional magnesium alloy extruded AZ31 (Mg–3 mass-% Zn–1 mass-% Al alloy), and heat-treated aluminum alloy A6061. The values are almost comparable to those of 235 $MPa \cdot (g \cdot cm^{-3})^{-1}$ of heat-treated strong aluminum alloy A7075-T6. The alloy should soon be put to practical use.[1]

Corrosion resistance is one of the main subjects for all magnesium alloys. There is no protective dense oxide film

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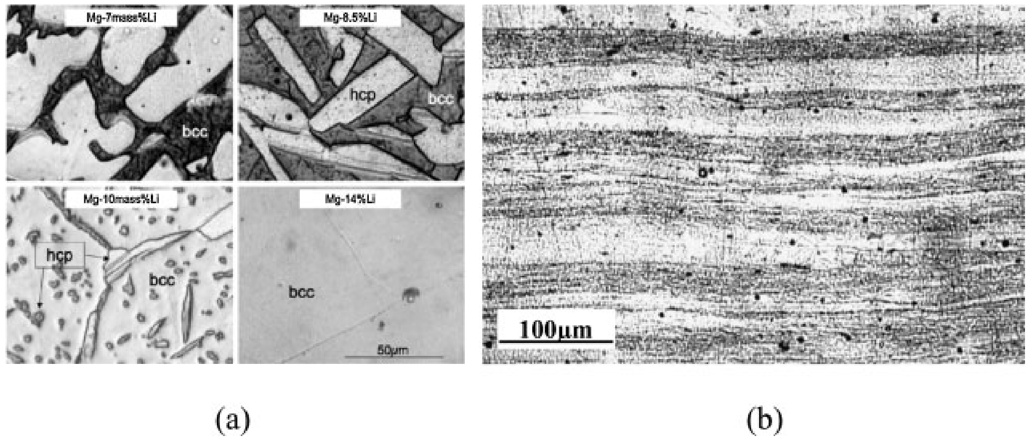

Figure 1. Microstructure of Mg-Li alloy (a) and cold-rolled Mg-14 wt.-% Li alloy (b).

on the surface of magnesium alloys, which is formed on the surface of aluminum alloy. There is also no effective sacrifice anode element for magnesium like zinc for steel surface. Therefore, no hairline crack is allowed for a protective surface of magnesium alloy.

A diamond-like carbon (DLC) coating can contribute to excellent tribological and corrosion protecting properties of materials. In most cases, a metallic film (e.g., Cr or Si) is used as an interlayer between DLC film and substrate to improve the adhesion of the coating. The adhesion of DLC on magnesium alloy is improved by substituting the interlayer with some kind of pretreatment.[2,3] In the same way, low temperature high voltage anodic oxidation forms effective[4,5] but hard and brittle protection layer on the surface. A brittle surface layer often gives rise to hairline cracks in the case of impact loading. Cracks reaching the substrate from local batteries in the moist environment.

In contrast, thin ductile metallic surfaces with corrosion resistance protect the substrate in the case of impact loading. This is because they have enough toughness to absorb such impact energy. If the aluminum thin layer can be formed on the magnesium alloy with adhesion, it will be an excellent protective surface for magnesium alloy.

In this paper, the corrosion resistance of plasma thermal spraying of aluminum on Mg-Li alloy was investigated.

Experimental Part

Preparation of Mg-Li Alloy

It is difficult to melt the alloy in air or in evacuated chambers because they have high reactivity and high vapor pressure. Because of their low density of 1.326 $g \cdot cm^{-3}$, flux melting is also prohibited. It causes oxide inclusion. Therefore, it is necessary to melt and cast under pressurized inert gas atmosphere. In this study, the alloys were melted at 953 K in a chamber of 0.15 MPa argon gas atmosphere. The degasification was done by argon gas bubbling for 1 h. After still standing for 15 min, the melts poured in the chamber into block molds under pressurized argon gas atmosphere. Obtained ingots were of 250 mm long, 250 mm and wide 50 mm thick with weights around 5 kg. These ingots were certified as defect-free by X-ray radiography. The chemical composition of an ingot is shown in Table 1. The ingots were homogenized at 673 K for 24 h.

The ingots were cut into a slab of $45 \times 300 \times 250$ mm^3. The slab was cold-rolled to 2 mm thickness with the rolling mill with 380 mm roll diameter in 12 reduction passes. The rolling reduction was 95.6%. The plate's microstructure is shown in Figure 1(b).

The strength of LA141 alloy is varied with the degree of cold working. The maximum value of the ultimate tensile strength of this alloy is 294 MPa, as mentioned above at the condition of 98% in reduction ratio at cold rolling. The 2 mm thick plates prepared for this investigation have 205 MPa in ultimate tensile strength.

Low Pressure Plasma Thermal Spraying of Aluminum on the Mg-Li Alloy

These Mg-Li alloy plates were ground using #120 emery paper and grit blasted using white #24 alumina particles as a pretreatment for thermal spraying. Then, the plates were plasma thermal sprayed with 99.7% pure aluminum particles of 50 μm diameter. Thermal spraying was carried out in the chamber filled with argon gas of 6.6 kPa. The apparatus used in this investigation has an output of 26 kW (TA-7050, Aero Plasma Co. Ltd.). The thermal spray distance was constant at 0.35 m.

Table 1. Chemical composition of Mg-Li alloy (wt.-%).

Li	Al	Mn	Fe	Si	Cu	Ca	Na	Mg
13.7	1.32	0.120	0.0001	0.013	0.003	0.000	0.001	Balance

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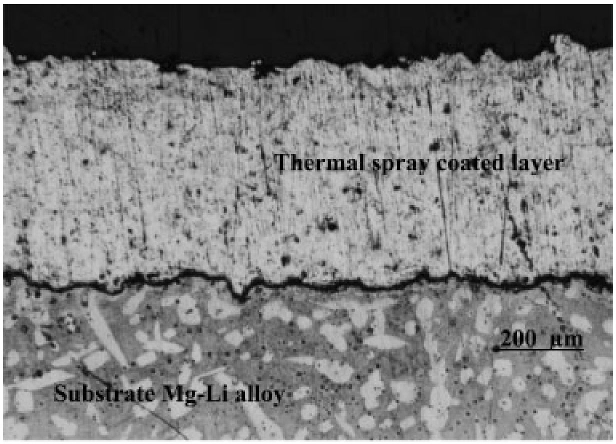


Figure 2. Example of cross-section view of plasma thermal sprayed surface.

Cold Rolling After Plasma Thermal Spraying

A portion of thermal sprayed plate was slightly cold-rolled. The reduction ratio was about 3%. The effect of rolling on corrosion protection was evaluated.

Salt Spray Test

Corrosion resistance was evaluated by the salt spray test. A thermal sprayed sample was cut to 30×50 mm^2, then the substrate side and end faces were polymer-coated for isolation. The test used a spray of 50 g $\cdot$ l^{-1} NaCl solution with pH 7.0, spray intensity of 125 ml $\cdot$ m^{-2} $\cdot$ h^{-1} and test temperature of 35 °C. A mechanically polished sample and a chemically polished sample were also tested simultaneously as reference. The duration of the salt spray test was 24 h.

Results and Discussion

Figure 2 shows the surface layer of thermal sprayed as-cast Mg-8 wt.-% Li alloy. Although there are many small black pores, the sprayed layer seems to be dense and the pores do not link each other. The thickness of the sprayed layer was about 500 µm and the hardness of deposit layer was 44HV0.1. The hardness of this as-cast Mg-8Li alloy was 56HV0.1. Also cold-rolled 3 mm thick plates were 55HV0.1.[1] The deposit layer is softer than the substrates.

The surfaces of specimen plates during the corrosion test were monitored. Unsprayed specimens started blistering before 4 h. No marked difference exists between the emery ground surface and the chemically polished surface. the thermally sprayed specimen started to stain obviously by 4 h. In contrast, a thermal sprayed and cold-rolled specimen surface was clear until the end of the testing. These features are listed in Table 2.

Figure 3 shows the specimen surfaces after a 24 h test and rinsed by deionized water in a dried state. Unsprayed surfaces, Figure 3(a) and 3(b), show vigorous corrosion. As thermal sprayed specimen, Figure 3(c) shows uneven stain. The thermal sprayed and cold-rolled surface, Figure 3(d), showed no evidence of blistering or considerable stain. It was found that the cold rolling of a thermal sprayed surface is effective for corrosion protection of Mg-Li alloy.

The reason why the thermally sprayed specimen easily stained is the presence of a microchannel between the specimen surface and substrate. Figure 4 shows the surfaces of a sprayed specimen (a), and a sprayed and rolled specimen (b), observed by SEM. As shown in Figure 4(a), the thermal sprayed surface consists of small particles. A microchannel must exist between them. The effect of rolling on the corrosion protection is due to the closing of the microchannels.

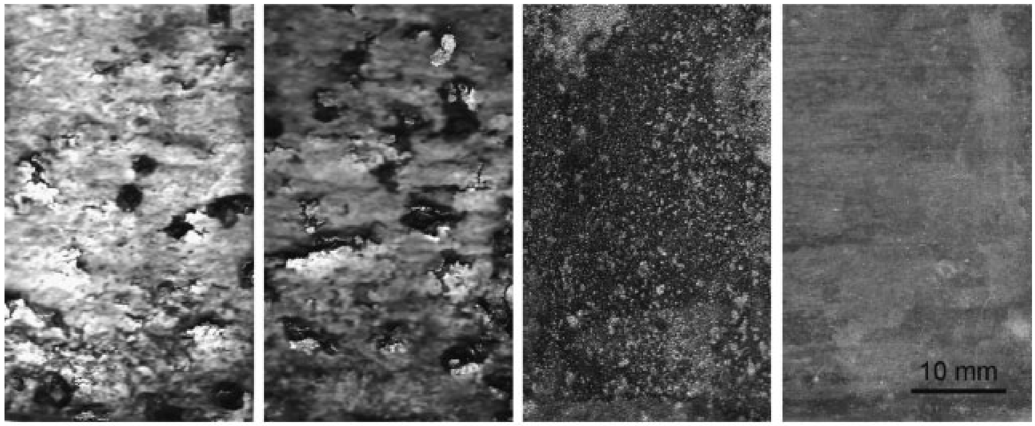
The Mg-Li alloys with lithium content above 11 wt.-% have a BCC crystal structure. It allows these magnesium alloys to be cold worked without cracking. Therefore, this slight cold working process of plasma thermal sprayed pure aluminum layer is ideal for the Mg-Li alloys. Furthermore, such type of clad plates will be the raw material for the cold press process.

Conclusion

A Mg-Li alloy is a lightweight structural material, but has poor corrosion resistance. A protective pure aluminum surface layer was build up by plasma thermal spraying. It was not enough, however, to avoid degradation of the

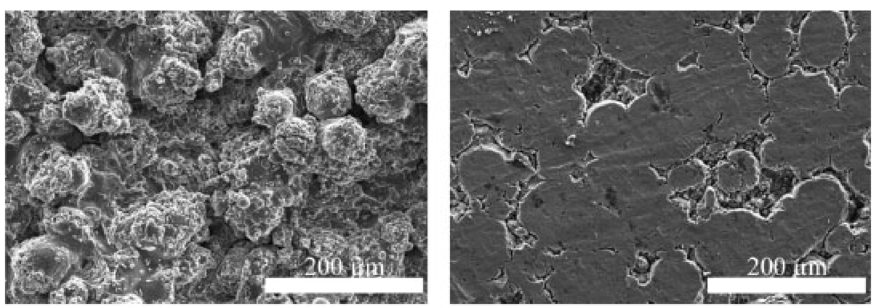
Table 2. Examination result of salt-spray test.

Sample	4 h	8 h	24 h
(a) Unsprayed #1000 emery-paper ground	Blistering	Blistering	Blistering
(b) Unsprayed chemically polished	Blistering	Blistering	Blistering
(c) Thermal sprayed	Stain	Stain	Stain
(d) Thermal sprayed and cold-rolled	Clear	Clear	Clear



(a) Un-sprayed (Emery-ground) (b) Un-sprayed (Chemically polished) (c) Sprayed (d) Sprayed (+cold rolled)

Figure 3. Surfaces after corrosion test (test duration: 24 h).



(a) As thermal sprayed (b) rolled surface

Figure 4. Features of surface: (a) as sprayed, (b) cold-rolled 3%.

material. Considerable stain was formed on the sprayed surface. Such a stain was eliminated by the cold rolling of the sprayed plate slightly. The effect of slight rolling follows the closing microchannels that exist in the sprayed layer between the surface and the substrate. This process is suitable for the cold workable magnesium alloy with BCC crystal structure.

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[1] M. Tsujikawa, Y. Abe, S. W. Chung, S. Oki, K. Higashi, M. Kamita, I. Hiraki, *Mater. Trans.* **2006**, *47,* 1077.
[2] N. Yamauchi, N. Ueda, A. Okamoto, T. Sone, M. Tsujikawa, S. Oki, *Surf. Coat. Technol.* **2007**, DOI: 10.1016/ j.surfcoat. 2006.07.080, available online 14 August 2006.
[3] N. Yamauchi, K. Demizu, N. Ueda, T. Sone, M. Tsujikawa, Y. Hirose, *Thin Solid Films* **2005**, *506–507,* 378.
[4] Y. Zhang, C. Yan, F. Wang, W. Li, *Corros. Sci.* **2005**, *47,* 2816.
[5] Y. Zhang, C. Yan, *Surf. Coat. Technol.* **2007**, DOI:10.1016/j.surfcoat.2006.04.015, available online 8 June 2006.