PLASMA THERMAL DEPOSITION OF ALUMINUM ON Mg-Li WORK-HARDENED ALLOY

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ABSTRACT
Magnesium-lithium alloys containing 14 mass% lithium are putatively the lightest metallic structural material that has good cold workability and high specific strength, which are attributable to the cubic crystalline structure of the lithium solid solution, which differs from the closely packed hexagonal crystalline structure of a magnesium solid solution. Unfortunately, the alloy’s poor corrosion resistance hinders its application. Alloy surface modifications have been tried, but vigorous corrosion has made aqueous treatments difficult. Moreover, dry processes are restricted thermally at temperatures less than about 150°C because of lithium’s low melting point and low re-crystallization temperatures of cold-worked alloy material.

Plasma-sprayed pure aluminum coatings on cold-rolled Mg-Li alloy plates were investigated. A Mg-14mass% Li-1mass% Al alloy ingot was cast in an argon atmosphere. After homogeneous heat treatment, the ingot was rolled to a 3-mm-thick plate under a reduction ratio of 95%. After grit blasting, plasma spraying of pure aluminum was performed under several conditions. The coated layer thickness was 50–300 µm. The substrates' temperature increases during spraying were small. Corrosion resistance of plasma sprayed plates, as evaluated by salt-water spraying tests, was improved through formation of a dense aluminum-coating layer.
INTRODUCTION

Mg-Li alloy

Lightweight materials are effective for reducing the mass of transportation-related devices. Magnesium alloys are the lightest of all practical metallic alloys for structures. They offer excellent mechanical properties including high specific strength and high specific rigidity. They are remarkable as materials of future-generation aircraft; studies of higher specific-strength alloys have been performed widely. Notwithstanding, high specific-strength, practically useful magnesium alloys have not attained the capabilities of high-strength aluminum alloys. It is important for expansion of magnesium usage that the specific strength of magnesium alloy be greater than the value of high-strength aluminum alloys.

Two means exist to increase the specific strength of magnesium alloys. One is the pursuit of high strength through addition of hardening elements such as yttrium and zinc, which usually increase the alloy’s density. The other means is addition of lithium, which is a lighter element than magnesium. First, the addition of Li decreases the resultant alloy’s density. Secondly, additional Li changes the crystal structure from CPH to BCC, thereby allowing cold-working. Using cold-working, work hardening, which is impossible for ordinary HCP magnesium alloys, is expected.

An alloy called LA141 includes 14 mass% Li and 1 mass% Al is an Mg-Li alloy. Its density is 1.326 g/cm³. 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/(g/cm³). 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-3mass%Zn-1mass%Al alloy, and heat treated aluminum alloy A6061. The values are almost comparable to those of 235 MPa/(g/cm³) of heat-treated strong aluminum alloy A7075-T6. The alloy should soon be put to practical use ¹.

Surface protection for Magnesium alloys

Corrosion resistance is an important subject for all magnesium alloys. No protective dense oxide film exists on the surface of magnesium alloys, such as that formed on an aluminum alloy surface. Furthermore, no effective sacrifice anode element exists for magnesium that would act similarly to zinc for steel surfaces. For those reasons, no hairline crack would be acceptable in a protective surface of magnesium alloys.

A diamond-like carbon (DLC) coating can contribute to excellent tribological and corrosion-protecting properties of materials. In most cases, a metallic film such as one of Cr or Si is used as an interlayer between DLC film and substrate to improve the coating’s adhesion. The adhesion of DLC film on magnesium alloy is improved through the use of some kind of pretreatment instead of an interlayer ²,³. Similarly, low-temperature high-voltage anodic oxidation forms a layer effectively ⁴,⁵ but it is hard and brittle on the surface. A brittle surface layer often engenders hairline cracks during impact loading. Cracks to the substrate form the local batteries in a moist environment.

In contrast, thin ductile metallic surfaces with corrosion resistance protect the substrate during impact loading because they have sufficient toughness to absorb such impact energy. Excellent protective surfaces for magnesium alloy can be formed if there were an adhesive thin aluminum layer on the magnesium alloy.
This study investigated the corrosion resistance of plasma thermal spraying of aluminum on Mg-Li alloy.

EXPERIMENTAL PROCEDURES
Preparation of Mg-Li alloy

It is very difficult to melt Mg-Li alloys in air or in an evacuated chamber because they have high reactivity and high vapor pressure. Because of their low density of 1.326 g/cm³, flux melting is also out of the question because it causes oxide inclusion. For these reasons, it is necessary to melt and cast these alloys in a pressurized inert gas atmosphere. In this study, the alloys were melted at 953 K in a chamber with 0.15 MPa argon gas. Degassing was done for one hour using argon gas bubbling. After standing for 15 min, the melts were poured in the chamber into block moulds under a pressurized argon gas atmosphere. The resultant ingots were 250 mm high and 250 mm wide, with 50 mm thickness and weight of around 5 kg. These ingots were certified as defect free by x-ray radiography. The ingots were homogenized at 673 K for 24 h.

The ingots were cut into 45 mm × 300 mm × 250 mm slabs. Each slab was cold rolled to 2-mm thickness using a rolling mill with 380 mm roll diameter in 12 reduction passes. The rolling reduction was 95.6%. The plate's microstructure is shown in Fig. 1.

The LA141 alloy strength varies according to 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.

![Microstructure of cold-rolled Mg-14mass%Li alloy.](image)

Plasma thermal spraying of aluminum onto 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 thermally sprayed with 99.7% pure aluminum particles of 50 μm diameter. 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 0.15 m.

Cold-rolling

A fraction of the thermally sprayed plate was slightly cold-rolled. The reduction ratio was 3%. The effect of rolling on corrosion protection was evaluated.

Salt-spray test

Corrosion resistance was evaluated using the salt spray test. A thermally sprayed sample was cut to 30 × 50 mm², then the substrate side and end faces were polymer-coated for isolation. The test used the spray of 50 g/l NaCl solution with 7.0 pH, the spray intensity was 125 ml/m²/h and the test temperature was 35°C. A mechanically polished sample and a chemically polished sample were also tested simultaneously as references.

The duration of salt spray testing was 24 h. Surface conditions were checked after 4 h and 8 h during the test.

![Figure 2. Exemplary cross section of a plasma thermally sprayed surface layer.](image)

RESULTS AND DISCUSSION

Figure 2 shows the surface layer of thermally sprayed as-cast Mg-8mass%Li alloy. The sprayed layers were dense and the pores were not mutually linked. The sprayed layer thickness
was about 500 μm and the deposit-layer hardness was 44HV0.1. The hardness of this as-cast Mg-8Li alloy is 56HV0.1; cold-rolled 3-mm-thick plates were 55HV0.1. The deposit layer is softer than the substrate.

![Image of test results](image)

Figure 3. Salt-spray test results Mg-14mass%Li alloy with various surface conditions.

The surfaces of specimen plates during testing are shown in Fig. 3. Untreated specimens (a) and (b) 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 markedly by 4 h. In contrast, the thermally sprayed, then cold-rolled specimen surface was clear until the end of testing.

Figure 4 shows specimen surfaces after 24-h testing and rinsing using deionized water in comparison to the dried state. The unsprayed surfaces depicted in Figs. 4(a) and 4(b) show vigorous corrosion. The thermally sprayed specimen portrayed in Fig. 4(c) show uneven staining. The thermally sprayed and cold-rolled surface showed no evidence of blistering or considerable staining. Results indicate that cold-rolling of the thermally sprayed surface is effective for corrosion protection of Mg-Li alloy.

The thermally sprayed specimen is easily stained because of microchannels between the specimen surface and substrate. Figure 5 shows surfaces of the as-sprayed specimen (a) and the sprayed, then rolled specimen (b). Figure 5(a) shows that the thermally sprayed surface includes small particles. A microchannel must exist between them. The effect of rolling on corrosion protection arises from closing of the microchannels.
The Mg-Li alloys with lithium contents of greater than 11 mass% have a BCC crystal structure. It allows these magnesium alloys to be cold-worked without cracking. Therefore, this slight cold-working process of plasma thermally sprayed pure aluminum layer is ideal for Mg-Li alloys. Furthermore, such clad plates will be a raw material for cold-press processing.

**CONCLUSION**

The Mg-Li alloy structural material is lightweight but has poor corrosion resistance. A protective pure aluminum surface layer was built up using plasma thermal spraying. Nevertheless, it was insufficient to prevent material degradation. Considerable staining occurred on the sprayed surface. Such staining was eliminated slightly by cold rolling of the sprayed plate. The effect of slight rolling follows the closing of microchannels that exist in the sprayed layer.
between the surface and substrate. This process is suitable for a cold-workable magnesium alloy with a BCC crystal structure.

REFERENCES


