Coating on Magnesium Alloy with Super Duralumin by Hot Extrusion and Evaluation of Its Surface Properties^{*1}

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The poor corrosion resistance of Mg alloys, which is well known as one of the lightest structural metal materials, limits a wide use of these alloys. In order to dramatically increase not only the corrosion resistance but also the surface hardness of Mg alloys (AZ80), coating with A2024 Al alloy by hot extrusion has been attempted in this study. The coating was successfully realized by hot extrusion of a Mg alloy (AZ80) billet together with an Al alloy plate placed between the billet and the extrusion die. The A2024 Al alloy-coated Mg alloy exhibited an excellent corrosion resistance and no weight loss was observed after immersion in a 5 mass% HCl aqueous solution for 10 min while a weight loss of about 1500 g·m⁻² was observed in case of AZ80 Mg alloy without coating under the same condition. The surface hardness of the coated alloy was increased to about 85 HV by aging for 144 h at room temperature after solution treatment for 3 h at 673 K.

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1. Introduction

Mg alloys are characterized by the lowest density among all the practical structural metals, and also by their high strength-to-weight ratio. Moreover, they have good recyclability and electromagnetic shielding ability¹⁾. Recently, as a solution to the environmental problems such as air pollution and global warming, improvements in fuel efficiency by weight saving of automobiles and air crafts have been attempted. One of the weight-saving strategies is replacement of steel with light metals, i.e., Al alloys, and further weight-saving is expected by replacement with Mg alloys¹⁾. However, the application of Mg alloys is still limited because of the poor corrosion resistance of Mg alloys.

In order to improve the corrosion resistance, the present authors have recently developed a simple method to coat Mg alloys with Al by using a hot extrusion process, and demonstrated that the pure Al-coated AZ80 Mg alloy exhibits a good corrosion resistance even in an aqueous solution of HCl acid²⁾. In addition, the Al-coated Mg alloy exhibited better strength and elongation than the conventional Mg alloys because of the grain refinement due to recrystallization during and after the extrusion. Moreover, the Al-coated Mg alloy was successfully hot-rolled without breaking or debonding of the Al coating layer, and the rolled sheet exhibited a superplastic elongation of 710%. This superior formability of the Al-coated Mg alloy is very useful for the production of the parts having extremely complex shapes. However, in the previous study on the Al-coated Mg alloy²⁾, pure Al was used as a coating material, which is soft and easily scratched, and it involves a risk of impairment in corrosion resistance when the coating is severely damaged. For the solution of such a problem, it will be useful to employ a high strength Al alloy instead of pure Al. In the present study, the possibility of the use of a super duralumin A2024

Al alloy is investigated, which possesses superior hardness and tensile strength, and the corrosion resistance and surface hardness of the A2024-coated AZ80 Mg alloy are investigated.

2. Experimental

2.1 Composite fabrication

The hot extrusion process was used to coat the A2024 Al alloy on Mg alloy substrate. The detail of the process can be found in the authors' previous study²⁾. The AZ80A-T5 Mg alloy commercial rod (Mg-8.2Al-0.6Zn-0.4Mn (mass%)), having a diameter of 42 mm was used. The rod was cut into a cylinder of 30 mm in thickness, and it was press-formed to the substrate with a rectangular cross section of 40 mm × 40 mm. The substrate was solution-treated at 673 K for 5 hours and then aging-treated at 623 K for 1 hour. On the other hand, a commercial rectangular bar of A2024P-T351 Al alloy (Al-4.4Cu-1.4Mg-0.6Mn (mass%)), having a cross section of 40 mm × 42 mm, was used for the coating material. The Al alloy bar was cut into a plate with a thickness of 7 mm and cross section of 40 mm × 40 mm.

The metals were put in an extrusion container, preheated up to 603 K in an electric furnace, in the order of the Mg alloy substrate and the Al alloy plate. The die was put on the Al plate, and the hot indirect extrusion was conducted by pressing the rams on the die downward. At the first trial, coating failed, since the extruded bar was only partially covered with the Al alloy coating. It was considered that the failure was due to a very high deformation resistance of the A2024 alloy at the extrusion temperature compared with that of the AZ80 alloy. In order to soften the A2024 alloy, the A2024 alloy was annealed at 683 K for 3 hours prior to the extrusion to remove the fine precipitates. After the extrusion, the alloy can be hardened by additional solution and aging treatments. The detailed explanation of the solution and aging treatments will be given in the next section.

Figure 1 shows the shape and dimensions of the die used in the present study. A die angle of 20° was chosen based on

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Fig. 1 Schematic images of a die used in the present study: (a) overhead view and (b) cross-section of the die.

the results of the authors' previous study²⁾, where the effect of the die angle on the uniformity of the coating layer was investigated and it was found that the thickness was most uniform when the die angle was 20°. The AZ80 alloy substrate and the A2024 alloy plate were put in the container and heated up to 643 K in 30 minutes, and they were indirectly extruded at a ram speed of 8.0 mm/min and at an extrusion ratio of 87.5%. The microstructure of the extruded composite was observed by optical microscope and Scanning Electron Microscopy (SEM). The concentration profiles of the elements were obtained across the A2024/AZ80 interface by Field Emission-Electron Probe Micro Analyzer (FE-EPMA).

The change in thickness of the A2024 alloy coating layer along the extrusion direction was investigated. The extruded bar was cut at every 10 mm from the tip, and on each cross section, the thickness of the coating layer was measured along 12 different lines perpendicular to the extrusion direction and the average was recorded as a thickness of the coating layer on the cross section.

2.2 Heat treatment of the composite

The heat treatment in this study includes solution and aging treatments, and their conditions are summarized in Table 1. Although the solution treatment is usually performed at approximately 773 K for A2024 alloy^{3–5)}, 673 K was chosen in this study to avoid the melting of the intermetallic compounds formed at the Al/Mg interface such as Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$, the melting temperatures of which are 723 and 733 K, respectively⁶⁾. The composite was held at 673 K for 2 or 3 hours and then water-quenched. Following the solution treatment, an artificial or a natural aging was performed at 453 K for 0 to 10 hours and at room temperature for 0 to 144 hours, respectively. After the artificial aging treatment, the samples were furnace-cooled to room temperature.

2.3 Characteristics investigation

Corrosion resistance of the composite was evaluated by monitoring the weight loss during the immersion in a 5.0 mass% HCl aqueous solution at room temperature. In addition to the corrosion test of the as-extruded composite, the as-received AZ80 Mg alloy and A2024 Al alloy were also corrosion-tested for a comparison purpose. In order to focus on the same area in the corrosion test for all the samples, the surface of each sample was covered by epoxy-based adhesive, leaving a non-covered square window of 10 mm × 10 mm.

Table 1 Heat treatment conditions.

Solution treatment		Aging treatment	
Temp. (K)	Holding time (h)	Temp. (K)	Holding time (h)
673	2	no aging	
		Room temperature	24
			48
			72
			96
			120
			144
	3	Room temperature	2
			4
			6
			8
			10
			10
673	2	no aging	
		Room temperature	24
			48
			72
			96
			120
	3	Room temperature	144
			2
			4
			6
			8
			10

The surface hardness was measured by using a Vickers Hardness tester. The applied load and the holding time were set at 500 g and 30 seconds, respectively. The testing was performed at 24 different points in each sample, and the maximum and the minimum values and the second maximum and the second minimum were removed when the average value was calculated. The hardness of the A2024 alloy coating layer was measured after the extrusion and also after the heat treatment shown in Table 1, and the effects of the solution and aging treatments on the hardness were investigated. Moreover, the hardness of the AZ80 alloy substrate was also measured. The applied load and the holding time were 100 g and 30 seconds for the AZ80 alloy substrate.

3. Results and Discussion

3.1 Microstructure and the coating thickness

Figures 2 (a) and (b) illustrate the overview of the extruded bar and its cross-section, respectively. The extruded bar is soundly coated by A2024 Al alloy on the whole surface. In Fig. 2 (b), no debonding or cracking can be seen at the A2024/AZ80 interface. The enlargement of the interface is shown in Fig. 3 (a). Between the A2024 alloy and the AZ80 alloy, a granular phase with a diameter of about 0.5 μm , a plate-like phase with a thickness of about 3 μm and a saw-like phase with a thickness of about 1 μm are observed from the A2024 alloy side to the AZ80 alloy side. Although a void of about 0.3 μm in a diameter can be seen near the center of Fig. 3 (a), formation of the above-

mentioned phases indicates the occurrence of sufficient interdiffusion of Al and Mg across the bonding interface which results in a strong bonding between the A2024 and AZ80 alloys. In order to identify these phases, composition analysis was conducted by using the FE-EPMA on the A-A' line shown in Fig. 3 (a). The results are shown in Fig. 3 (b). Since the atomic composition of the above-mentioned three phases were detected as 65Al-5Cu-30Mg, 60Al-40Mg and 35Al-65Mg, those phases can be considered as Al_6CuMg_4 , Al_3Mg_2 , and $\text{Al}_{12}\text{Mg}_{17}$, respectively, based on the phase diagram shown in Fig. 4.

Figure 5 shows the thickness change of the coating layer with respect to the distance in the extrusion direction. At the initial stage of the extrusion, the Al alloy plate near the die hole did not undergo severe plastic deformation, and thus the coating is very thick near the tip of the extruded bar. After the distance of around 50 mm, the coating thickness was uniform at approximately 400 μm . The thickness of the coating layer was 200 to 300 μm when AZ80 alloy was similarly coated with the pure Al using the Al plate of 3 mm in the initial thickness in the present authors' previous study²⁾. The difference in coating thickness between the present and previous studies is considered to be due to the initial thickness of the coating material, since a sensitivity analysis has revealed that the initial thickness of the coating material strongly affects the coating thickness of the extruded clad bar⁸⁾. However, it is also considered that the difference in the coating thickness is affected by the difference in the deform-

ability of the coating material.

3.2 Corrosion resistance of the composite

Figure 6 illustrates the weight loss behavior during the corrosion test where the samples were immersed in a 5.0 mass% HCl aqueous solution. The results of AZ80 Mg alloy and A2024 Al alloy are also shown for comparison.

Fig. 4 Al-Cu-Mg ternary phase diagram at 298 K⁷⁾.

Fig. 2 (a) The overview of the extruded bar and (b) cross-sectional picture of the extruded bar.

Fig. 5 Thickness change of A2024 Al alloy coating layer with respect to the distance from tip of the extruded bar.

Fig. 3 (a) SEM image of Al/Mg interface after extrusion, and (b) EPMA results obtained from the line A-A' shown in (a).

The bare AZ80 alloy severely reacted with the HCl aqueous solution to form a lot of small bubbles from the beginning of the immersion. On the other hand, the A2024 alloy and the as-extruded composite did not react at all, and no weight loss was observed. Thus, the present composite exhibited a good corrosion resistance of the same level as the A2024 alloy. A slight weight gain is observed for the A2024 alloy and the as-extruded composite, the reason for which may be due to imperfect drying of the epoxy-based adhesive using for the masking of the samples. The same weight gain should have occurred in the AZ80 alloy sample, however, the weight gain was negligibly small compared with the significantly large weight loss.

3.3 Surface hardness of the composite

Due to the annealing before the extrusion, the hardness of the A2024 alloy plate significantly decreased from 120 with a standard deviation of 6.9 to 53 with a standard deviation of 1.8. After extrusion, the hardness of the A2024 alloy slightly increased to 60 with a standard deviation of 1.1. The extrusion led an increase in hardness of the A2024 alloy. The

Fig. 6 Weight loss behavior of the A2024 Al alloy, AZ80 Mg alloy and the as-extruded composite immersed in 5.0 mass% HCl aqueous solution at room temperature.

hardness of the AZ80 alloy also increased to a small extent by the extrusion, which was 60 and 64 with standard deviations of 2.5 and 2.2 before and after the extrusion, respectively.

The coating layer was softer than the substrate just after the extrusion, which is against with the present purpose, i.e., coating of Mg alloy with a hard Al alloy. In order to increase the hardness of the coating layer, a variety of heat treatments listed in Table 1 were performed. The effect of the heat treatment on the hardness was investigated by the Vickers hardness test, and the optimal condition of heat treatment was studied.

Figures 7 (a) and (b) illustrate the results of hardness test after solution treatment followed by the artificial aging at 453 K or natural aging at room temperature. The error bar on each plot indicates the standard deviation. In the solution-treated composite, before the aging treatment, the hardness of the A2024 alloy coating layer was 62 irrespective of the solution treatment time of 2 or 3 hours. Also, in those samples, remarkable difference in the standard deviation was not observed, and the standard deviations were 0.8 and 1.3, respectively. All the solution-treated samples before aging treatment (shown as symbol × and ○ in Fig. 7) show slight increase in hardness compared to the as-extruded sample (shown as symbol ◆ in Fig. 7).

Aging treatment significantly contributes to the increment in hardness of the A2024 alloy coating layer. The A2024 alloy coating layer, which was solution-treated at 673 K for 3 hours followed by the aging treatment at 453 K for 4 hours, shows the maximum hardness of 77 with a standard deviation of 1.2. After showing the maximum hardness, viz. more than 4 hours of aging time, the hardness gradually decreases. This decrement can be considered as a result of overaging, associated with a coarsening of hardening precipitates. On the other hand, the hardness of the A2024 alloy coating layer subjected to the natural aging treatment (Fig. 7 (b)) in-

Fig. 7 Vickers hardness test results obtained from composite after solution treatment and (a) artificial aging at 453 K and (b) natural aging at 298 K. The solution treatment was performed at 673 K.

creases as the aging time increases, and it remains constant after 72 hours. The maximum hardness of 85 was obtained from the sample solution-treated at 673 K for 3 hours followed by natural aging treatment for 144 hours. The standard deviation was 0.77. The hardness of the coating layer measured in 3 weeks after the solution treatment was 83 with a standard deviation of 0.87, which indicates that no significant change in hardness occurs after showing the maximum hardness. In any aging condition, the coating layer exhibited higher hardness than the Mg alloy substrate.

As for the A2024 alloy coating layer in both composites subjected to the artificial and the natural aging, the hardness was higher when the solution treatment time was longer. The increase in solution treatment time leads to the increase in concentration of the solute elements in the Al matrix phase closer to the solubility limit, and consequently, it leads to the increase in the amount of the precipitation after the aging treatment.

The hardness of the AZ80 alloy substrate in the composite solution-treated for 2 and 3 hours are also shown in Fig. 7 by symbols $\square$ and $\triangle$, respectively. The hardness of AZ80 alloy substrate was not changed significantly by the solution treatment at 673 K. Generally, heating of Mg alloys causes deterioration in mechanical properties. However, in the present study, since the hardness of the Mg alloy did not decrease after heating to the solution treatment temperature, it is considered that the aging treatment at an appropriate low temperature gives no deterioration in mechanical properties. Consequently, the improvement in surface hardness of the A2024 alloy coating layer was succeeded by using the aging condition shown above without any hardness deterioration of the AZ80 alloy substrate. However, it should be noted that the hardness of 120 in the as-received A2024 alloy was not achieved in the A2024 alloy coating layer in the composite. The reason for this is discussed below.

As mentioned in section 2.2, in the present study, the solution treatment temperature was set at 673 K, which is approximately 100 K lower than a commonly employed solution treatment temperature of 773 K. Although this low solution temperature was chosen to avoid melting of the intermetallic compound, it is known that this difference of 100 K in the solution treatment temperature is large enough to influence mechanical properties obtained by the subsequent aging treatment⁹⁾. This is why it was not possible to retrieve the hardness to the level of the as-received A2024 alloy.

By applying solution treatment for longer time than that in the present study, better solution of the alloying elements might be possible, and higher hardness could be obtained, although there may be a limit of hardening.

4. Conclusions

In order to improve the corrosion resistance and surface hardness of Mg alloys, coating on AZ80 Mg alloy with A2024 Al alloy, having superior corrosion resistance and high hardness, was attempted and the following conclusions were obtained.

- (1) A2024 alloy-coated AZ80 alloy was successfully fabricated by hot extrusion, and it exhibited a good corrosion resistance.
- (2) The hardness of the A2024 alloy coating layer increased and exceeded that of the AZ80 alloy substrate by applying the solution and aging treatments. A maximum hardness of 85 HV was achieved by a solution treatment at 673 K for 3 hours and the natural aging at room temperature for 144 hours.

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