World Academy of Science, Engineering and Technology
International Journal of Mechanical and Mechatronics Engineering
Vol:4, No:9, 2010

Microstructure and Corrosion Behavior of Laser Welded Magnesium Alloys with Silver Nanoparticles

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***Abstract*—**Magnesium alloys have gained increased attention in recent years in automotive, electronics, and medical industry. This because of magnesium alloys have better properties than aluminum alloys and steels in respects of their low density and high strength to weight ratio. However, the main problems of magnesium alloy welding are the crack formation and the appearance of porosity during the solidification. This paper proposes a unique technique to weld two thin sheets of AZ31B magnesium alloy using a paste containing Ag nanoparticles. The paste containing Ag nanoparticles of 5 nm in average diameter and an organic solvent was used to coat the surface of AZ31B thin sheet. The coated sheet was heated at 100 °C for 60 s to evaporate the solvent. The dried sheet was set as a lower AZ31B sheet on the jig, and then lap fillet welding was carried out by using a pulsed Nd:YAG laser in a closed box filled with argon gas.

The characteristics of the microstructure and the corrosion behavior of the joints were analyzed by opticalmicroscopy (OM), energy dispersive spectrometry (EDS), electron probe micro-analyzer (EPMA), scanning electron microscopy (SEM), and immersion corrosion test. The experimental results show that the wrought AZ31B magnesium alloy can be joined successfully using Ag nanoparticles. Ag nanoparticles insert promote grain refinement, narrower the HAZ width and wider bond width compared to weld without and insert. Corrosion rate of welded AZ31B with Ag nanoparticles reduced up to 44 % compared to base metal. The improvement of corrosion resistance of welded AZ31B with Ag nanoparticles due to finer grains and large grain boundaries area which consist of high Al content. β-phase $Mg_{17}Al_{12}$ could serve as effective barrier and suppressed further propagation of corrosion. Furthermore, Ag distribution in fusion zone provide much more finer grains and may stabilize the magnesium solid solution making it less soluble or less anodic in aqueous

***Keywords*—**Laser welding, magnesium alloys, nanoparticles, mechanical property

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I. Introduction

THE welding of thin sheets is usually more problematic than welding thick sheet metal. Such problems are usually related to the high heat input of conventional arc welding processes. This high heat input leads to various problems such as cutting, burn through, distortion, porosity, cracking, etc. Thus, the selection of an appropriate welding process, procedure and technique are important in order to prevent these problems. Compared with arc welding, laser welding and electron beam welding are excellent methods that offer many advantages, such as narrow welds and impressive penetration depths. However, laser beam welding is the best choice because it can be used at ambient pressures and temperatures. However, the laser welding of thin sheet metals can still be problematic. Issues include the loss of material due to evaporation and inadequate control of heat, which leads to cutting and melt-through issues [1-3]. There are plenty of reports on the welding of copper, stainless steel and aluminum alloys [1-3] in thin sheets of less than 1 mm thickness, but few studies have been published to date that focus on thin sheets of similar thickness in the case of magnesium alloys.

In order to improve weld quality, this research examines the use of a metal insert for lap fillet welding of thin AZ31B sheets. Thin silver foil has been successfully applied to resistance spot welding of Mg and Al alloy plates, in which Ag bonds better with the Mg alloy than with Al alloy [1]. It is difficult to use Ag foil in laser lap fillet welding of magnesium alloy sheets with a thickness of 0.3 mm; first, the melting point of the silver foil (1233K) is much higher than that of AZ31B (905 K), and second, it is not easy to set a thin foil between the sheets with a clearance less than 35 μm, which creates inconsistent contact between the sheets and foil [2]. Therefore, in this research, an attempt has been made to use Ag nanoparticles as an insert material. The microstructure and corrosion resistance of welded magnesium alloy by using Ag nanoparticles with 5 nm diameter in size is discussed in this paper.

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II. Experimental Methods

A. Experimental set-up

Ag nanoparticles paste was used as an insert material between the two magnesium sheets. Prior to welding, the AZ31B sheet was coated by the Ag nanoparticles paste using a spin-coating machine with a rotational speed 1,000 rpm for 30 s. Next, the coated sheet was heated on a hot plate at a temperature of 100°C for 60 s to dry the organic solvent. Finally, the coated sheet was set as the lower sheet on a jig.

A pulsed Nd:YAG laser with a wavelength of 1.06 μm, a beam spot diameter of 0.4 mm and a focal length of 100 mm was used for this experiment. Lap welding was carried out by overlapping the two sheets and then irradiating the edge side of the upper sheet with the laser beam. The distance between the clamps was 4 mm, and the edge of the upper sheet was equidistant from them. The specimen was fixed with the jig in a closed box located on a CNC X-Y table. The top surface of the box was a heat-resistant glass through which the laser beam was transmitted. Prior to welding, the box was filled with argon gas with a flow rate of 20 l/min to prevent oxidation; the argon flowed continuously during the course of welding.

B. Macro and microstructure observation

Cross-sectional samples for metallurgical examination were cut from the weld joint at four locations. The samples were mounted in polymer resin and etched in a solution composed of either 10 ml acetic acid diluted with 100 ml distilled water for macroscopic observation or a solution of 5 ml acetic acid + 5 g picric acid + 10 ml distilled water and 70 ml ethyl alcohol for microscopic observation. Macrostructure and microstructure were examined by using an optical microscope and scanning electron microscope (SEM), respectively. The bond width and penetration depth were measured at all four locations using image analysis software. The element compositions were analyzed by EDX.

C. Corrosion test

Immersion tests were carried out for 24, 72, 120 and 168 hours in 5 wt. % sodium chloride solution at 20 °C, with a pH 7.0. The test periods and condition were chosen based on many studies. The welded specimens were cut into 2 mm width and 20 mm length. The specimens were cleaned in acetone with ultrasonic cleaner machine. Then, specimens were immersed in 50 cm^3 of 5 % NaCl solution in a beaker. At the end of the immersion period, corrosion products were immersed in acetone and cleaned using ultra-vibration machine. The specimens were weighed on an analytical balance to an accuracy of ±0.1 mg. Corrosion rates are determined as in equation below:

$$\text{Corrosion rate, mm/y} = 87.6 \times \frac{W}{D \times A \times T} \quad (1)$$

where, W= weight loss (mg), A = area of sample (cm^2), D= metal density (g/cm^3) and T = time exposure of metal sample (hr).

For surface observation, specimens were mounted in polymer resin, and then were immersed in 5 % NaCl solution at 1, 3 and 5 days. Prior to observation, specimens were cleaned in acetone with ultrasonic cleaner machine.

III. Results and Discussions

A. Macro and microstructure

Microstructure of welded AZ31B without Ag nanoparticles shows three different areas as shown in Fig. 1. From Figs. 5-15 and 5-16, the use of the Ag nanoparticles increased the width of the fine-grain region. No regions similar to Region II in Fig. 1 when weld without Ag nanoparticles were observed. The reduced grain size was similar to the result of extruding Mg-Zn, where the addition of Ag promoted grain refinement compared with the as-extruded alloy [4]. In addition, the length of the columnar region was reduced compared to the weld without an insert. The large fine-grain area arises from the enhancement of the heat absorption with the use of Ag nanoparticles.

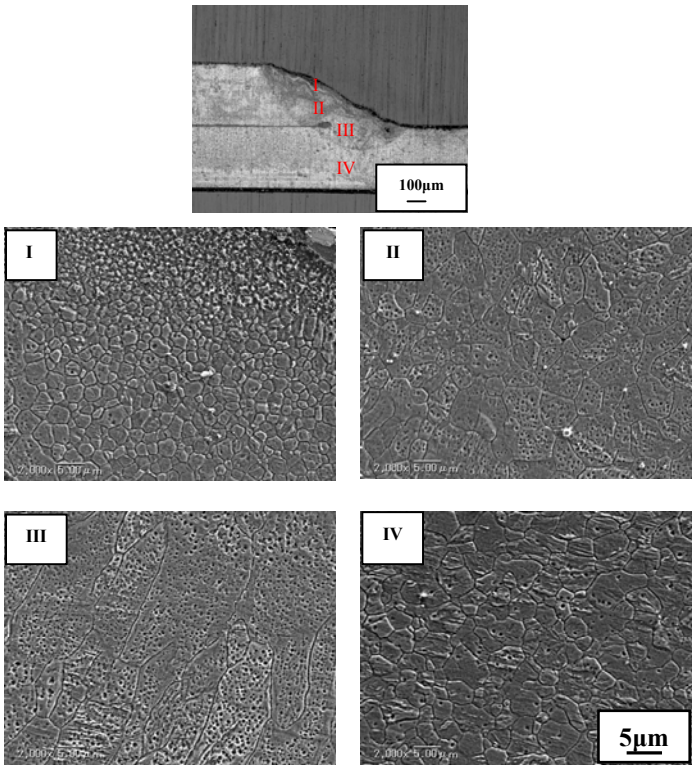


Fig.1 Microstructure of specimen without insert at different region

A lower scan speed or higher heat input caused a lower cooling rate during solidification, leading to larger grain sizes. As the scanning speed decreased, both the solidification rate of the weld and the growth rate of the grains decreased, which changed the solidification mode from equiaxed to columnar

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[5]. Thus, the increase in the scan speed also caused the smaller grain area.

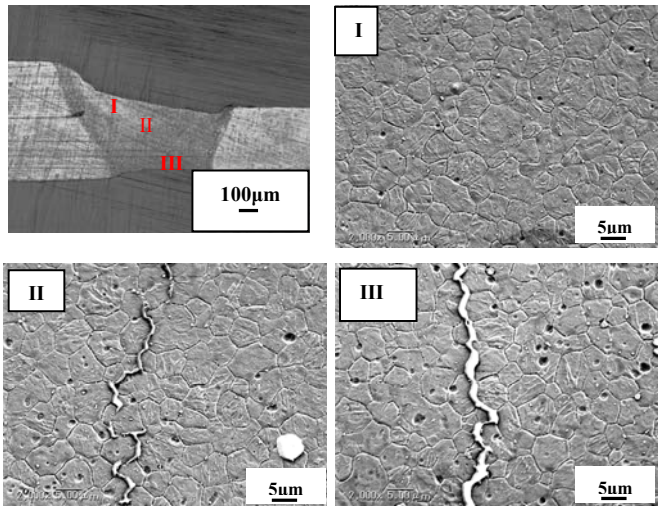


Fig.2 Microstructure of specimen with Ag nanoparticles at scan speed of 450 mm/min.

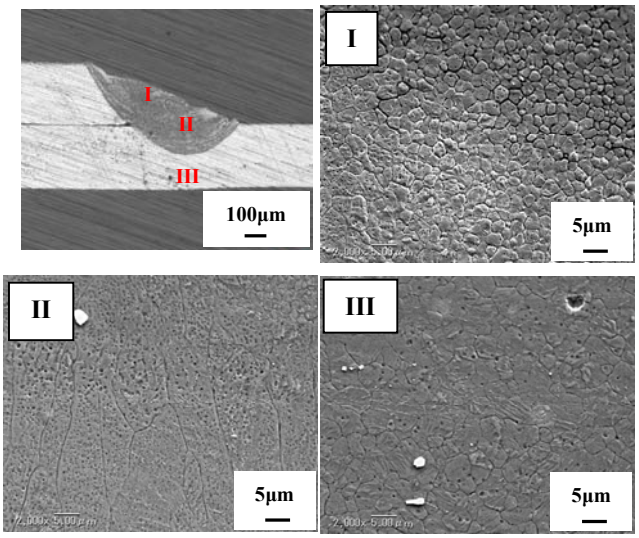


Fig.3 Microstructure of specimen with Ag nanoparticles at scan speed of 550 mm/min

To verify the presence of Ag, element analysis was carried out using EPMA and EDX at a selected location in the weld. As shown in Fig. 4, Ag was well distributed in the fine-grain area, but almost no Ag was detected in the large-grain area. Table 1 lists the result of the spot analysis at Points 1 and 2 in Fig. 4. Silver existed in the weld zone, though its amount was small. Silver circulated with other liquid metal elements in the weld pool during welding, so the Ag was uniformly distributed in the weld area and could be detected in high concentration at Point 1 in the fusion zone. At Point 2 in the heat affected zone HAZ, however because melting did not occur, the Ag concentration was almost zero. The reason for such a low concentration in the weld area was the low content of Ag nanoparticles in the paste (about 55 mass %) in the thin coating (around 3.0 μm) on the lower sheet. The distribution of Ag in the weld indicated high heat transfer from the upper to the lower sheet, thus providing enough heat to melt the upper sheet down to the lower sheet.

The thermal conductivities of silver, aluminum, pure magnesium, zinc and AZ31B are 432 W/mK, 248 W/mK, 161 W/mK, 122 W/mK and 96 W/mK [6], respectively. The heat conductivity of Ag is 2.7 times higher than that of pure magnesium and 4.5 times higher than that of AZ31B. The insertion of the high-heat-conductive Ag nanoparticles into the microscale gap between the two sheets improved heat transfer from the upper sheet to the lower one. Furthermore, Ag paste coating improved the surface roughness of the thin sheet from around $R_z = 4.7$ μm to $R_z = 0.9$ μm and decreased the clearance of the two sheets. These combined factors played a role in the increase of the bond width and penetration depth as well as the enlargement of the fine-grain area.

The mechanism of the refining grains is still unclear. However, the suggestion of mechanism can be based on the result of refining grain size in the casting process. In casting process, the grain size can be manipulated by altering various casting parameters, such as cooling rate, or by adding alloying elements and nucleants (a grain refiner) before or during the casting process. However, unlike aluminum alloys, where established, reliable grain refiners system does not exist for the range of magnesium alloys.

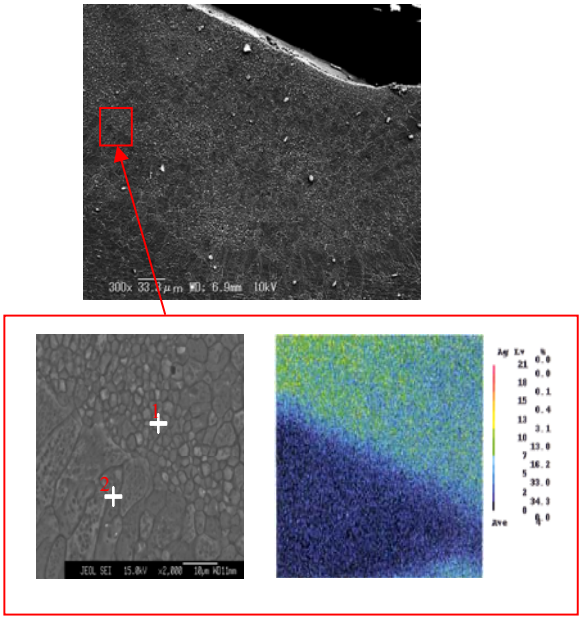


Fig.4 EPMA analysis at fusion and large grain zone boundary

TABLE I
CONTENTS OF ELEMENTS IN WELD AND LARGE GRAIN AREA

Area	Element wt %				
	Mg	Al	Zn	Mn	Ag
1	89.330	2.705	0.933	0.186	0.389
2	88.560	2.141	0.518	0.106	0.046

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There are many studies regarding grain refiners on magnesium alloys but the mechanism of grain refining in casting process even still not clear. There are many grain refining agents in casting that has been reported, such as Zr, Ca, C, Fe, Al, Mn, Ti and etc [7-11]. The two main reasons of grain refining in casting process as following:

This elements could produce potent nucleant particles in melt, promotes the formation of fine equixed macrostructure by deliberately suppressing the growth of columnar and twin columnar grains. Many nucleants particles could produce large number of fine grain sizes [7-12].

Some of these agents have strong segregation ability generates constitutional under cooling in a diffusion layer ahead of the advancing solid/liquid interface, which restricts grain growth since the diffusion of the solute occurs slowly, thus limiting the rate of crystal growth [10-12].

It has been reported that by addition of Ag in Mg-Zn cast alloy significantly reduced the grain sizes [13]. Increase in Ag contents up to 3 % furthermore decrease the grain sizes. The grain refining occurred because of precipitate formations ($Ag_{17}Mg_{54}$) in grain interior and boundaries, and the resulting inhibition of grain growth during recrystallization [13].

Based on the microstructure observation of welded samples, grain size reduces as Ag nanoparticles were introduced between the thin sheets. From EPMA results it was found that Ag nanoparticles are uniformly distributed in the weld zone, rather than only accumulated at grain boundary. Therefore, it is suggested that the Ag could primarily causes the formation of precipitate in the melt. This precipitate particle could act as nucleation sites for fine primary magnesium grains in Mg-Al-Zn alloys.

The identification of effective nucleant particles is commonly based on the assumption that after nucleation on any particle existing in the melt, latent heat release will decrease the likelihood of nucleation on neighbouring particles, which will subsequently be pushed to grain boundaries or into interdendritic spaces. Therefore, an effective nucleant particle is expected in the central regions of grains. Based on the EPMA observation the Ag nanoparticles are uniformly distributed in all grain regions, which it is high possibility that precipitate that act as nucleants could exist within grain area. In addition, the precipitate may also formed at grain boundaries could restrict the grain growth which limiting the rate of crystal growth.

High cooling rate in laser welding, Ag nanoparticles which act as nucleants catalyst in interior grain and precipitate formation at grain boundaries, promote to the development of fine equiaxed grain.

C. Corrosion resistance

It is well known that magnesium alloys are very low in corrosion resistance compared with other metals [14, 15]. The corrosion resistances of welded samples were improved compared with base metals at different test periods as shown in Fig.5. The averages corrosion rates over the 7 days being reduced by about 44 % and 27 % for welded sample with and without Ag nanoparticle, respectively.

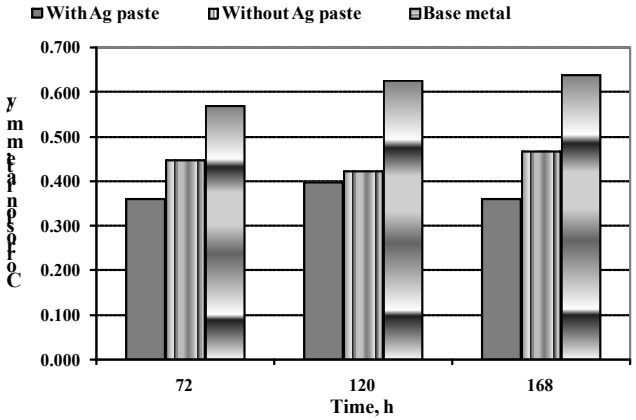


Fig. 5 Corrosion rates of base metal, welded samples with and without Ag nanoparticles paste.

The macrostructure of transverse observation before and after immersed in 5 % NaCl solution in 1, 3 and 5 days of specimen welded with Ag nanoparticle as shown in Fig. 6. The base metal area corroded after 1 day immersed. After 3 and 5 days immersed in the solution, severe corroded area can be observed at base metal area.

In contrast, weld area shows almost no corrosion happened after 1 day immersion because of short time. After 3 to 5 days immersion, smaller corroded area observed at weld area compare with base metal area. The corrosion surface shows pitting appeared to be the main corrosion model at base metal area and weld area. The corrosion in magnesium alloys usually preferentially occurred in matrix of α-Mg phase. This is because of the matrix of α phase in the magnesium is normally anodic to intermetallic compound $Mg_{17}Al_{12}$ [14-18]. The corrosion happened according to the chemical reaction:

Anodic reaction:

$$Mg \rightarrow Mg^{2+} + 2e \quad (2)$$

Cathodic reaction:

$$2H_2O + 2e \rightarrow 2H_{2\uparrow} + 2OH^- \quad (3)$$

Total reaction:

$$Mg^{2+} + 2H_2O = Mg(OH)_2 + 2H_{2\uparrow} \quad (4)$$

The corrosion attack on the welded area was decreased which may attributed due to the several reasons. Grains sizes of welded specimens are finer than the base metal. The finer the grain means that higher the grain boundaries areas. Therefore, more precipitate will reduce the anode and cathode ratio because of β-phase $Mg_{17}Al_{12}$ distributed along the grain boundaries. This β-phase suppressed the corrosion process [14, 18]. In addition, the grains boundaries have high amount of Al level in solid solution, which cause higher corrosion resistance compared with grains interior. Therefore, β-phase could serve as effective barrier and suppressed further propagation of corrosion.

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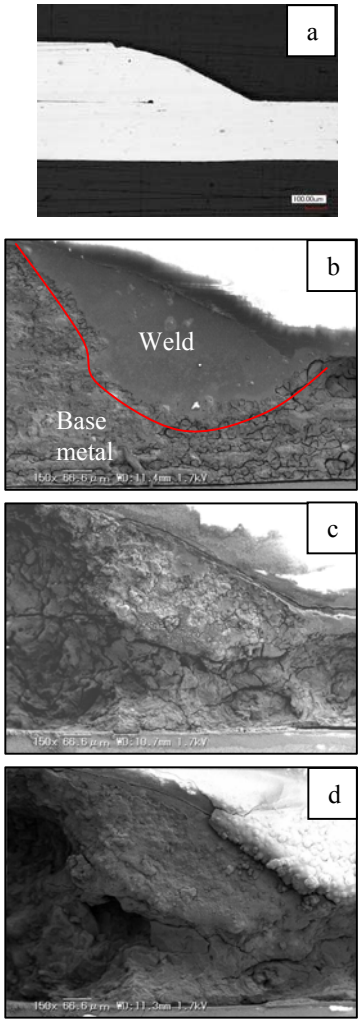


Fig.6 Images a) before corrosion test, b) after 24 h, c) after 72 h and c) after 120 h.

The result of corrosion test shows that specimen welded with Ag nanoparticles demonstrate highest corrosion resistance. The grain refining effect provided by Ag nanoparticles led to much finer grain size and smaller HAZ area could be the reason of higher corrosion resistance. In addition, small amount of silver elements were uniformly distributed in the fusion zone. Small amount Ag elements in fusion zone could also give an effect on corrosion resistance of the alloy. Ag is much more cathodic than magnesium. Ag element may stabilize the magnesium solid solution making it less soluble or less anodic in aqueous solutions, therefore, further improve the corrosion resistance of welded specimen.

IV. Conclusion

The following conclusions can be drawn from the investigations conducted on the lap fillet laser-welded thin sheets of AZ31B magnesium alloys using Ag nanoparticles as insert material:

Introduction of the Ag nanoparticle paste insert promoted grain refinement and broadened the acceptable range of scanning speed parameters compared to welds without an insert. Ag nanoparticles which may act as nucleants catalyst in interior grain and precipitate formation at grain boundaries, furthermore promote to the development of fine equiaxed grain. The weld bead geometry improved, the area of fine grains was larger, the HAZ width was narrower and the bond width was wider, but still very narrow (below 1.0 mm). The narrower HAZ width significantly reduced the voids and cracks.

Corrosion rates of welded samples with and without Ag nanoparticles significantly reduced up to 44 % and 27 %, respectively, compared to base metal. Finer grains mean increase in grain boundaries area, which consist of high Al content. β-phase $Mg_{17}Al_{12}$ could serve as effective barrier and suppressed further propagation of corrosion. Furthermore, Ag distribution in fusion zone provide much more finer grains and may stabilize the magnesium solid solution making it less soluble or less anodic in aqueous solutions, therefore, further improve the corrosion resistance of welded specimen.

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