Introduction

Automotive manufacturers are coming under increasing regulatory pressure to improve the overall fleet mileage of their automobiles. This has created a need to develop and assess new advanced materials and manufacturing technologies that will allow fabrication of lighter weight automotive bodies and structural components, thereby increasing fuel efficiencies and lowering environmental impact of vehicles. While magnesium alloys, with their combination of low density and high specific tensile strengths, could potentially be used to advantage to reduce the overall weight of a vehicle (Refs. 1, 2), sheet steels remain the most commonly used material in the automotive industry, due to their consistent properties, excellent ductility, and their lower material and fabrication costs (Ref. 3). Thus, the ability to make hybrid structures of magnesium alloy and steel sheet would facilitate the increased use of magnesium alloys and light-weighting of automotive structures. This will require the development of new techniques and processes that can be used to make reliable and low cost dissimilar metal joints between magnesium alloy and steel sheet (Refs. 4–11).

It is difficult to join magnesium alloys directly to steel by conventional fusion welding technologies due to the large difference in their melting temperatures and the nearly zero solubility of magnesium and iron (Ref. 4). The melting point of steel (≈ 1823 K [1550ºC]) is well above the boiling point of magnesium (1380 K [1107ºC]), and this can cause catastrophic vaporization of the molten magnesium during a fusion welding process. In addition, the maximum solid solubility of Fe in Mg is only 0.00041 at.-% Fe (Ref. 4). There is also clear evidence that magnesium and steel do not react with each other and do not mix in the liquid state at ambient pressure (Ref. 4). Thus, metallurgical bonding between these two metals...
will only be possible provided another element that can interact and bond with both of them can be applied between the Mg and Fe and act as an intermediate interlayer element or alloy. The weldability of magnesium to steel using various processes such as hybrid laser-arc welding (Refs. 4, 7, 9, 11), resistance spot welding (RSW) (Ref. 10) and friction stir welding (FSW) (Refs. 12, 13) have been examined. In addition, the benefits of using various interlayer alloys and elements such as Al-12Si (Ref. 14), Ni (Refs. 7, 15), Cu (Refs. 7, 11), and Zn (Refs. 8, 10, 16–18) have been explored. In more recent studies, the feasibility of using the laser brazing or laser weld-brazing processes in conjunction with different interlayers have been explored (Refs. 14–18). The laser-brazing process combines attributes of furnace brazing and laser welding (Ref. 19). Also, laser brazing and laser welding-brazing can prevent or minimize excessive formation of detrimental brittle intermetallic phases (Ref. 20). However, if intermetallic layers can be limited to thicknesses below 10 μm, then acceptable joint strengths and mechanical properties may be realized (Refs. 5, 21).

In previous studies (Refs. 14, 15), a diode laser brazing process was developed for joining Mg alloy sheet to coated steel sheet where the Al-12Si and Ni coatings served as the interlayers. These coatings were found to promote wetting of the steel by the magnesium brazing alloy; however, in the case of the Al-12Si coating layer, a preexisting layer of brittle θ-FeAl₃ along the braze-steel interface was found to degrade the mechanical properties of the joint. Nasiri et al. (Ref. 15) also showed that improved wetting and bonding between the magnesium brazing alloy and electroplated Ni steel sheet was facilitated by the formation of an Fe(Ni) solid solution on the steel surface. The average fracture shear strength of the metallic bond reached 96.8 MPa and the joint efficiency was 60% with respect to the AZ31B-H24 Mg alloy base metal. Clearly, selection of an appropriate interlayer for joining Mg to steel depends on identification of an interlayer composition that promotes both good wetting and bonding between the brazing alloy and the steel without generating layers of brittle intermetallics or other reaction products at the joint interface that limit the joint strength.

Following a review of binary and ternary phase diagrams, Sn was identified as a potentially viable interlayer element between the steel and the Mg-Al-Zn brazing alloy used in our previous studies (Refs. 14, 15). Therefore, the objectives of the present study were to investigate the brazeability, interfacial microstructure, and mechanical properties of the laser brazed AZ31B-H24 magnesium alloy to steel sheet with a layer of Sn on the steel to act as the interlayer element. It is expected that development of this laser brazing technology for joining of steel-interlayer-Mg alloy combinations with a strong metallurgical bond between the steel and Mg alloy will facilitate increased application and use of Mg alloys in the automotive industry.

| Table 1 — Measured Chemical Composition of the AZ31-H24 Mg Alloy Sheet and TiBraze Mg 600 Filler Metal (wt-%) |
|---------------------|------------------|-------------|-------|-------|------------------|
|                     | Al       | Zn         | Mn    | Si    | Mg               |
| AZ31B-H24           | 3.02     | 0.80       | 0.30  | 0.01  | Bal.             |
| TiBraze Mg 600      | 9.05     | 1.80       | 0.18  | —     | Bal.             |

| Table 2 — Measured Chemical Composition of the 0.6-mm-Thick Steel Sheet (wt-%) |
|---------------------|------------------|-------------|-------|-------|------------------|
|                     | C        | Mn         | P     | S     | Fe               |
|                     | 0.01     | 0.5        | 0.010 | 0.005 | Bal.             |
Experimental Apparatus and Procedures

The laser brazing process was carried out on 60 × 50-mm specimens sheared from 2-mm-thick, commercial-grade, twin-roll strip cast AZ31B-H24 Mg alloy sheet and 0.6-mm-thick Sn-coated, cold-rolled AISI 1008 plain carbon steel sheet in a lap joint configuration. The electroplated Sn coating layer on the steel sheet was 3.7 ± 0.7 μm thick. Figure 1 shows a SEM micrograph of the cross section of the Sn electroplated steel. The brighter layer on top of the steel is the Sn coating layer. The coating was of uniform thickness with a void-free interface. EDS analysis of the Sn layer on the steel showed a pure Sn coating layer. The chemical compositions of the base materials are given in Tables 1 and 2.

A 2.4-mm-diameter TiBraze Mg 600 filler metal (Mg-Al-Zn alloy) with solidus and liquidus temperatures of 445° and 600°C, respectively, was chosen for this study. The commercial flux used in the experiments was Superior No. 21 manufactured by Superior Flux and Manufacturing Co. This powder flux was composed of LiCl (35–40 wt-%), KCl (30–35 wt-%), NaF (10–25 wt-%), NaCl (8–13 wt-%), and ZnCl₂ (6–10 wt-%) (Ref. 22).

Prior to laser brazing, the oxide layers on the surfaces of the magnesium sheets were cleaned by stainless steel wire brushing. All of the specimens were ultrasonically cleaned in acetone to remove oil and other contaminants from the specimen surfaces. The AZ31B sheet was then clamped on top of the steel sheet to make a lap joint configuration as shown in Fig. 2A. The filler metal was cut and set along the joint line with flux before heating and brazing by the laser beam. An integrated Panasonic 6-axis robot and NuVonyx diode laser system with a maximum power of 4.0 kW and a 0.5 × 12-mm rectangular laser beam intensity profile at the focal point were used for laser brazing. This energy distribution is more suitable for brazing processes compared with the nonuniform Gaussian-distributed circular beams generated by CO₂ and Nd:YAG lasers (Ref. 23). The beam was focused on top of the filler metal. Helium shielding gas was provided in front of the molten pool at a flow rate of 30 L/min from a 6-mm-diameter soft copper feeding tube. Laser brazing was performed using a range of laser powers, travel speeds and beam offset positions.

After laser brazing, 10-mm-wide rectangular-shaped specimens were cut from the brazed joints and subjected to tensile-shear tests with a crosshead speed of 1 mm/min. As shown in Fig. 2B, shims were used at each end of the specimens to ensure shear loads in the lap joint while minimizing induced couples or bending of the specimens.

Transverse sections of the brazed specimens were cut and mounted in epoxy resin. The samples were then mechanically ground using 300, 600, 800, 1000, and 1200 grades of SiC grinding papers followed by polishing using a 1-μm diamond suspension. The polished specimens were etched to reveal the microstructure of the braze metal and AZ31B base material. The etchant was comprised of 20 mL acetic acid, 3 g picric acid, 50 mL ethanol, and 20 mL water (Ref. 24). Macro- and microstructures of the etched joints were examined using an optical metallographic microscope. The microstructure and composition of different zones of the joint cross section were determined using a JEOL JSM-6460 SEM equipped with an Oxford INCA energy dispersive X-ray spectrometer (EDS). A TEM foil of the steel-fusion zone interfacial region was also prepared using a focused ion beam (FIB) and in-situ lift out technique. After attaching the TEM foil to a copper grid, final Ga-ion beam thinning was performed on the sample using an acceleration voltage of 30 kV,
followed by 10 kV, and 1 kV for the final polishing step to get a 100-nm-thick TEM sample. The TEM studies were performed with a Titan 80-300LB, a high-resolution transmission electron microscope (HR-TEM) made by FEI Company.

Results

Visually acceptable laser brazed joints were made using 2.2-kW laser power, 8 mm/s travel speed, and 0.2 mm beam offset to the steel side. These conditions resulted in melting of the filler metal to form a fillet with triangular cross section between the AZ31B Mg and steel base metals — Fig. 3. There was a uniform brazed area with good wetting of the Mg-Al-Zn brazing alloy to the steel base metal and some melting of the AZ31B base metal. The average leg length of the Mg-Al-Zn alloy filler metal-steel interface was 7.5 ± 2.1 mm.

Figure 3A shows a typical tensile shear test of a laser-brazed specimen. All tensile-shear specimens fractured in the steel base metal well away from the brazed joint. The average fracture load of 10-mm-wide tensile shear specimens was found to be 2064 ± 85 N. This value was exactly the same as fracture load of the steel base metal with the same size tensile specimen, confirming that fracture of the laser brazed joint always occurred in the steel base metal. With an average interface area between the braze alloy and the steel sheet was 75 mm²; therefore, the tensile shear strength of the interface was greater than 2064/75 = 27.5 MPa.

A cross-sectional view of a typical laser brazed specimen is shown in Fig. 3B. The average contact angle of the fusion zone (FZ) on the steel substrate was measured to be 35 ± 5 deg, which is indicative of good wetting of the Sn-coated steel substrate by the molten Mg filler metal (Ref. 25). Defects such as porosity or cracks were not observed in the joint. In contrast, when bare steel was used, no metallic bonding occurred between the steel sheet and the braze alloy (fusion zone) and wetting of the steel by the braze metal was very poor (Ref. 14).

Microstructural Analysis of the Steel-FZ Interface

The microstructure in the AZ31B-H24 Mg base metal and filler metal were similar to that observed in previous studies with these alloys (Refs. 14, 15). As indicated in Fig. 3B, in the base metal, continued recrystallization and grain growth occurred in the AZ31B heat-affected zone (HAZ). In the partially melted zone (PMZ), localized melting or liquation of the intergranular regions occurred. The solidification microstructure of the FZ was a combination of columnar and equiaxed α-Mg dendrites with a divorced eutectic β-Mg17Al12 intermetallic phase at the dendrite boundaries. A more detailed microstructural analysis of the fusion zone and AZ31B Mg alloy microstructure may be found in Ref. 14.

Figure 4 shows a typical SEM image of the microstructure along the steel-fusion zone interface. After the laser brazing process, the Sn coating was not detected as a separate layer along the interface. This suggests that the low melting point Sn (Tₘₚ = 505 K [232 ºC]) layer had been entirely melted and mixed with the molten Mg filler metal immediately adjacent to the interface. The microstructure of the steel-FZ interface was the same along the entire length of the interface. The contrast of α-Mg adjacent to the interface looks darker than the α-Mg in the fusion zone, meaning lower Al content of α-Mg adjacent to the interface — Fig. 4. Therefore, Al atoms near the interface should be consumed in a way, which is unclear according to the SEM photomicrograph. While this SEM photomicrograph might suggest that the α-Mg phase has bonded directly to the steel substrate, it is well known that this will not occur due to the very large lattice mismatching of Fe and Mg (Refs. 4, 5). In our previous studies (Refs. 14, 15), a submicron-thick transitional layer or phase was found to exist at the steel-magnesium interface that could not be resolved by optical microscopy or the SEM. This intermediate phase was found through TEM examination to be responsible for the observed microstructure.
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Figure 6A shows a scanning transmission electron microscopy (STEM) image of the steel-fusion interface. Complete metallurgical bonding appears to have occurred along the entire length of the interface; however, there is a band of nanoscale pores with an average diameter of 145 ± 22 nm in the steel substrate adjacent to the interface. As shown at even higher magnification in Fig. 5B, a very thin layer of a distinctly different phase exists between the steel and the fusion zone, which appears to have created a transitional interlayer between these two alloys that forms a bond with the steel substrate on one side as well as the magnesium filler alloy on the other side.

STEM-EDS compositional mapping and point scan analysis were used to identify the composition of the phases formed at the steel-fusion zone interface shown in Fig. 5. Figure 6A shows a STEM image of a representative area of the interface and concentration maps of this same area for Mg, Fe, Al, Mn, and Sn. Mg is seen to be present primarily in the fusion zone, but nowhere else. Similarly, Fe from the steel exists up to the interlayer, but is not present in the fusion zone. The nanoscale pores are within the Fe.

There is a significant concentration of Al from the braze alloy within the interlayer and also to a depth of about 270 nm into the steel substrate and past the band of pores. Mn, also from the braze alloy, is concentrated primarily within the interlayer and is not detected in significant quantities elsewhere in the braze alloy and only in small concentrations in the steel. Finally, there appears to be very low concentrations of Sn only within the steel close to the interface.

The composition and distribution of elements across the interface between the steel and fusion zone was also analyzed using STEM-EDS point analysis along the line shown in Fig. 5B. These results are shown in Fig. 6B and are consistent with those shown in the element maps in Fig. 6A, e.g., the Mg exists only in the filler metal and Sn is detectable in only very small concentrations within the steel. While the Al concentration in the fusion zone is close to the nominal 9 wt-% Al of the braze alloy, the concentration increases in a step-wise fashion to about 48 wt-% Al in the interlayer and then drops to about 31 wt-% followed by a continual decrease of the Al concentration to a distance of about 270 ± 46 nm into the steel, which is past the band of pores. This is indicative of solid-state diffusion of the Al into the steel. With the increased Al concentration in the steel, there is a complementary decrease of the Fe concentration at the steel surface approaching the interlayer. The Fe concentration appears to drop to about 15 wt-% in the interlayer and is not detected in the fusion zone. Mn, also present in concentrations less than 1 wt-% in all three alloys, is concentrated up to 40 wt-% primarily within the interlayer and is not detected in significant quantities elsewhere in the braze alloy and only in small concentrations in the steel. The average thickness of the interlayer was 45 ± 10 nm and it contained only 60.9 ± 0.2 at.-% Al, 34.8 ± 0.6 at.-% Mn, and 4.3 ± 0.4 at.-% Fe. This suggests that the interlayer is composed of the Al(3Mn,Fe)5 intermetallic compound.

The range of composition in the Fe-Al diffusion layer evident in Fig. 6B is consistent with the range of Al composition over which the disordered α-Fe and ordered Fe-Al solid solution phases exist in the Fe-Al binary phase diagram (Ref. 26). This was confirmed using selected area diffraction pattern analysis (SADP). Figure 7A shows a bright field TEM image of the interface region between the steel substrate, the Al(3Mn,Fe)5 interlayer and the Mg braze alloy and Fig. 7B shows a SADP obtained from the Fe-Al phase region. Analysis of this pattern indicated that this phase is a Fe(Al) solid solution with a body-centered cubic (BCC) crystal structure. The SADP was taken along the [111] zone axis of the phase. The lattice parameter of Fe(Al) was calculated to be a = 2.885 Å, which is similar to the lattice parameter of Fe (aFe = 2.8606 Å). Thus, the crystal structure and the lattice parameter of Fe(Al) were similar to Fe. The Fe-Al binary phase diagram shows up to 55 at.-% solid solubility for Al in Fe (Refs. 26, 27). The Fe(Al) is well-known for its relatively high strength, high oxida-
tion resistance, low cost, and excellent fracture toughness (Refs. 18, 28). Figure 7C shows a SADP analysis of the Fe(Al)-Al<sub>8</sub>Mn<sub>5</sub> interface, where the lattice of Fe(Al) was exactly located on the [111] zone axis of the phase. The diffraction spots from the Fe(Al) were indexed accordingly. The extra spots in Fig. 7C are from the Al<sub>8</sub>Mn<sub>5</sub> phase. This figure shows that while the Fe(Al) is in the [111] zone axis orientation, the Al<sub>8</sub>Mn<sub>5</sub> intermetallic compound is off any low index orientation.

According to the results of thermodynamic calculations performed by Kim et al. (Ref. 29), during solidification of the Mg-Al-Zn brazing alloy, the sequence of phase formation during solidification is first Al<sub>8</sub>Mn<sub>5</sub>, then α-Mg and finally the β-phase (Mg<sub>17</sub>Al<sub>12</sub>). Therefore, it is expected in the present study that a thin layer of Fe(Al) at the steel-FZ interface forms first by solid-state diffusion of Al in the FZ liquid into the steel. Upon further cooling, the Al<sub>8</sub>Mn<sub>5</sub> intermetallic nucleates and grows on the Fe(Al) surface layer that has formed on the steel and there is time for a thin layer to grow and cover the Fe(Al) (BCC) surface. Therefore, the remaining FZ liquid will be in contact with only the thin Al<sub>8</sub>Mn<sub>5</sub> layer and this new interlayer phase now plays the role of the substrate for subsequent reactive wetting, nucleation and growth of the remaining α-Mg liquid onto the thin surface layer of Al<sub>8</sub>Mn<sub>5</sub>. A SADP analysis of the Al<sub>8</sub>Mn<sub>5</sub>-Mg interface is shown in Fig. 7D. When the Mg phase was parallel to the [1100] zone axis of the Mg, the Al<sub>8</sub>Mn<sub>5</sub> phase was off any low indexed orientation.

Measurements of the Crystallographic Orientation Relationships at the Steel-FZ Interface

When reaction products form at the interface of dissimilar metals, the bond strength between the two phases is directly affected by the interfacial energy density of the interface, which in turn depends on the degree of crystallographic registry, i.e., the crystallographic orientation relationship (OR) and lattice matching, that exists between the two phases at their interface (Refs. 25, 30). In the present study, in order to identify the OR and lattice matching between the Al<sub>8</sub>Mn<sub>5</sub> phase with a rhombohedral crystal structure and the FCC Fe(Al) phase on the one side (steel) and the hexagonal close-packed (HCP) α-Mg phase on the other side (fusion zone), high-resolution (HR)-TEM analysis of the interface was performed.

Figure 8A shows a HR-TEM image of the Al<sub>8</sub>Mn<sub>5</sub>-Fe(Al) substrate interface. When the specimen was aligned with the direction of Al<sub>8</sub>Mn<sub>5</sub> [011], the (110)<sub>FeAl</sub> was within 4.2 deg of the (0002)<sub>Mg</sub> and the measured interplanar spacing for these planes were d<sub>1101</sub><sub>FeAl</sub> = 2.095 Å and d<sub>0002</sub><sub>Mg</sub> = 2.204 Å, which represents only 5.2% interplanar mismatch at the interface. Thus, good lattice matching with low angle rotation of matched lattice planes exists between the Fe(Al) and Al<sub>8</sub>Mn<sub>5</sub> phases at this interface. This good match of lattice sites between Al<sub>8</sub>Mn<sub>5</sub> and Fe(Al) leads to a low energy density at their interface.

Figure 8B shows the HR-TEM image of the Al<sub>8</sub>Mn<sub>5</sub>-α-Mg interface. Using HR-TEM, it was found that when [1011]<sub>Al8Mn5</sub>//[1010]<sub>Mg</sub>, the (3033)<sub>Al8Mn5</sub> was within 47.4 deg of the (0002)<sub>Mg</sub>. Similarly, the measured d-value for the (0002)<sub>Mg</sub> was 2.574 Å. This represents 16.8% mismatch with that of the (3033)<sub>Al8Mn5</sub>. This analysis showed a poor crystallographic matching between Al<sub>8</sub>Mn<sub>5</sub> and α-Mg with a large angle rotation of matching planes and therefore high energy density at their interface.

Discussion

Analysis of the Interface Orientation Relationships at the Steel-FZ Interface

The HR-TEM measurements indicated that good OR and lattice match-
ing exists between the Al₈Mn₅ and Fe(Al) phase on the steel side and poor crystallographic matching was found between the Mg and the Al₈Mn₅ layer on the Mg-Al-Zn brazing alloy side. However, the observed ORs were more like a local observation at the interface than a general trend of OR. Therefore, further analysis of the possible formed ORs at the interface is required. Due to different lattice parameters between Al₈Mn₅, Fe(Al) and Mg, an intrinsic strain in their adjoining lattices arises. If this strain is not relaxed by the introduction of misfit dislocations, the magnitude of this extensional strain will be proportional to the lattice mismatch between Al₈Mn₅ and Fe(Al) from one side and Mg from the other side (Ref. 31). This strain will increase the total interfacial energy. As a result, the strength of the formed interfaces decreases. In such a way, the interfacial energy and metallic bond strength can be dependent on the crystallographic disregistry and lattice matching along Fe(Al)-Al₈Mn₅-Mg adjoining lattices. In addition, the effectiveness of a substrate in promoting heterogeneous nucleation, such as Fe(Al) for Al₈Mn₅ or Al₈Mn₅ for Mg, depends on the crystallographic OR and lattice matching between the substrate and the solidified region (Ref. 32).

Using the edge-to-edge matching model, the interatomic spacing misfits along matching directions and mismatches between matching planes can be calculated. It is assumed that the matching directions and matching planes are the close or nearly close-packed directions and planes (Refs. 33, 34). The lattice parameters of Fe(Al) used in this study was \( a_{Fe(Al)} = 0.2885 \) nm (measured from the SADP of the Fe(Al) phase in Fig. 8B). In the BCC crystal structure, there are four possible close-packed or nearly close-packed directions must first be identified.

Al₈(Mn,Fe)₅ is a substitutional solid solution of Al₈Mn₅, in which some Mn atoms are replaced by Fe. Solution of the Fe atoms into Al₈Mn₅ and replacement of the Mn atoms by Fe atoms do not cause significant variation in the lattice parameters, since the atomic radius of Mn and Fe are very close (0.112 and 0.124 nm, respectively). Therefore, Al₈(Mn,Fe)₅ can be treated as Al₈Mn₅ with Al₁₈Cr₅ type of rhombohedral structure. In this case, the lattice parameters for Al₈Mn₅ are \( \alpha = 1.2645 \) nm and \( c = 1.5855 \) nm (Ref. 35).

The unit cell of Al₈Mn₅ (or Al₈(Mn,Fe)₅) contains 48 Al atoms and 30 Mn/Fe atoms. From these atoms’ positions in the unit cell to together with the X-ray diffraction intensity data (Ref. 36), the close-packed or nearly close-packed planes of Al₈(Mn,Fe)₅ were identified to be \{3033\}Al₈Mn₅ and \{3360\}Al₈Mn₅. Similarly, the close-packed or nearly close-packed directions are \( \{1120\} \), \( \{0001\} \), \( \{1102\} \) and \( \{1011\} \).

The lattice parameters of Fe(Al) used in this study was \( a_{Fe(Al)} = 0.2885 \) nm (measured from the SADP of the Fe(Al) phase in Fig. 8B). In the BCC crystal structure, there are four possible close-packed or nearly close-packed
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The BCC crystal structure, there are planes that have to be identified. In Fe(Al) and Al8Mn5, possible matching directions between δ interatomic spacing misfits, along the calculated results for the relative pairs can be calculated. Table 3 shows the interatomic spacing along these directions; (111)_{Fe(Al)}, (100)_{Fe(Al)}, and (110)_{Fe(Al)} planes. The interatomic spacing along these four directions are

\[ f = \frac{\sqrt{2}}{2} a_{Fe(Al)} \]

for (111)_{Fe(Al)}, \( f = a_{Fe(Al)} \) for (100)_{Fe(Al)}, \( f = \frac{\sqrt{3}}{2} a_{Fe(Al)} \) for (110)_{Fe(Al)} and \( f = 0.25\sqrt{3} a_{Fe(Al)} \) for (113)_{Fe(Al)}. Therefore, there will be sixteen direction pairs between Fe(Al) (BCC) and Al8Mn5 (rhombohedral) that can be potential matching directions. If we assumed that the Fe(Al) phase is the substrate and Al8Mn5 is the reaction product on the Fe(Al), the variation of interatomic spacing misfit along these direction pairs can be calculated. Table 3 shows the calculated results for the relative interatomic spacing misfits, \( \delta \), along possible matching directions between Fe(Al) and Al8Mn5.

To predict the ORs, the matching planes have also to be identified. In the BCC crystal structure, there are three close-packed or nearly close-packed planes, i.e., \{110\}_{Fe(Al)}^p, \{200\}_{Fe(Al)}^p and \{111\}_{Fe(Al)}^p. Thus, there are a total of six possible plane pairs between Fe(Al) (BCC) and Al8Mn5 (rhombohedral) that are potential matching planes. For the BCC crystal structure, the interplanar spacing, \( d \), between adjacent \{110\}_{Fe(Al)}^p, \{200\}_{Fe(Al)}^p and \{111\}_{Fe(Al)}^p planes are

\[ \frac{\sqrt{2}}{2} f_{Fe(Al)} \times 0.5 a_{Fe(Al)} \text{ and } \frac{\sqrt{3}}{3} f_{Fe(Al)} \text{, respectively. Table 4 shows the calculated interplanar spacings for the Al8Mn5 phase and the Fe(Al) substrate as well as the interplanar spacing mismatches.}

According to the data shown in Table 3, the matching directions with interatomic spacing misfits less than the critical value of 10% between the Fe(Al) substrate and Al8Mn5 phase at the interface are:

- \{111\}_{Fe(Al)}^p/\{1120\}_{Al8Mn5}^s
- \{111\}_{Fe(Al)}^p/\{1121\}_{Al8Mn5}^s
- \{110\}_{Fe(Al)}^p/\{1120\}_{Al8Mn5}^s
- \{110\}_{Fe(Al)}^p/\{1121\}_{Al8Mn5}^s
- \{100\}_{Fe(Al)}^p/\{1010\}_{Al8Mn5}^s
- \{100\}_{Fe(Al)}^p/\{1011\}_{Al8Mn5}^s
- \{113\}_{Fe(Al)}^p/\{1120\}_{Al8Mn5}^s

The selection of these directions is further supported by the calculated interplanar spacings for the Al8Mn5 phase and Fe(Al) substrate, as shown in Table 4.

Table 3 — Interatomic Spacing Misfits along Possible Matching Directions between Al8Mn5 Phase and Fe(Al) Substrate

<table>
<thead>
<tr>
<th>Matching Directions</th>
<th>Fe(Al) Interatomic Spacing, nm</th>
<th>Al8Mn5 Interatomic Spacing, nm</th>
<th>Interatomic Misfit (%)</th>
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<tbody>
<tr>
<td>&lt;111&gt;<em>{Fe(Al)}^p/{1120}</em>{Al8Mn5}</td>
<td>0.250</td>
<td>0.244</td>
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<td>&lt;113&gt;<em>{Fe(Al)}^p/{1101}</em>{Al8Mn5}</td>
<td>0.239</td>
<td>0.264</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Table 4 — Calculated Interplanar Spacing for Al8Mn5 Phase and Fe(Al) Substrate and Interplanar Spacing Mismatch between Possible Matching Planes of Al8Mn5 and Fe(Al)

<table>
<thead>
<tr>
<th>Matching Planes</th>
<th>Fe(Al) Interplanar Spacing, nm</th>
<th>Al8Mn5 Interplanar Spacing, nm</th>
<th>Interplanar Mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110]<em>{Fe(Al)}^p/{3033}</em>{Al8Mn5}</td>
<td>0.204</td>
<td>0.221</td>
<td>8.3</td>
</tr>
<tr>
<td>[110]<em>{Fe(Al)}^p/{3360}</em>{Al8Mn5}</td>
<td>0.204</td>
<td>0.217</td>
<td>6.3</td>
</tr>
<tr>
<td>{200}<em>{Fe(Al)}^p/{3033}</em>{Al8Mn5}</td>
<td>0.144</td>
<td>0.221</td>
<td>53.5</td>
</tr>
<tr>
<td>{200}<em>{Fe(Al)}^p/{3360}</em>{Al8Mn5}</td>
<td>0.144</td>
<td>0.217</td>
<td>50.7</td>
</tr>
<tr>
<td>{111}<em>{Fe(Al)}^p/{3033}</em>{Al8Mn5}</td>
<td>0.166</td>
<td>0.221</td>
<td>33.1</td>
</tr>
<tr>
<td>{111}<em>{Fe(Al)}^p/{3360}</em>{Al8Mn5}</td>
<td>0.166</td>
<td>0.217</td>
<td>30.7</td>
</tr>
</tbody>
</table>
of 10% as the critical value for the interatomic spacing misfit is based on van der Merwe’s energy calculation, which was done along the close-packed directions between face-centered cubic (FCC) and BCC (Ref. 37). Similar to the interatomic spacing misfit along matching directions, it has been reported that the approximate critical value of 6%; {110}_{Fe(Al)}//{3360}_{AlMn_5} with 6.3% interplanar mismatch. This plane pair does not contain all the possible matching directions with small misfit values. It only contains three direction pairs, i.e., (111)_{Fe(Al)}//(1120)_{AlMn_5}, (111)_{Fe(Al)}//(1011)_{AlMn_5}, and (110)_{Fe(Al)}//(0001)_{AlMn_5}. Therefore, combination of {110}_{Fe(Al)}//{3360}_{AlMn_5} plane pair and these direction pairs have the potential to form an OR. These conditions lead to a low-angle rotation of the lattice planes along the matching directions and a low mismatch strain at the interface of these two phases. Thus, the Fe(Al) phase can be regarded as an effective nucleating substrate for the AlMn_5 phase. The plane pair of {110}_{Fe(Al)}//{3360}_{AlMn_5} might also have this potential to form an OR, but this would require a higher angle rotation of the matching plane. The HR-TEM experimental results in this study also showed that the OR at the interface between the Fe(Al) and AlMn_5 was [1011]_{AlMn_5}//[111]_{Fe(Al)}, 4.2 deg from (3033)_{AlMn_5} with 5.2% interplanar mismatch between them — Fig. 8A. Therefore, presented results in this study suggest that the Fe(Al) phase has small interatomic spacing misfit along the matching direction and very low d-value mismatch between the matching planes with AlMn_5 phase. This leads to a low energy density and strong Fe(Al)-AlMn_5 interface.

The edge-to-edge crystallographic matching model was also applied to the AlMn_5-Mg interface. For Mg with a HCP crystal structure, there are three possible close-packed or nearly close-packed directions (directions with low indexes), i.e., (1120)_{Mg}, (1010)_{Mg}, and (1123)_{Mg}. The interatomic spacing along these three potential matching directions can be expressed in terms of the lattice parameters, a_{Mg} and c_{Mg}. If f is used to represent interatomic spacing, then f = a_{Mg} for (1120)_{Mg}, f = 0.5 \sqrt{3} \frac{a_{Mg} + c_{Mg}}{2} for (1010)_{Mg}, and f = 0.5 (a_{Mg} + c_{Mg})^{0.5} for (1123). The lattice parameters of Mg used in the current study are a_{Mg} = 0.320 nm and c_{Mg} = 0.520 nm (Ref. 39). In the HCP crystal structure, the close-packed or nearly close-packed planes are (0002), (1011), and (1010) with d-spacings of c_{Mg}/2, 

\[
\frac{a_{Mg} + c_{Mg}}{2},
\]

and \sqrt{3}a_{Mg}/2, respectively.

If it is assumed that during cooling, the Mg (HCP) nucleates and grows onto the preexisting AlMn_5 surface layer, the variation of interatomic spacing misfit along twelve possible close-packed or nearly close-packed directions pairs and also the variation of interplanar spacing mismatch among six possible close-packed or nearly close-packed planes between Mg phase and AlMn_5 substrate can be calculated (Tables 5, 6). If 10% is selected as the critical value of the interatomic spacing misfit, then three direction pairs satisfy this condition; (1120)_{AlMn_5}//(1010)_{Mg}, (1120)_{AlMn_5}//(1123)_{Mg}, and (1101)_{AlMn_5}//(1100)_{Mg}. However, Zhang et al. (Ref. 36) reported that the first two direction pairs are combinations of straight AlMn_5 atom rows and nonstraight Mg atoms rows and as a result they cannot be matched. Therefore, the direction pair of (1011)_{AlMn_5}//(1010)_{Mg} is the only possible matched pair with interatomic spacing misfit.
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spacings mismatch less than 10%. This direction pair involves two plane pairs, i.e., $\{003\}_{\text{AlMn}_5}/\{002\}_{\text{Mg}}$ with 17.6% $d$-value mismatch and $\{1350\}_{\text{AlMn}_5}/\{002\}_{\text{Mg}}$ with 19.8% $d$-value mismatch (Table 6). Again, if 6% is used as the critical data of the $d$-value mismatch (Ref. 38), in both cases the $d$-value mismatches are much larger than the critical value. Therefore, the formed OR between $\text{Al}_8\text{Mn}_5$ and $\text{Mg}$ will have a large angle rotation of the matching planes — Fig. 8B. Qui et al. (Ref. 40) also reported that $\text{Al}_8\text{Mn}_5$ has a high interplanar mismatch energy against $\text{Mg}$. Therefore, the formed $\text{Al}_8\text{Mn}_5$ phase cannot act as an effective site for heterogeneous nucleation and growth of the $\text{Mg}$ from the molten FZ. Zhang et al. (Ref. 36) reported that the metastable $\text{Mg}$ phase possesses significantly better crystallographic matching with the $\text{Mg}$ matrix than the other Al-Mn intermetallic phases, such as $\text{Al}_8(\text{Mn,Fe})_5$ phase.

Porosity Formation at the Steel-FZ Interface

In Figs. 5 and 6, there is evidence of a band of spherical, nonscale pores that have formed parallel to the interface and within the single-phase $\text{Fe(Al)}$ surface layer that was created during the laser brazing operation. This type of porosity is very similar to the Kirkendall porosity observed by Saiz et al. (Ref. 41) within a layer of FeSn$_x$ which formed parallel to the interface during soldering of a Fe-Ni alloy using Sn-Ag solder at 523 K (250°C). Salamon and Mehrer (Ref. 42) have observed Kirkendall porosity formation in the diffusion zone of a $\text{Fe}_8\text{Al}_{17}/\text{Fe}_5\text{Al}_{42}$ diffusion couple. Springer et al. (Ref. 43) reported formation of Kirkendall porosity in the reaction layer $\text{Fe}_{\text{Fe}}\text{Al}$ formed at the interface of friction stir welded steel to Al alloy joints. Finally, Tiwari and Mehrotra (Ref. 44) have observed Kirkendall effect and Kirkendall porosity in their recent study of interphase interdiffusion mechanisms in NiAl and FeAl intermetallic compounds.

The necessary condition for occurrence of Kirkendall effect and formation of Kirkendall porosity in a binary diffusion couple is that two diffusing species should have unequal intrinsic diffusion coefficients (Ref. 42). In the present study, considering the location of the porosity (Fig. 6), the Kirkendall porosity is formed during inter-diffusion of the Al and Fe atoms within the Fe-Al diffusion layer; however, since the diffusivity of Al in Fe is greater than Fe in Al, there is a net flux of vacancies in the opposite direction of the Al diffusion that results in vacancy concentrations that exceed equilibrium values and ultimately result in nucleation and growth of nanoperoporo pores similar to those shown in Figs. 5 and 6 (Refs. 42, 44, 45).

In Figs. 5 and 6, the average area fraction of Kirkendall porosity in the shear plane parallel to the interface is about 15%. However, this reduction in throat area due to the porosity was not sufficient to compromise the strength of the interface, primarily because of the significant strength of the $\text{Fe(Al)}$ layer relative to the steel and the Mg-Al-Zn brazing alloy. The ultimate tensile strength (UTS) of $\text{Fe(Al)}$ along the [001] crystallographic direction has been reported to be 19,000 MPa (Ref. 46), whereas the UTS for the steel sheet was 344 MPa and the Mg-Al-Zn brazing alloy was 170 MPa (Ref. 47). Thus, even with the Kirkendall porosity defects, the strength of the $\text{Fe(Al)}$ layer far exceeds the strength of the steel and $\text{Mg-Al-Zn}$ brazing alloy so that the Kirkendall porosity did not limit the overall tensile strength of the joint.

Sequence of Phase Formation along the Interface (Bonding Mechanism)

Based on the results described above, a sequence of events may be surmised to take place during laser brazing of the Sn-plated steel and the AZ31B Mg sheet. These are shown in the schematics in Fig. 9 starting with the original joint configuration at room temperature shown in Fig. 9A. During initial heating (Fig. 9B), the electroplated Sn layer melts when the electroplated Sn layer exceeds the melting temperature of the Sn (505 K [232°C]). At this stage, the steel surface is still covered by Sn$_{\text{Fe}}$, which continues to pre-
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Katayama (Ref. 48) in laser welding of AZ31B magnesium alloy to Zn-coated steel, where Zn played the role of the interlayer.

Conclusions

It has been shown that diode laser brazing can be successfully performed between 2-mm-thick AZ31B-H24 Mg alloy sheet and 0.6-mm-thick Sn-coated plain carbon steel sheet in the lap joint configuration using a Mg-Al-Zn brazing alloy wire.

In all cases, tensile shear tests failed in the steel sheet indicating that the Mg-Al-Zn brazing alloy-to-steel sheet interface and braze joint were always stronger than the steel sheet. The formation of nano-scale layers of Fe(Al) solid solution and Al(Mn,Fe)5 intermetallic compound was found to be responsible for the formation of a metallurgical bond between the steel and Mg-Al-Zn brazing alloy.

HR-TEM analysis of the Fe(Al)-Al8Mn5 interface showed that a crystallographic orientation relationship with low angle rotation of the matching planes and low interplanar mismatch existed at the Fe(Al)-Al8Mn5 interface. However, Al8Mn5-Mg interface showed a poor crystallographic matching between Al8Mn5 and α-Mg with a large angle rotation of matching planes at their interface.

These results were further confirmed by the predictions of an edge-to-edge crystallographic matching model of the Fe(Al)-Al8Mn5 and Al8Mn5-Mg interfaces. These conditions will result in an interface with low interfacial energy density and strong metallic bond between the Fe(Al) and the Al8Mn5 and an interface with high interfacial energy density and weak bond between the Al8Mn5 and the Mg in the filler metal. The Sn coating on the steel sheet does not appear to contribute to the final metallic bonding of the steel to the AZ92 filler metal. Instead, its primary role is to prevent contamination and oxidation of the steel surface until molten Mg-Al-Zn brazing alloy can come into direct contact with the steel surface.

Acknowledgments

The authors wish to acknowledge support of the American Welding Society (AWS) Graduate Fellowship program and the Magnesium Network of Canada (MgNET) supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) for sponsoring this work.

References

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