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A study on the SCC susceptibility of friction stir welded AZ31 Mg sheet

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Abstract

In this study, the stress corrosion cracking (SCC) behavior of friction stir welded (FSW) AZ31 Mg alloy was examined using slow strain rate tensile (SSRT) test method. Electrochemical impedance spectroscopy (EIS) and salt spray tests were carried to understand the general corrosion behavior. The FSW AZ31 Mg samples exhibited higher SCC susceptibility than the base material during SSRT in corrosive environment. The failure of the FSW AZ31 Mg samples occurred in the stir zone (SZ) when tested in corrosive environment, in contrast to the failure in the thermo mechanically affected zone (TMAZ) observed in tests in air. However, the EIS and salt spray test results showed a higher general corrosion resistance of the SZ than the base material. The study suggests that hydrogen assisted cracking could be a reason for the higher SCC susceptibility of FSW AZ31 Mg samples than the base material.

Keywords: Magnesium alloy; Stress corrosion cracking; Friction stir welding

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1. Introduction

High specific strength of Mg based alloys makes them very attractive for automotive and aerospace applications. However, the applications of these alloys require welding and joining procedures. Unfortunately, the conventional fusion welding for Mg alloys often produces some porosity in the weld joint, which deteriorates the mechanical properties [1, 2].

Friction Stir Welding (FSW) is a solid state joining technique patented in 1991 by TWI Ltd., England [3]. The process typically employs a cylindrical and non-consumable tool consisting of a shoulder and smaller diameter pin. The tool is rotated and plunged into the joint line between clamped and abutting work pieces so that the shoulder is in intimate contact with the work piece surface and the pin is buried within the through thickness of the work pieces. Friction between the tool and the work pieces generates heat causing a plasticized zone to form under the tool shoulder and around the pin. The rotating tool is then transversed along the join line, whereby the pin stirs the locally plasticized material forcing it to flow in the direction of tool rotation to be deposited behind the pin where it cools and consolidates [4].

The major advantage of FSW over conventional fusion welding techniques is that a metallic bond is achieved below the melting point of the base material thus avoiding many of the metallurgical problems associated with the solidification process [5]. Moreover, the joining process requires no additional filler material or shielding gas in the joining of Mg and Al alloys [5]. A number of investigations have shown that under the influence of the FSW tool (i.e. mechanical deformation) and processing temperatures a fine recrystallised microstructure is formed in the stir zone [6]. Thus, the finer and more equiaxed the grains in the stir zone compared to that of the base material the higher the local strength levels. It is also reported that the high dislocation density in the weld region further contributes to a more homogeneous hardness profile in FSW Mg alloys [7].

It is well known that Mg alloys are susceptible to localized corrosion such as pitting and stress corrosion cracking (SCC) [8-10]. Major studies show that SCC susceptibility of Mg alloys in chloride containing solutions, and some even in distilled water [8, 9]. The welding process inevitably causes changes in the original microstructure of the alloy due to welding thermal cycles. These microstructural changes can affect the localized corrosion behavior of the alloy. A recent study on the SCC behavior of laser butt welded AZ31 Mg alloy showed high SCC susceptibility and consequent failure in the fusion boundary of the sample [11]. Such a failure was attributed to the electrochemical potential gradients between the weldment and base material causing a localized attack along the fusion boundary. However, the microstructural changes occurring in Mg alloys through the FSW process are different from that of the laser butt welding process due to the difference in the processing techniques. To the best knowledge of the authors, the effect of such changes on the SCC behavior of Mg alloy has not yet been studied. Hence, in this work AZ31 Mg alloy was used to study the SCC behavior of FSW of this material. Slow strain rate tensile (SSRT) test method was adopted for this study. In addition, electrochemical impedance spectroscopy (EIS) and salt spray tests were carried out on the material to understand the general corrosion behavior.

2. Experimental procedure

AZ31 alloy sheet (Mg-3Al-1Zn-0.2Mn, by wt.%) was used for this investigation. The friction stir butt welds were produced in extruded AZ31 Mg alloy having a plate thickness of 1.9 mm. Welding was performed at the GKSS-Forschungszentrum Geesthacht, Germany, using a Tricept 805 Robot. Further details concerning the robot and FSW unit can be found elsewhere [12]. The FSW tool consisted of a 13 mm diameter shoulder coupled to cylindrical and threaded pin, the diameter of which measured 5 mm. Pin stick out length was 1.7 mm with tool tilted 1.5° away from direction of the weld travel. The butt weld examined in this study was welded in the extrusion direction utilizing a tool rotation speed of 1400 rpm, a weld travel speed of 300 mm/min and an axial load or down force of 5.5 kN.

For microstructural examination, the weld joints were sectioned and prepared by standard metallographic procedures. The specimens were etched in a solution containing 3.5 g picric acid, 6.5ml acetic acid, 20ml water and 100ml ethanol, and were examined by optical microscopy. The Vickers hardness was measured on a polished surface across the weld, using HV 0.2 and a load time of 10 s. Microhardness evaluation was performed on a fully automatic UT100 – Hardness Scanner. In total, 81 indentations were performed where the selected distance between two consecutive indentations measured was 0.5 mm. After removing 0.5 mm thickness of the material from both the top and bottom surface of the weldment, two rows of indentations were produced across the weldment.

The SCC susceptibility of the samples was studied by SSRT tests. The tests were performed on flat tensile specimens with gauge dimensions 24 x 6 x 1.8 mm. In the case of FSW tensile samples, the weld region was located in the middle of the gauge section. These samples were ground with SiC paper up to 1200 grit on all sides of the gauge section to obtain a flat region between the base material and the weldment, and were cleaned with acetone prior to testing. In the SSRT tests, the samples were tested in an inert environment (air) at a strain rate of 2 x 10^{-6}/s, and the test results were compared with those obtained in corrosive environment (test solution according to ASTM D1384, containing 148 mg/l Na_2SO_4, 165 mg/l NaCl and 138 mg/l $NaHCO_3$) at a strain rate of 10^{-7}/s. The SCC susceptibility was evaluated using the mechanical properties such as elongation to failure (ε_f), reduction in area (RA) and ultimate tensile strength (UTS) both measured in air and in corrosive environment. The reported values are an average of three test results. The SCC susceptibility indices (Iscc) were calculated by taking the ratio of a particular mechanical property obtained from SSRT tests in corrosive environment to its corresponding value in air. The lower the Iscc values the higher is the SCC susceptibility. After testing, the fracture surfaces were examined by scanning electron microscopy (SEM).

It should be pointed out that all values of strain rates given in this paper are nominal ones, based on the elongation measured by a pair of linear variable displacement transducers, LVDTs, which were attached at two opposite sides of the specimen fixtures. These readings were used to control in a feed-back circuit the crosshead speed of the test machine, so that a constant rate of increase in displacement, measured by these LVDTs and according to the selected nominal strain rate, was achieved. Here, a uniform deformation over the entire gauge section of the specimen under test was assumed. The actual strains and hence the actual strain rate at the site of failure, caused by either mechanical rupture or by SCC, could not be measured with the equipment used.

Electrochemical impedance spectroscopy (EIS) was used to study the electrochemical corrosion behavior of the alloy. A typical three electrode system, consisting of samples as working electrode, Pt gauze as counter electrode and Ag-AgCl electrode as a reference electrode was used in the study. EIS was performed between 0.01Hz and 30 kHz frequency range using a frequency response analyzer (Gill AC, ACM Instruments, UK). The experiments were conducted at corrosion potential in ASTM D1384 solution. Salt spray test was carried out in 5% NaCl solution at pH 6.5 for 48 h according to DIN 50021 standard. Prior to the test, the samples were polished with SiC paper up to 2500 grit, washed in distilled water, and ultrasonically cleaned in acetone.

3. Results and discussion

The overview of the cross-section of an FSW AZ31 Mg sample is shown in Fig.1. The different regions such as stir zone (SZ), thermo mechanically affected zone (TMAZ) and base material are shown in Fig. 2(a-c). The base material shows equiaxed grains with some evidence of twins (Fig. 2a). Slightly larger grains were observed in the TMAZ

(Fig.2b) just outside the SZ. However, the SZ exhibited refined grains as compared to the TMAZ and the base material (Fig. 2c). This could be attributed to the dynamic recrystallisation process occurring during friction stir welding [6]. Esparza et al. [7] also reported recrystallized and equiaxed grain structure in the SZ of the FSW AZ31B Mg alloy.

Fig. 3 shows the Vickers hardness values measured across the weld of one of the samples. No significant differences in the hardness values are seen between the two profiles measured across the weldment in the top and bottom region of the specimen. A slight decrease in the hardness values is noticed in the SZ towards the advancing side. In contrast, Esparza et al.[7] reported a slight increase in hardness in the SZ of FSW AZ31B Mg samples, which has been attributed to the relatively high dislocation density in the recrystallized grains. However, in this work detail analysis of the microstructure using transmission electron microscopy was not performed.

Stress-strain curves of the base material and of the FSW AZ31 Mg sample tested in air and in corrosive environment are shown in Figs. 4a and b. The base material tested in air exhibited 37 % ε_f, 46 % RA and 237 MPa UTS. In the tests in corrosive environment, conducted at a nominal strain rate of 10^{-7}/s, the base material showed a significant loss in ductility. Thus, the base material exhibited only 2.3 % ε_f and 7 % RA. The failure stress levels also decreased to 175 MPa due to the exposure to corrosive environment.

The FSW samples tested in air failed in the TMAZ and exhibited lower ductility and strength as compared to that of the base material. The FSW sample showed 9 % ε_f , 19 % RA and 184 MPa UTS. Woo et al. [13] and Park et al. [6] also reported a similar loss in ductility and strength levels in FSW AZ31B and AZ61 alloys, respectively. Park et al. [6] attributed the loss in the mechanical properties in FSW AZ61 to the difference in crystallographic orientation of the grains between the regions.

The macrograph of the FSW sample failed in air is show in Fig. 5a. The figure reveals higher deformation in the edges of the weldment. It can be noticed that the failure of the sample occurred towards the advancing side of the weldment. The cross-sectional view of one part of the failed sample is show in Fig. 5b. The sample was etched to reveal the failure region. The micrograph clearly shows that the failure of the sample occurred in the TMAZ adjacent to the base material.

When tested in corrosive environment at a nominal strain rate of 10^{-7}/s, the FSW samples showed a drastic loss in ductility and in strength. Thus, the alloy exhibited 0.9 % ε_f, 1 % RA and a failure stress of 71 MPa. Fig. 6a shows the macrograph of one of the sample just before the complete fracture of the sample. The figure shows cracking of the sample near the centre region of the weldment. The cross-sectional view of one part of the failed sample is show in Fig. 6b. The etched micrograph reveals that the failure of the sample occurred in the SZ.

The SCC susceptibility indices of base material and FSW samples, calculated based on their respective mechanical properties in corrosive environment / in air are given in Table. 1. The low Iscc (ε_f), and Iscc (RA) values of the base material show their susceptibility to SCC. However, in the FSW sample the Iscc (ε_f), and Iscc (RA) values further decreased as compared to the base material. Moreover, the Iscc (UTS) of FSW sample is significantly lower than that of the base material. This reveals the higher susceptibility of the FSW sample to SCC as compared to the base material.

The SSRT fracture surfaces of the base material tested in air and in corrosive environment are shown in Fig. 7. The base material which failed in air shows fibrous features due to ductile tearing (Fig. 7a). In corrosive environment, the base alloy exhibited typical brittle fracture revealing cleavage facets (Fig. 7b). This type of failure was also earlier observed in AZ31 Mg alloys [10, 11]. The fracture surface of FSW samples tested in air also showed ductile features (Fig. 8) as that of the base material under similar test conditions. However, the fracture surface of FSW samples tested in corrosive environment shows mix mode of failure (Fig. 9a-d). The near edge of the fracture surface shows brittle failure revealing cleavage facets as well as some pitting. The other area of the fracture surface shows predominately transgranular cracking (Fig. 9c), however intergranular cracking was also observed in some areas (Fig. 9b).

The electrochemical impedance spectroscopy results of base material and SZ exposed to ASTM D1384 solution for 2 h and 48 h are plotted in Fig.10a,b shows that the

SZ exhibits a slightly higher electrochemical corrosion resistance (i.e.1x 10^4 ohm. cm^2) than the base material (i.e. 8 x 10^3 ohm. cm^2). The higher electrochemical corrosion resistance of the SZ compared to the base material is also observed after 48h of exposure in the corrosive environment. A macrograph of an FSW AZ31 Mg sample exposed to a salt spray test is shown in Fig. 11. The base region shows severe corrosion whereas the weldment region shows a significant improvement in corrosion resistance. Fig. 12a, b shows the SEM micrographs of base region and SZ, respectively. The base region exhibits large pits whereas SZ shows no such pitting morphology. A large reduction in the thickness was observed in the base region as compared to the weldment. This further confirms the higher corrosion resistance of the SZ as compared to the base material which could be due to the finer grain size [14].

It is interesting to note that, although the SZ exhibited higher general corrosion resistance than the base material, the samples failed in the SZ during SSRT tests in corrosive environment. The probability of the FSW samples to fracture in the weldment is high due to the slightly lower hardness values observed in the weldment. Accordingly, the FSW samples failed in the weldment in both the test environments i.e., air and corrosive environment. However, what makes the difference is that in air tested samples the failure location was in the TMAZ towards the advancing side of the weldment whereas in corrosive environment the failure location was in the SZ. Slightly lower hardness values observed in the advancing side as compared to the retreating side of the weldment could have caused such a failure in air tested samples. However, it is not clear whether the shift in the failure location to SZ in the corrosive environment is due to its higher SCC susceptibility. In fact, according to the Iscc indices, the FSW samples exhibit higher SCC susceptibility as compared to the base material. In addition, the fracture surface of the FSW samples also showed intergranular cracking in addition to the transgranular cracking occurring predominantly in the base material. The intergranular cracking could be due to the hydrogen assisted grain boundary decohesion. It should also be noted that the SZ exhibited higher general corrosion resistance than the base material, hence, the probability of anodic dissolution assisted cracking in the SZ is less. Thus, the hydrogen assisted cracking could be a reason for the higher SCC susceptibility of the FSW AZ31 Mg samples. A literature review shows that the SZ usually exhibits higher dislocation density than the base material [6, 7]. This higher dislocation density can accelerate the hydrogen embrittlement susceptibility as observed in high strength Al alloys [15, 16]. In fact, Kuramoto et al. [17] reported an accelerated diffusion of hydrogen by dislocation motion causing brittle stress corrosion cracking in AZ31 Mg alloy. However, another point to be noted from the literature is that increased dislocation density in SZ increases the hardness [7]. But in this study, the hardness value in the weldment is slightly lower than that of the base material. Hence, further work has to be carried out in order to substantiate the mechanistic understanding of the cracking phenomenon in FSW samples.

4. Conclusions

The SSRT experimental results showed higher SCC susceptibility of the friction stir welded (FSW) AZ31 Mg samples compared to the base material. The failure of the FSW samples occurred in the stir zone (SZ) when tested in corrosive environment, in contrast to the failure in the thermo mechanically affected zone (TMAZ) observed in tests in air.

However, electrochemical impedance spectroscopy (EIS) and salt spray test results showed a higher general corrosion resistance of the SZ compared to the base material. Hydrogen assisted cracking could be a reason for higher SCC susceptibility of the FSW AZ31 Mg samples compared to the base material.

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References

[1] A. Weisheit, R. Galun, B.L Mordike , Welding J. 77 (1998) 149s.

[2] S. Jüttner, Weld Met. Fabr. 66 (1998) 11.

[3] W.M. Thomas, U.S. Patent No. 5, 460, 317.

[4] B. London, M. Mahoney, W. Bingel, M Calabrese, R.H. Bossi, D. Waldron, in: Proceedings of Friction Stir Welding and Processing II, TMS Annual Meeting, San Diego, California, 2003.

[5] R. Zettler, A.C. Blanco, J.F. dos Santos, S. Marya, in : N.R. Neelameggham, H.I. Daplan, B.R. Powell (Ed.), Magnesium Technology, TMS (The Minerals, Metals & Materials Society), 2005.

[6] S.H.C. Park, Y.S. Sato, H. Kokawa, Scripta Mater. 49 (2003) 161.

[7] J. A. Esparza, W.C. Davis, E.A. Trillo, L. E. Murr, J. Mater. Sci. Letters 21 (2002) 917.

[8] E. Ghali, W. Dietzel, K.U. Kainer, J. Mater. Eng. Performance 13 (2004) 7.

[9] N. Winzer, A. Atrens, G. Song, E. Ghali, W. Dietzel, K.U. Kainer, N. Hort, C. Blawert, Adv. Eng. Mater. 7 (2005) 659.

[10] R.G. Song, C. Blawert, W. Dietzel, A. Atrens, Mater. Sci. Eng. A 399 (2005) 308.

[11] M. Bobby Kannan, W. Dietzel, C. Blawert, S. Rikher, M. Kocak, Mater. Sci. Eng. A, (2006), doi:10.1016/j.msea.2006.08.075

[12] A. Von Strombeck, C. Schilling, J.F. dos Santos, in Proceedings of the 2nd International Symposium on Friction Stir Welding, Gothenburg, Sweden, 2000.

[13] W. Woo, H. Choo, D.W. Brown, P.K. Liaw, Z. Feng, Scripta Mater. 54 (2006) 1859.

[14] G. Abbas, Z. Liu, P. Skeldon, Appl. Surface Sci. 247 (2005) 347.

[15] M.Talianker, B. Cina, Metall. Trans. A 20 (1989) 2087.

[16] M. Bobby Kannan, V. Raja, A.K. Mukhopadhyay, Scripta Mater. 51 (2004) 1075.

[17] S. Kuramoto, I. Araki, M. Kanno, J. Japan Institute of Light Metals 51 (2001) 397.

Table 1

SCC susceptibility indices calculated by taking the ratio of a particular mechanical property obtained from SSRT tests in corrosive environment to its corresponding value in air.

Sample	Iscc (ε_f)	Iscc (RA)	Iscc (UTS)
Base material	0.06	0.15	0.73
FSW	0.01	0.05	0.38

Figure captions

Fig. 1. Cross-sectional view of an FSW AZ31 Mg sample. Note: (a), (b) and (c) corresponds to base material (BM), thermo mechanically affected zone (TMAZ) and stir zone (SZ), respectively.

Fig. 2. Optical micrograph of (a) base material (b) TMAZ and (c) SZ of FSW AZ31 Mg sample.

Fig. 3. Vickers hardness values (0.5 mm removed from top and bottom of plate surface) as measured across the FSW AZ31 Mg sample with 0.5 mm indent spacing. Note: The average hardness of the base material measured i.e., 60 HV0.2.

Fig. 4. Stress-strain curves of (a) base material and (b) FSW AZ31 Mg sample, measured in air and in ASTM D1384 solution (corrosive environment).

Fig. 5. FSW AZ31 Mg sample failed during SSRT test in air (a) macrograph and (b) micrograph, shows failure in the TMAZ.

Fig. 6. FSW AZ31 Mg sample failed during SSRT test in ASTM D1384 solution (a) macrograph and (b) micrograph, shows failure in the SZ.

Fig. 7. Fracture surfaces of base AZ31 Mg sample tested in (a) air and in (b) ASTM D1384 solution.

Fig. 8. Fracture surfaces of FSW AZ31 Mg sample tested in air.

Fig. 9. Fracture surfaces of FSW AZ31 Mg sample tested in ASTM D1384 solution, (a) overview of the fracture surface (b) edge of the fracture surface showing pitting (c) intergranular cracking, and (d) transgranular cracking .

Fig. 10. Electrochemical impedance spectroscopy plots of the base material and the SZ of FSW AZ31 Mg sample exposed to ASTM D1384 solution for (a) 2 h and (b) 48 h.

Fig. 11. Macrograph of FSW AZ31 Mg sample exposed to salt spray test.

Fig. 12. SEM micrographs of (a) base region (c) SZ of FSW AZ31 Mg sample exposed to salt spray test.