CORROSION PROPERTIES IN FRICTION STIR WELDED 304 AUSTENITIC STAINLESS STEEL

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ABSTRACT

A 304 austenitic stainless steel was friction stir welded using polycrystalline cubic boron nitride (PCBN) tool. Relationship between corrosion properties and microstructure was examined in the weld using several corrosion tests and microstructural observation techniques. The stir zone (SZ) had better corrosion properties than the base material (BM). The corrosion tests showed that the intergranular corrosion was developed in the heat-affected zone (HAZ) compared to the BM and SZ although the grain boundaries were not severely corroded. TEM/EDS analysis revealed that Cr depletion zone near grain boundary in the HAZ was shallow and narrow. Friction stir welding (FSW) suppressed sensitisation in the HAZ, which could be explained by short duration at sensitisation temperatures during welding. On the other hand, many grain boundaries were deeply corroded in the AS, where the corrosion resistance was significantly degraded. The microstructural observation revealed that sigma phase was formed in the AS during FSW. Sigma formation produced the wide and deep Cr depletion zone with the minimum Cr content less than 12 wt % in the vicinity of the grain boundary in the AS, which severely deteriorated the corrosion resistance in the AS.

IIW Thesaurus keywords: *Friction stir welding; Friction welding; GTA welding; Arc welding; Gas shielded arc welding; Austenitic stainless steels; Stainless steels; Steels; Microstructure; Corrosion; Comparisons; Practical investigations; Reference lists.*

1 INTRODUCTION

Austenitic stainless steels are widely used in many industries utilizing high temperature components such as heat exchangers and chemical reactors because of their good mechanical properties at elevated temperatures and their excellent corrosion resistance. However, when an austenitic stainless steel is welded, its heat-affected zone (HAZ) is often sensitised by formation of intergranular Cr-rich carbides, which deteriorates the corrosion properties of the welded joint. Since the formation of the Cr carbides is caused by exposure to the temperature range of 773 to 1 073 K, rapid cooling in the welding cycle is preferable for prevention of sensitisation. Friction stir welding (FSW), which is a relatively new solid state joining process and has been the focus of constant attention in joining low and high temperature materials [1-25], holds promise as an effective method of suppressing development of sensitisation in HAZ because it is a low heat input welding process.

In a previous study [26], Park *et al*. examined the microstructural evolution in a friction stir welded (FSWed) 304 stainless steel and reported that small sigma phases are rapidly formed along the grain boundaries in the advancing side of the stir zone having a dynamically recrystallised grain structure. Generally, sigma formation in austenitic stainless steels deteriorates the corrosion resistance [27], but the effect of the local small sigma formation on corrosion properties in the FSWed 304 stainless steel has not yet been clarified.

The objective of the present study was to evaluate the corrosion properties of an FSWed 304 stainless steel, especially the advancing side of the stir zone and the HAZ. Corrosion properties of these regions were investigated using the ferric sulfate-sulfuric acid test and the double-loop electrochemical potentiokinetic reactivation (DL-EPR) test, and corrosion properties of the HAZ were compared with those in a gas tungsten arc (GTA) weld.

2 EXPERIMENTAL PROCEDURES

The base material was a 6 mm-thick 304 austenitic stainless steel, whose chemical composition (wt %) was 18.10 Cr, 8.56 Ni, 0.59 Si, 1.08 Mn, 0.040 C, 0.032 P

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and 0.003 S. A bead-on-plate friction stir (FS) weld was produced on the base material plate at a travel speed of 1.33 mm/s and a rotational speed of 550 rpm using a polycrystalline cubic boron nitride (PCBN) tool with a length of 4.75 mm [28]. The welding processes used for the present study, including the welding equipment and the other FSW parameters, were the same as those for a previous study [26].

Corrosion resistance in the as-welded specimen containing both the base material and the stir zone was qualitatively examined by a ferric sulfate-sulfuric acid test for 72 h. Since the specimen for this test had dimensions of $10^W \times 40^L \times 6^T$ mm, two cross sections perpendicular to the welding direction, the top surface and the bottom surface of the weld were in contact with the test solution during the test. The tested specimens were observed by optical microscopy (OM) and scanning electron microscopy (SEM). The corrosion resistance in the HAZ of the FS weld was compared to that in the HAZ of the GTA weld by the DL-EPR test. The bead-on-plate GTA weld was made on a base material plate in an Ar atmosphere at a welding current of 300 A and a travel speed of 0.67 mm/s. Depth of the fusion zone was roughly the same as that of the stir zone in the FS weld.

Detailed microstructures were observed by transmission electron microscopy (TEM). Thin disks for TEM with a diameter of 3 mm were cut from various locations of the weld using an electrical-discharge machine and were electrolytically polished in a 10 % perchloric acid + 90 % ethanol solution. The thin foils were observed at 200 kV using a JEOL-2000EXII transmission electron microscope (TEM) and a Philips CM200FEG TEM equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis system, using a 0.6 nm electron probe with a spatial resolution of 1.2 nm. The grain boundary plane was aligned as parallel as possible with both the incident electron beam and the direction of the X-ray detector.

3 RESULTS AND DISCUSSION

3.1 Corrosion resistance in FSWed 304 stainless steel

Figure 1 (a) shows the cross section perpendicular to the welding direction in an FSWed 304 stainless steel after the ferric sulfate-sulfuric acid test. The weld was classified into four characteristic regions, i.e., base material (BM), HAZ, stir zone (SZ) and advancing side of the stir zone (AS), which are indicated as BM, HAZ, SZ and AS, respectively, in Figure 1 (a). The sensitised region of the HAZ can be faintly observed in the cross section. The AS is remarkably corroded and has the worst corrosion resistance in the weld. A cross section perpendicular to the welding direction of the 304 GTA weld after the ferric sulfate-sulfuric acid test is also shown in Figure 1 (b). The sensitised region of the HAZ is distinctly located further outside the fusion zone (FZ), and the width of the sensitised region is much larger than that in the FS weld.

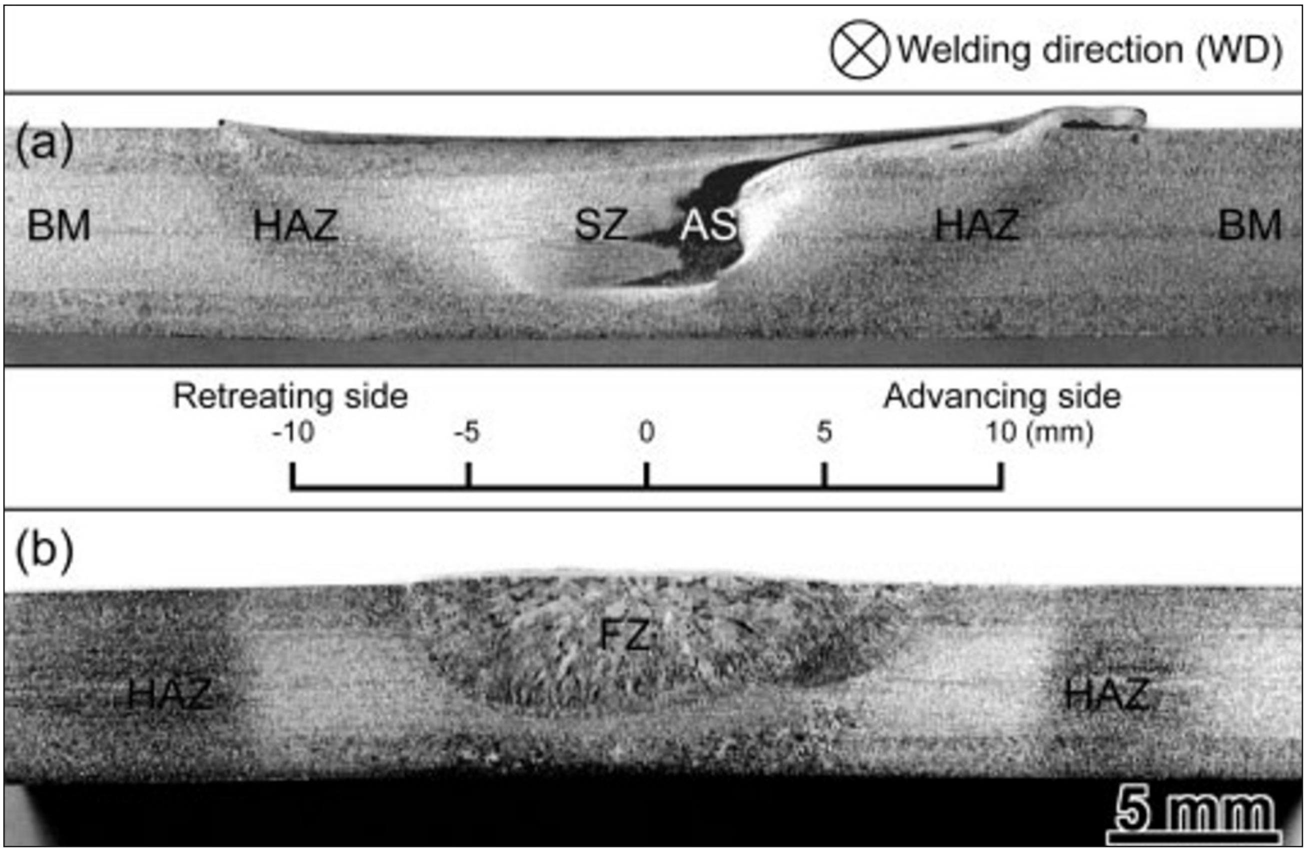

Figure 1 – Cross sections perpendicular to the welding direction after application of ferric sulfate-sulfuric acid in the FS weld (a) and GTA weld (b)

SEM images in these regions are indicated in Figure 2 (a)-(e). The BM has some grooved grain boundaries and pits after the ferric sulfate-sulfuric acid test, as shown in Figure 1 (a), because the base material often contains some amount of Cr-rich carbides and residual ferrites. The SZ has better corrosion resistance than the BM, as shown in Figure 2 (c). This suggests that Cr-rich carbides and residual ferrites pre-existing in the BM are dissolved in the matrix during formation of recrystallised grains in FSW. The HAZ has more corroded grain boundaries than the BM and SZ, as represented in Figure 2 (b). However, the degree of the corrosion in the HAZ of the FS weld is much lower than that in the HAZ of the GTA weld [see Figure 2 (e)]. Figure 2 (d) shows deeply grooved grain boundaries in the AS and a very slightly corroded region outside the AS. The SEM image suggests that the corrosion resistance is significantly degraded in the AS.

In order to quantitatively evaluate distribution of corrosion resistance in the weld, the DL-EPR test was carried out for the four above-mentioned regions. The reactivation current ratio was determined by the ratio of the maximum current in the reactivation loop, I_r, to that in larger anodic loop, I_a [29], and the higher current ratio means that more grain boundaries have larger Cr depletion. The current ratios in the BM, HAZ, SZ and AS in the FS weld obtained by the DL-EPR test are indicated in Figure 3. The current ratio in the HAZ of the GTA weld is also included in this figure. The BM and SZ show low current ratios, which indicates that the grain boundaries having Cr depletion hardly exist in the BM and SZ. The HAZ shows a slightly higher current ratio than the BM and SZ. It should be noted that the current ratio in the HAZ of the FS weld is approximately one-third of that in the HAZ of the GTA weld. This result indicates that the corrosion resistance in the HAZ of the FS weld is much superior to that in the HAZ of the GTA weld. On the other hand, the AS has a much higher current ratio, about 5 %, than the other regions. This high current ratio can be attributed to Cr depletion due to the presence of the sigma phase, as mentioned above. The effect of the

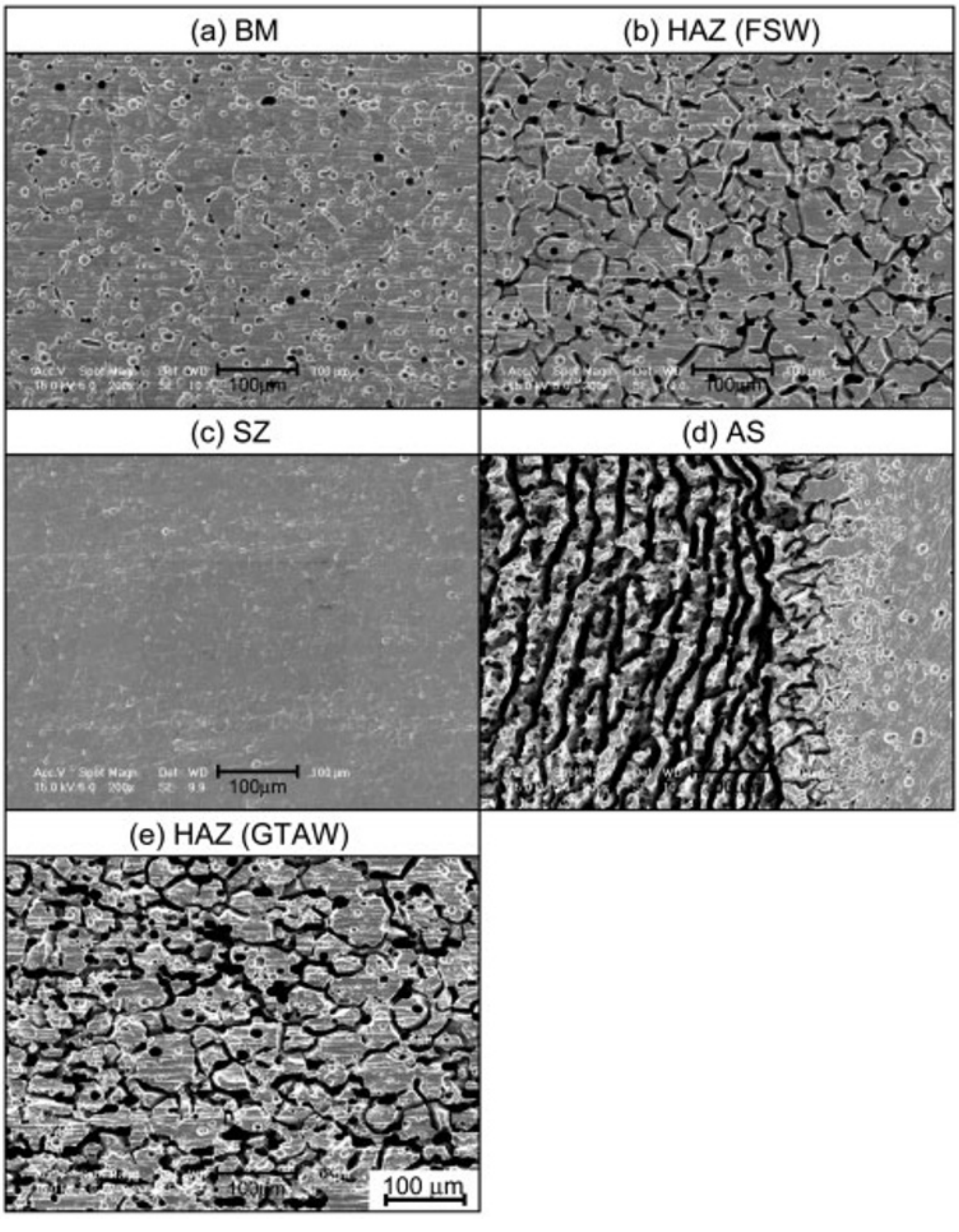

Figure 2 – SEM images of several regions indicated in Figure 1

sigma phase on corrosion properties in the FS weld is discussed in section 3.3.

3.2 Sensitisation in the HAZ

A slightly higher current ratio was detected in the HAZ of the FS weld (see Figure 3), although the grain boundaries were not severely corroded [see Figure 2 (b)]. TEM images in the sensitised region of the HAZ are shown in Figure 4 (a) and (b). A small amount of Cr-rich carbides smaller than 100 nm in length are observed along the grain boundaries. Figure 4 (d) shows the Cr content profile along the dotted line in Figure 4 (b) measured by the EDS system. A shallow, narrow Cr depletion developed near the grain boundary in the sensitised region. The minimum Cr content was about 16 wt % in the vicinity of the grain boundary. Based on electron diffraction Kikuchi patterns, the grain boundary misorientation analysis showed that the grain boundary in Figure 4 (b) was a general high angle boundary (random boundary). The smaller Cr depletion in the present HAZ is not attributed to reasons of grain boundary energy, although special low energy boundaries, typically coincidence site lattice (CSL) boundaries, have Cr depletions which are much smaller than those of random boundaries [30-32].

It is well known that exposure to the temperature range between 823 and 1073 K leads to precipitation of Cr-rich carbides directly associated with sensitisation in austenitic stainless steels. Since formation of Cr-rich carbides accompanies diffusion of Cr atoms to grain boundaries, the shorter exposure time to the sensitization temperatures reduces the amount of Cr-rich carbides formed on the grain boundaries. Using K-type thermocouples, in previous studies [25-26], the temperature hysteresis during FSW of a 304 stainless steel under the same FSW parameters as in the present study was measured. According to the temperature hysteresis, the

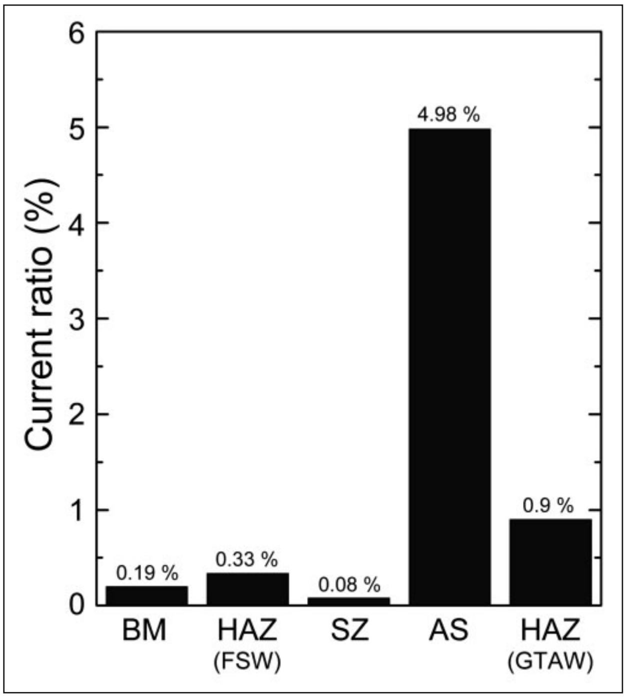

Figure 3 – Reactivation current ratios in the base material, the heat-affected zone in the FS weld, the stir zone, the advancing side of the stir zone and the heat-affected zone in the GTA weld

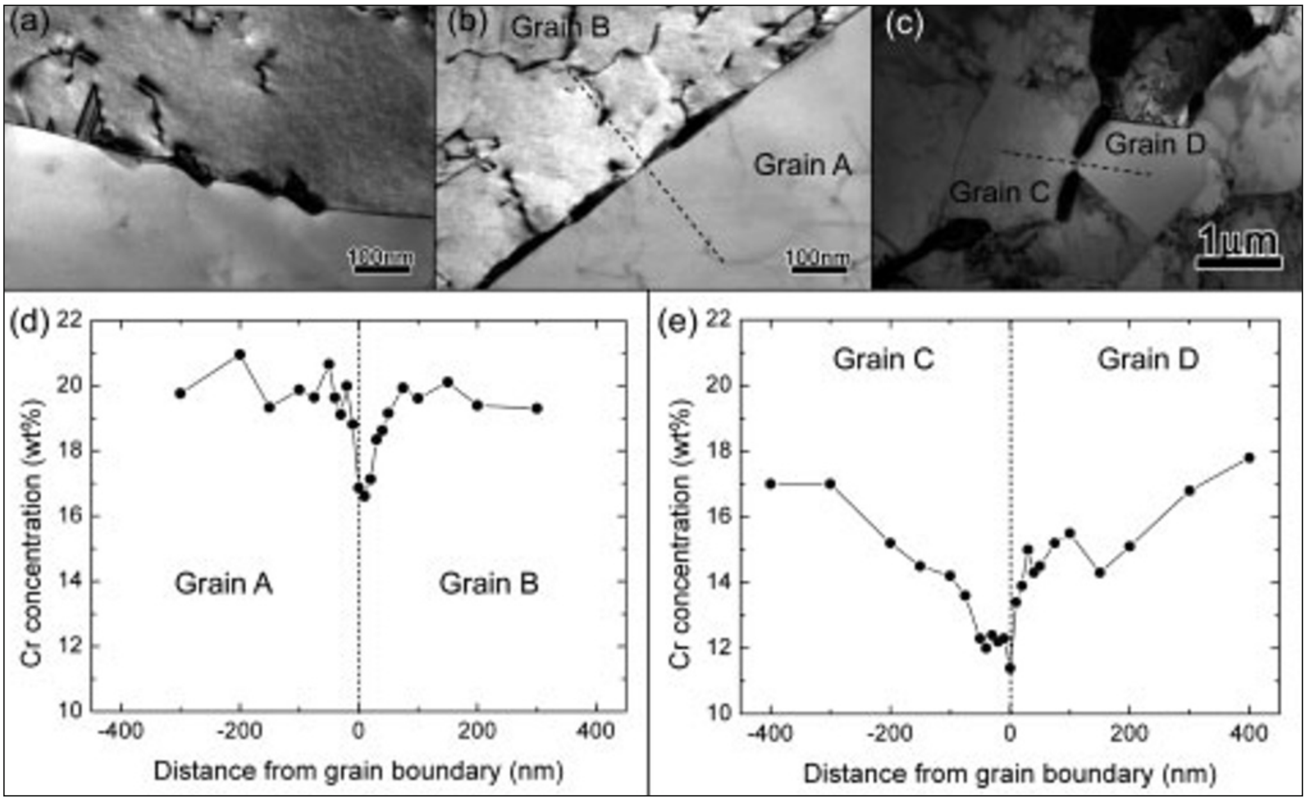

Figure 4 – TEM images and Cr content profiles near grain boundaries by EDS analysis in the HAZ and the advancing side of the stir zone

exposure time to the sensitisation temperature range was estimated to be about 18 s in the HAZ of the FS weld. A conventional GTA weld of comparably sized fusion zone to the FS weld stir zone would be expected to dissipate more heat. Therefore the HAZ of the GTA weld would have a longer duration in the sensitisation temperature range. The actual temperature hysteresis of the HAZ of the GTA weld using K-type thermocouples showed approximately 5 times longer duration in the sensitisation temperature range than that of the FS weld. This should lead to more extensive corrosion of HAZ grain boundaries in the GTA weld as compared to those of the FS weld.

3.3 Effect of sigma formation on corrosion resistance in the FS weld

FSW hardly resulted in sensitisation in the HAZ, but the corrosion resistance was significantly reduced in the AS. A TEM image of the AS is shown in Figure 4 (c). This figure reveals that relatively large particles, 500-1 000 nm in length, are formed on the grain boundaries in the AS. A previous study [26] determined that those particles, having a band or lamellar structure, observed along grain boundaries in the AS are sigma phase. A profile of Cr content measured by EDS along the dotted line indicated in Figure 4 (c) in the AS is shown in Figure 4 (e). A widely and deeply Cr-depleted zone with minimum Cr content less than 12 wt % is created in the vicinity of the grain boundary in the AS. The grain boundary in the AS was a general high angle (random) boundary.

Park *et al*. [26] have suggested that the sigma phase can be rapidly formed by the transformation of austenite to delta-ferrite at high temperatures and the subsequent decomposition of the ferrite under the high strain and recrystallisation induced by friction stirring. At such high temperature and strain conditions, the mutual diffusion between Cr and Fe in the austenite matrix can be promoted in a very short time, so that Cr content would be reduced near grain boundaries having the sigma phases. As shown in Figure 3 (c), a fine recrystallised grain structure is formed in the AS [26]. Since the grain boundary acts as a high diffusivity path [33], it is likely that grain boundary diffusion of Cr rapidly occurs between the fine grains so as to form the sigma phase rapidly in the AS. This probably causes a deep Cr depletion at the grain boundary in the AS. Additionally, the fine grains contain relatively many dislocations introduced by dynamic recrystallisation during FSW in the AS. Dislocation also acts as a diffusion path [34], so that intragranular diffusion would be also promoted during FSW. Such diffusion may be a reason why the sigma phase widely produces Cr depletion near the grain boundary for a short time during FSW. Grain boundary migration enhanced by high strain in the SZ can also result in a wide Cr depletion region [35]. The largely degraded corrosion resistance in the AS is due to the wide and deep Cr depletion produced by formation of the sigma phase during FSW.

4 CONCLUSION

Corrosion properties were evaluated in an FSWed 304 stainless steel. FSW led to a relatively low degree of sensitisation in the HAZ, which could be explained as being due to the short duration of sensitisation temperatures. However, many grain boundaries were deeply corroded in the advancing side of the stir zone. The severely deteriorated corrosion resistance was attributed to the formation of the sigma phase during FSW.

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