The influence of pre-plating on the LME phenomenon of advanced high strength steel

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Abstract: The galvanized steel plate is developed to protect the car from corrosion. During the resistance spot welding, the liquid metal embrittlement (LME) phenomenon occurs because of the lower melting temperature of zinc, then the melted Zn would get penetrating into the austenite grain boundaries which would cause the LME embrittlement. The high-temperature three-point tests at 600°C, 1 mm/min could be used as experimental simulation procedure. The pre-plating technology has been used to improve the LME resistance property of the galvanized steel. It could be found from the microstructure analysis that the pre-plating Ni technology could partly solve LME issue.

1. Introduction
Reducing fuel consumption, as well as the exhaust emissions calls the lightweight of vehicle. Therefore, the usage of the ultra-high strength steel has been promoted [1]. The advanced high-strength steels (AHSS) widely used in body in white could enhance the safety and crashworthiness [2]. There are some factors, such as the industrial pollution, solar radiation, marine air and the road anti-skid salt, leading to the acceleration of the vehicle body corrosion. Hot-dip galvanized coatings could provide both the barrier protection and the sacrificial protection on steels. Therefore, the high strength galvanized steel could meet the requirement for the excellent corrosion resistance.

As the galvanized steel take up a very high percent usage, the welding failure issue should be paid more attention. The melting temperature of Zn is around 420°C, and the vaporization temperature of Zn is around 907°C. Due to the low melting temperature of Zn and Fe-Zn intermetallic compounds, most of the Zn or Zn-alloy coatings would partially turn to liquid at the austenitizing temperature. The melted Zn appears to penetrate into the austenite grain boundaries causing an embrittlement characterized by surface crack formation under the influences of high temperature and complex stress, leading to the phase-transformation of austenite to ferrite [3]. The penetration of Zn is the main reason causing embrittlement, which called liquid metal embrittlement (LME)[4]. The brittle intermetallic compound Y phase Fe3Zn10 formed during the resistance spot welding is found to be the main reason for the LME. Furthermore, the welding stress promotes the occurrence of the LME micro-cracks. J.K. Chang and C.S. Lin [2] have studied the 11Al-3Mg-Zn ternary alloy-coated hot stamping steels, found that. N. Ding et.al [5] mentioned that the compressive stress produced by the nitriding layer on the surface prevents the expanding of the LME micro-cracks between grain-boundaries. However, once this compressive stress is easily affected by the external or vibration force, then the multiple-sites LME micro-cracks begin to expand rapidly. J. La and M. Song et al. [6] found that adding Mg in the
galvanizing process to form Mg2Zn11 and MgZn2 could improve the melting temperature of the surface layer. But it still could not solve the LME problem in the spot welding process.

The micro-cracks found in the resistance spot welded AHSS could be attributed to tensile-stress corrosion by liquid zinc that penetrate into the grain boundaries of the substrate [7, 8]. The LME cracks degraded the mechanical properties of the high strength steel [3, 9]. The reliability and mechanical performance of the welds are affects with the growth of these cracks by the vibrations of the automobiles [10]. Thus, the LME problem should be solved. Because the Ni could improve the LME resistance of the galvanized steel, we used pre-plating technology to add Ni pre-plating film before galvanized.

2. Experimental methods

2.1. Spot-welding and Microstructure
The material used in this research is DP980. The two series of samples used in the welding tests are high and low yield-point (YP) samples. The resistance spot welding (RSW) equipment used in this study is OBARA DB-220 stationary inverter welding machine with 6mm tip diameter Cu-Cr dome radius (DR) type electrode. In this research, we should firstly choose a specific spot-welding parameter routine, to study the LME phenomenon. The welding parameters is listed in Table 1. Then the welded samples are cross sectioned, mounted and then polished. The LME cracks have been investigated by the field-emission electron probe microanalysis (FE-EPMA).

| Number | Current/kA | Pressure/kN | Welding time/ms | Holding time/ms | LME cracks |
|--------|------------|-------------|-----------------|-----------------|------------|
| L/H 1  | 6          | 4           | 320             | 200             |            |
| L/H 2  | 7          | 4           | 320             | 200             |            |
| L/H 3  | 8.2        | 4           | 320             | 200             | √          |
| L/H 4  | 8.2        | 4           | 320             | 200             | √          |

2.2. Mechanical properties test
After welding, the samples were undergoing two types of mechanical properties tests to evaluate the properties of the welding-spot, the cross-tensile test and shear test. The cross-tensile test has been employed to evaluate the 6, 7, 8.2 kA samples, while the shear test has been used to evaluate the 8.2 kA sample.

2.3. The high-temperature three-point bending
In this paper, the high-temperature three-point bending has been used to simulate the LME phenomenon during the RSW process. The parameters are shown in table 2.

| No. | Temperature/ºC | Strain Rates | Bending/mm | LME cracks |
|-----|----------------|--------------|-------------|------------|
| 1   | 600            | 1mm/min      | 4           | √          |
| 2   | 700            | 1mm/min      | 4           |            |
| 3   | 800            | 1mm/min      | 4           |            |
| 4   | 800            | 1mm/s        | 4           |            |

2.4. Pre-plating Ni
This technology pre-plates Ni before galvanizing (GI). The solution of pre-plating Ni is 120 g/L NiSO4ꞏ7H2O, 8g/L NaCl, 30g/L orthoboric acid, 60 g/L Na2SO4, and 0.5 g/L lauryl sodium sulfate.
3. Results and discussion

3.1. Microstructure and welding morphology

The original microstructure of DP980 is consisted of ferrite and martensite-austenite islands. The percentage of martensite-austenite islands represents the mechanical property. The following Figure 1 shows the internal defects of GI plate after spot-welding. From Figure 2, it could be found that there are many LME micro-cracks in the welding joint shoulder welded under 8.2 kA. The highest peak temperature and effective stress in the RSW process determine the position of LME cracks. The coating layer of biphasic Fe-Zn ferrite/liquid zinc structure [11] formed in the RSW would lead to the LME-induced cracking.

Figure 1. Internal defects of GI plate after spot-welding

| Cr  | Mn  | Fe  | Zn  |
|-----|-----|-----|-----|
| 0.10| 0.91| 36.89| 2.68|
| 0.06| 0.80| 22.27| 1.53|
| 0.12| 2.57| 61.58| 0.85|
| 0.23| 1.63| 79.64| 0.18|

Figure 2. The welding morphology of DP980 under 8.2 kA

3.2. The elements distribution along LME cracks

It could be found from Figure 3 that the LME crack is about 50µm, and Zn and O elements distribute along LME cracks. Then it could be verified that in the RSW process, the LME cracks are mainly caused by the melted Zn. Around the welding spot shoulder, the temperature range would be room temperature to 1000°C from base metal to the spot centre. At the position which temperature is higher than 420°C, Zn would get melted and decline along austenite grain boundaries, then there would be LME cracks under the tensile stress during the welding cooling process. It is reported that the LME firstly causes multiple-sites of intergranular micro-cracks, and then turns to transgranular fracture during the high speed crack propagation [5]. The liquid Zn penetrates into the steel matrix by a process of grain boundary decohesion [12], leading to the grain-boundary micro-cracks. Around 600°C, Zn is easily to form intermetallic compound, brittle Fe$_3$Zn$_{10}$ phase. Besides, as the electrode is made of Cu-Cr alloy, the liquid Zn could also form the Cu$_5$Zn$_8$ brittle phase when touching with the electrode under pressure stress and high temperature in the resistance spot welding process [13]. The brittle phases Fe$_3$Zn$_{10}$ and Cu$_5$Zn$_8$ would all be the weak position in the following cooling process. The shrinkage of the material will lead to the inner-tensile stress, leading to the LME micro-cracks. The austenitic microstructure has been investigated to be more sensitive to liquid metal embrittlement and particularly to liquid Zn embrittlement [14]. In DP steel, the temperature at which austenite starts to form is about 720°C, and microstructure is fully transformed to austenite at about 810°C. The austenite is formed to make the steel sensitive to liquid zinc embrittlement [15]. Furthermore, the retained austenite already inside during heating would also contribute to the occurrence of LME.
3.3. Mechanical properties
The evaluation results of the mechanical properties of welded samples are shown in Figure 4, in which Figure 4a shows cross-tensile test results and Figure 4b shows shear test results. The cross-tensile test results show that the higher current sample possesses the higher strength, but the one is also tends to have the LME cracks. The residual stress is higher in the high YP sample than in the low YP one. Since LME is sensitive to the residual stress, the tensile strength \( F_m \) of high YP sample is lower than the low YP one (Figure 4a). And the difference value between the high and low YP sample increases with the increase of the welding-current. As for the shear strength (Figure 4b), the dispersion of the shear strength value of the high YP sample is bigger than that of the low YP sample. The reason is attributed to the unstable residual stress of the high YP sample.

3.4. The high-temperature three-point bending simulation
In this study, the three-point bending tests are employed to simulated the LME phenomenon during RSW process through different strain rate under 600、700、800°C. Different strain rates have been used to study the simulation effect of the high-temperature three-point tests. Among the samples obtained by different parameters, the sample under 600°C, 1 mm/min has the apparent LME cracks (shown in Figure 5). At 700 and 800°C, the Zn and Zn-intermetallic alloy layer on top of samples would become vapor. In Figure 5, it could be obviously seen the Zn element distribute along the grain.
boundaries. Therefore, this high-temperature three-point tests at 600°C, 1 mm/min could be used as experimental simulation procedure.

Figure 5. The microstructure of high-temperature three-point bending sample under 600°C, 1mm/min

3.5. The Ni pre-plating

Figure 6 shows the welding morphology of sample without Ni-layer and the pre-plating sample. The interface of the without Ni-layer welding plate displays roughly (Figure 6a). And there is no Zn layer left. The surface of the molten metal in the nugget will bend and shaped into spherical surface [16, 17]. The pressure in molten metal would force the liquid penetrating into austenite grain boundaries. Comparatively, Figure 6b shows the morphology of Ni pre-plating sample. The interface looks smooth after welding. And there is still Zn layer left on the top surface. The penetration of Zn in Figure 6b has been reduced to about 10 μm, which distributes homogeneously, and there are not large cracks. The pre-plating layer are highly suitable for avoiding LME based on their high thermal stability and their specific solid alloying process [18]. Ashiri et al. [19, 20] also find that the Zn-Ni alloy coating sample has the lowest LME susceptibility compared with other different coated samples. The pre-plating Ni layer is expected to prevent the penetration of Zn. It could be concluded that the pre-plating technology could be used to reduce the LME sensitivity.

Figure 6. The comparison of the Ni, (a) LME cracks, (b) Ni pre-plating

4. Conclusion

After the pre-plating technology, the LME resistance is improved. Based on the above analysis, the conclusions could be found as follows,

(1) The melted Zn penetrates along austenite grain boundaries;
(2) The high-temperature three-point tests at 600°C, 1 mm/min could be used as experimental simulation procedure;
(3) The penetration of Zn has been reduced after pre-plating Ni;
(4) The pre-plating technology could be used to reduce the LME sensitivity.

References:
[1] Q. Wu, L.Y. Xu, (2013) Study on Quality Control of the Laser Welding Joint, Appl. Mech. Mater., 442: 276-281.
[2] J.K. Chang, C.S. Lin, (2017) Microstructural Evolution of 11Al-3Mg-Zn Ternary Alloy-Coated Steels During Austenitization Heat Treatment, Metall. Mater. Trans A, 48A: 3734-3744.
[3] C.W. Lee, W.S. Choi, L. Cho, et al., (2015) Liquid-Metal-Induced Embrittlement Related Microcrack Propagation on Zn-coated Press Hardening Steel, ISIJ Int., 55: 264-271.

[4] L.G. Wang, T. Zhou, Y. Huang, (2014) Zinc Coating Failure Analysis and Sheet Formability during Hot-Dip Galvanized Sheet Stamping, Key Eng. Mater., 575-576: 501-514.

[5] N. Ding, N. Xu, W.M. Guo, et al., (2016) Liquid metal induced embrittlement of a nitrided clutch shell of a motorbike, Eng. Fail. Anal., 61, 54-61.

[6] J.H. La, M.G. Song, H.K. Kim, et al., (2018) Effect of deposition temperature on microstructure, corrosion behavior and adhesion strength of Zn-Mg coatings on mild steel, J. Alloys Compd, 739, 1097-1103.

[7] M. Takahashi, M. Nakata, K. Imai, et al., (2017) Liquid Metal Embrittlement of Hot Stamped Galvannealed Boron Steel Sheet–Effect of Heating Time on Crack Formation, ISIJ Int., 57, 1094-1101.

[8] J. Frei, M. Rethmeier, (2018) Susceptibility of electrolytically galvanized dual-phase steel sheets to liquid metal embrittlement during resistance spot welding, Welding in the World, 62, 1031-1037.

[9] H. Kang, L. Cho, C. Lee, et al., (2016) Zn Penetration in Liquid Metal Embrittled TWIP Steel, Metall. Mater. Trans. A, 47A, 2885-2905.

[10] R. Ashiri, M. Shamanian, H.R. Salimijazi, et al., (2016) Liquid metal embrittlement-free welds of Zn-coated twinning induced plasticity steels, Scr. Mater., 114, 41-47.

[11] A. Pradeep, P. Priyadharsini, G. Chandrasekaran, (2011) Structural, magnetic and electrical properties of nanocrystalline zinc ferrite, J. Alloys Compd, 509, 3917-3923.

[12] C.W. Lee, D.W. Fan, I.R. Sohn, et al., (2012) Liquid-Metal-Induced Embrittlement of Zn-Coated Hot Stamping Steel, Metall. Mater. Trans. A, 43, 5122-5127.

[13] Y.G. Kim, I.J. Kim, J.S. Kim, et al., (2014) Evaluation of Surface Crack in Resistance Spot Welds of Zn-Coated Steel, Mater. Trans., 55, 171-175.

[14] C. Beal, (2011) Mechanical behaviour of a new automotive high manganese TWIP steel in the presence of liquid zinc. INSA de Lyon Publishing, The Lyon.

[15] E. Tolf, J. Hedegard, A. Melander, (2013) Surface breaking cracks in resistance spot welds of dual phase steels with electrogalvanised and hot dip zinc coating, Sci. Technol. Weld. Joining, 18, 25-31.

[16] G. Jung, I.S. Woo, D.W. Suh, et al., (2016) Liquid Zn Assisted Embrittlement of Advanced High Strength Steels with Different Microstructures, Met. Mater. Int., 22, 187-195.

[17] D. Kim, J.H. Kang, S.J. Kim, (2018) Heating rate effect on liquid Zn-assisted embrittlement of high Mn austenitic steel, Surf. Coat. Technol., 347, 157-163.

[18] J.K. Chang, C.S. Lin, (2017) Microstructural Evolution of 11Al-3Mg-Zn Ternary Alloy-Coated Steels During Austenitization Heat Treatment, Metall. Mater. Trans A, 48A, 3734-3744.

[19] J. Kondratiuik, P. Kuhn, E. Labrenz, et al., (2011) Zinc coatings for hot sheet metal forming: Comparison of phase evolution and microstructure during heat treatment, Surf. Coat. Technol., 205, 4141-4153.

[20] R. Ashiri, M.A. Haque, C.W. Ji, et al., (2015) Supercritical area and critical nugget diameter for liquid metal embrittlement of Zn-coated twining induced plasticity steels, Scr. Mater., 109, 6-10.