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Effect of Process Parameters on the Structure and Properties of Galvanized Sheets

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The effect of galvanizing parameters on the structure (spangle size and coating microstructure) and properties (formability and corrosion resistance) of galvanized sheets was studied in a hot dip process simulator (HDPS) in a conventional Pb bearing (0.08-0.10%) zinc bath by varying zinc bath Al level (0.10-0.28%), bath temperature (718-743 K), dipping time (1.5-3.5 s), wiping gas flow rate (200-450 lpm), nozzle distance (15-17 mm) and wiping delay time (0.1-2.1 s). Al level in the range of 0.18-0.24% in combination with dipping time of 1.5-2.5 s and bath temperature of 718-733 K results in superior formability (E_{cv}: ~9.3 mm) of the composite (thickness: 0.8 mm). High post-dip cooling rates (~25 K/s) suppress spangle growth (spangle size: ~2 mm). The spangle size of the GI sheet strongly influences the corrosion rate which increases from 5.8 to 9.2 mpy with a decrease in spangle size from 17.5 to 3 mm. By controlling the Al level (0.20%) in zinc bath and bath temperature (733 K), the corrosion rate of mini-spangle GI sheet can be controlled to a level of 5.5 mpy.

Keywords corrosion resistance, formability, galvanized sheets, simulation, spangle

1. Introduction

Galvanized steel sheets are characterized by their superior corrosion resistance, spangled appearance and formability properties along with adequate peel-off resistance and adherence of the coating with the steel substrate. These properties of the galvanized sheets vary widely depending on thickness, microstructure and spangle size of the coating as well as on substrate surface quality (Ref 1). Hot dip galvanized (HDG) sheets produced conventionally by passing clean steel strip through a conventional Pb bearing (0.08-0.10%) molten zinc bath have characteristic large spangles/frost flowers of zinc crystals. Galvanized sheets, with spangled appearance, are mainly used for applications like roofing, trunk, A.C. duct making etc. However, during the last few years, there has been significant increase in the demand for mini-spangle/spangle-free galvanized strip for its wide application in the White Goods/Consumer Durables and Automotive Sectors. To meet stringent 'Surface Quality Requirements' in these sectors for good paintability, lower paint consumption, improved formability and aesthetics, mini-spangle/spangle-free (spangle size: fraction of mm) formable quality galvanized sheets are required. One way of producing spangle-free coating is to use Pb-free zinc bath.

However, the manufacture of non-spangled coatings, free of lead (or antimony), is not so easily done. The reason relates to the influence of even a small amount of these additions on the viscosity of the molten zinc. Due to its higher viscosity, it is difficult to avoid small sags and ripples in the zinc coating when lead/antimony is not present. Hence, it is preferable to produce spangle-free/mini-spangle galvanized sheets using Pb bearing zinc bath. Moreover, when it is desirable to produce both spangled and non-spangled galvanized sheets on the same line without having to change the composition of the zinc bath, an alternate approach like spraying the surface of the molten coating with steam, water, fine zinc powder etc. is required to increase post-dipping cooling rate for suppressing the spangle growth (Ref 2). Recent research work (Ref 3, 4) carried out on spangle formation of galvanized sheets focuses mainly on understanding the effect of zinc bath Pb content on spangle shape and size and its effect on corrosion behavior of GI sheets and in classifying different types of spangles using image processing and ANN technique. In the present work, an effort has been made to examine the effect of post-dip cooling rate on the spangle size for a conventional (~0.10% Pb) zinc bath and its effect on the corrosion rate of GI sheets.

Further, in order to improve the formability characteristics of these mini-spangle/spangle-free galvanized sheets, thickness and microstructure of the coating should also be controlled in such a manner so that the formability of the composite is similar to that of the substrate. During hot dip galvanizing of the strip, as soon as the strip enters the bath, Fe reacts with molten zinc and form Fe-Zn inter-metallic compounds (IMC). This reaction continues till the strip is in bath and also after it emerges from the bath. These IMCs are detrimental to adhesion and formability characteristics of the Zn-coating due to their inherent brittleness and the formation of these IMCs should be suppressed to the maximum possible extent (Ref 5). In order to examine the effect of galvanizing parameters on the formability characteristics and spangle formation of galvanized sheets, number of experiments were conducted in a controlled manner

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in the hot dip process simulator (HDPS) by varying critical process parameters of galvanizing such as zinc bath Al level, bath temperature, dipping time, nozzle distance, wiping gas flow rate and wiping delay time. In this paper, effect of these parameters on the structure (spangle size and coating microstructure) and properties (formability and corrosion rate) of galvanized sheets have been presented.

2. Experimental

Simulation studies were conducted in HDPS on commercial quality (CQ) CR steel sheets with process variables such as zinc bath aluminium level, bath temperature, dipping time, wiping gas flow rate, wiping delay time and strip to nozzle distance as shown in Table 1.

During coating simulation test, cold rolled sheets (thickness: 0.80 mm) of size 200 mm (L) × 120 mm (W) were heated at the rate of 30 K/s to annealing temperature of 1023 K and soaked at this temperature for 60 s in annealing atmosphere of 20% H_2 + 80% N_2. Dew point of annealing atmosphere was kept 253 K during experimentation. Subsequent to annealing, samples were cooled with N_2 gas up to near bath temperature (5 K more than the bath temperature) and then dipped in conventional Pb bearing (0.08-0.10% Pb) molten zinc bath followed by wiping by N_2 gas and then cooling through N_2 gas up to room temperature.

Experimental galvanized sheet samples were characterized in terms of coating thickness, spangle size, Erichsen cup value, corrosion rate and microstructures. Coating thickness (CT) of the galvanized samples was measured using Defalsko Coating Thickness Gauge (model: Positector 6000). Spangle size of the coated sheets was measured by linear intercept method. Formability characteristics of GI sheets were evaluated through Erichsen Cup Tester. The point, at which the cracks/peel-off of the coating begins, during Erichsen Cup Test, was taken as the Erichsen cup value of the composite. Corrosion characteristics of GI sheets were assessed through Linear Polarization Tests using potentiostat under the following conditions:

Test solution: 3.5% NaCl
Reference electrode: silver-silver chloride
Scan rate: 0.1 mV/s
Scan range: ±20 mV.

Metallographic analysis of simulated GI sheet samples was carried out using scanning electron microscope (model: JSM-840A; make: JEOL, Japan) attached with EDAX system (model: 7663; make: Oxford Instruments, UK).

Table 1 Process variables and their ranges during simulation experiments

No.	Process variable	Range
1	Al level in zinc bath (AL), wt.%	0.10-0.28
2	Bath temperature (BT), K	718-743
3	Dipping time (DT), s	1.5-3.5
4	Wiping gas flow rate (WFR), lpm	200-450
5	Wiping delay time (WDT), s	0.1-2.1
6	Nozzle distance (ND), mm	15-17

3. Results and Discussion

3.1 Effect of Process Variables on Coating Thickness, Microstructure and Formability

Coating thickness of simulated galvanized sheets varied widely in range of 7 to 35 μm, depending on the process parameters. It has been found that the wiping gas flow rate and bath temperature significantly affect the coating thickness. Variation of coating thickness with wiping gas flow rate, for a particular bath composition and other galvanizing parameters, is shown in Fig. 1.

Coating thickness decreases with increase in wiping gas flow rate, as the quantum of impingement energy of gas jet increases with high flow rate. Further, it has been found that higher is the bath temperature, lower is the thickness of the pure zinc layer (η phase) and higher is the thickness (10-15% of total thickness) of the alloy layer (ζ and δ phase), particularly for lower Al level (0.10-0.16%) zinc bath. This happens because increase in bath temperature is generally associated with enhancement in the kinetics of the formation of Fe-Zn intermetallics, which results in thicker alloy layer. However, for zinc bath Al level of 0.18-0.28%, relative proportion of alloy layer thickness (2-5% of total thickness) decreases. In the subsequent section, the effect of process parameters on the microstructures (phase formation) and formability characteristics of simulated galvanized sheets have been discussed.

The formability characteristics of the simulated galvanized sheets were quantified in terms of Erichsen cup value (E_{cv}) of the composite. In the simulated GI sheets, E_{cv} of the composite varied in a very wide range, from 5.8 to 9.3 mm depending on the processing conditions of the sheet. Variation of E_{cv} of simulated galvanized sheets with zinc bath Al level is shown in Fig. 2. It can be seen from the graph that Erichsen cup value of GI sheets initially increases (from ~7.0 to 8.5 mm) with increase in zinc bath Al level from 0.10 to 0.18%; thereafter, it remains more or less constant (8.8-9.3 mm) for the Al range of 0.18 to 0.24%. Again it decreases with further increase in Al content from 0.24 to 0.28%. So, there are three distinct regions for the variation of GI sheet E_{cv}. In the subsequent sections, variation of GI sheets E_{cv} vis-à-vis their microstructures and galvanizing parameters in these three regions have been discussed.

E_{cv} of 6.5-8.5 mm was observed for the samples, which was galvanized in 0.10-0.16% Al bath. This is because of the formation of thick alloy layer (sometimes outbursts of brittle

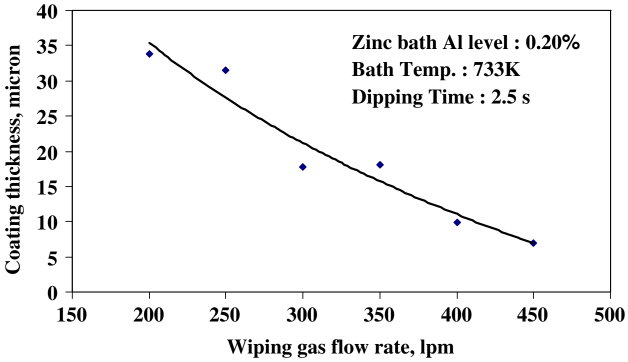


Fig. 1 Variation of coating thickness with wiping gas flow rate

Fe-Zn crystals) at the steel-zinc interface, leading to poor coating adherence of the zinc coating with the steel substrate. This was evident during the Erichsen cup tests, as the cracks in the coating were very much visible before the fracturing of the substrate.

Microstructure of one such coated sheet galvanized in 0.14% Al-Zn bath is shown in Fig. 3(a). EDAX analysis (1.24% Al, 10.30% Fe, 82.41% Zn and 6.05% O) of the above sample, carried out at ~1.0 μm from the coating-steel interface ($D_{surface}$), indicates presence of Fe-Zn crystals (δ phase), as shown in Fig. 3(b). Formation of irregular IL with appearance/outbursts of Fe-Zn crystals was noticed in most of the GI sheets, which were galvanized in 0.10-0.16% Al-Zn bath for almost all the combination of bath temperature and dipping time considered under the experimentation. This kind of outburst is generated by diffusion of Zn through the thin Fe-Al layer and rupture of the Fe-Al film due to volume expansion associated with the formation of Fe-Zn IMCs, which in turn causes rapid Fe-Zn reactions giving the outburst (OB) structure (Ref 6). In the EDAX analysis of almost all the samples some oxygen is also present, which may be because of the oxidation of the coating during sample preparation for metallography or from the Al_2O_3 solution used during polishing.

However, samples that were galvanized in 0.18-0.24% Al bath at bath temperature of 718-733 K and dipped for 1.5-2.5 s generally manifested superior Erichsen cup values ranging from 7.8 to 9.3 mm. Metallographic examination of these samples revealed formation of a very thick, uniform and continuous inhibition layer formation at the steel-coating interface. The thickness of these IL varied from 1.0 to 2.25 μm. Thick and uniform IL of maximum thickness (~2.25 μm) having composition 13.91% Al, 48.96% Fe, 27.98% Zn and 9.15% O ($D_{surface}$: ~1.0 μm) was observed in specimen which was galvanized in a 0.20% Al bath and dipped for 1.5 s at 733 K bath temperature (Fig. 4a, b). The formation of thick and continuous IL may be attributed to the higher affinity of the Al for Fe than Zn, so that immediately (within 0.15 s) after the

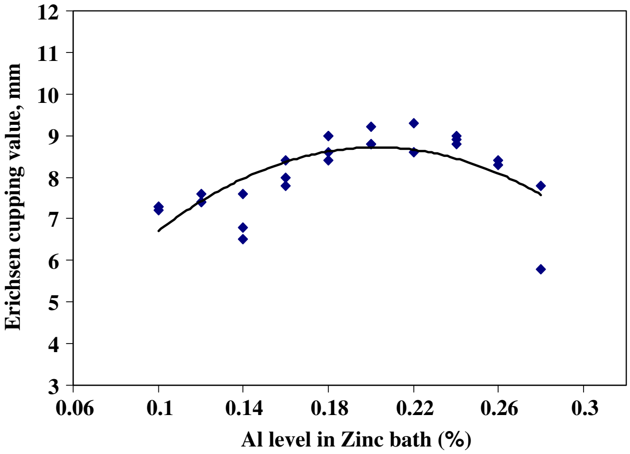
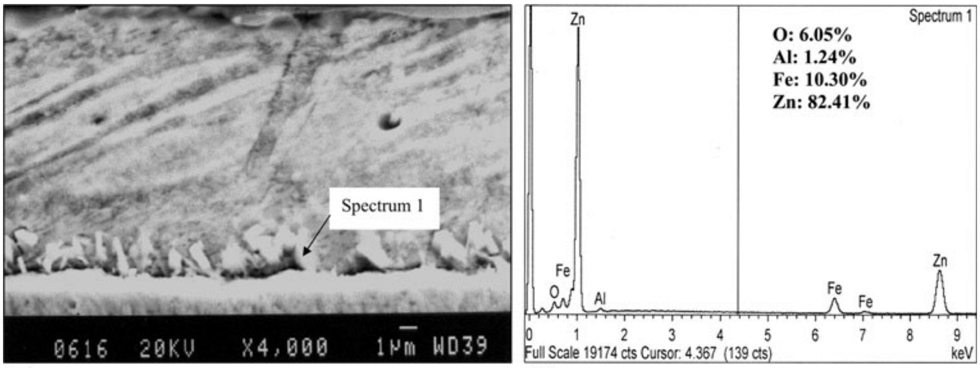
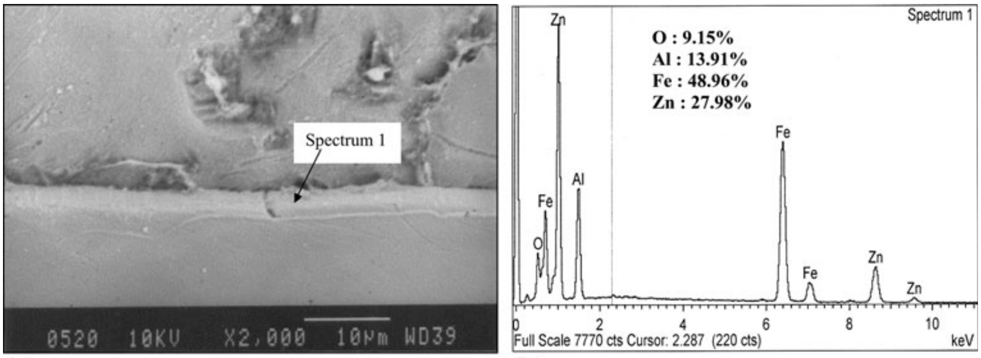


Fig. 2 Variation of E_{cv} of GI sheets with zinc bath Al level (%)



(a) (b)

Fig. 3 (a) SEM micrograph of GI sheet galvanized in 0.14% Al-Zn bath; (b) EDAX analysis of spectrum 1 (a)



(a) (b)

Fig. 4 (a) SEM micrograph of GI sheet galvanized in 0.20% Al-Zn bath; (b) EDAX analysis of spectrum 1 (a) steel enters the coating bath, the stable intermetallic compound, i.e. Fe_2Al_5 (known as inhibition or barrier layer), forms and retards the zinc-iron reaction (Ref 7). The reaction between zinc and iron gets delayed, and the net result is that the final thickness of the alloy layer is much less. When the alloy layer is thin, the coated sheet can be bent or shaped into many useful shapes without the alloy layer cracking and causing loss of coating adhesion.

However, in some of the sheets which were galvanized in 0.18-0.24% Al zinc bath at higher bath temperature of 743 K and dipping time of 3.5 s, appearance of Fe-Zn crystals was observed particularly for thicker coated samples (Fig. 5a), resulting in slightly inferior E_{cv} (7.3 mm). This is because at such a higher bath temperature, kinetics of the formation of Fe-Zn IMCs (alloy layer) gets enhanced and because of higher dipping time sufficient time is available for the breakdown of the inhibition layer and appearance of the Fe-Zn crystals (ζ phase) through IL. This was evident in EDAX analysis (Fig. 5b), which shows a layer of composition of 9.49% O, 3.56% Al, 3.13% Fe, and 83.81% Zn ($D_{surface}$: $\sim$3.0 μm) adjacent to IL at coating-steel interface confirming the formation of alloy layer.

In GI sheets, which were galvanized in 0.26-0.28% Al bath, generally very thick and broken IL was observed (Fig. 6a), which may be attributed to a very high Al level of the IL, leading to its brittle nature. This resulted in inferior formability property of the composite (E_{cv}: 5.8-7.4 mm). The composition of the broken IL pieces was estimated through EDAX (Fig. 6b) and it comprised of 38.62% Al, 42.40% Fe, 16.68% Zn and 2.30% Si ($D_{surface}$: $\sim$8.0 μm), indicating very high level of Al in the inhibition layer.

3.2 Effect of Process Variables on Spangle Size

Spangle size of the simulated GI sheets varied from 2 to 17.4 mm. Data analysis of the spangle size with processing parameters revealed that the spangle size of the GI sheets is influenced by the zinc bath Al level and post-dipping cooling rate. However, the effect of post-dipping cooing rate was found more pronounced. The effect of zinc bath Al level on the spangle size for a particular processing condition (bath temperature: 733 K; wiping gas flow rate: 300 lpm; dipping time: 2.5 s; wiping delay time: 1.1 s; nozzle distance: 15 mm) is shown in Fig. 7. It can be seen that the spangle size of the simulated GI sheets decreases with increase in zinc bath Al level. This is because higher Al in the melt increases the growth undercooling more than nucleation undercooling, leading to high nucleation site density and lower growth rate of the solidified zinc crystals (Ref 8). This resulted in lower average spangle size of the coated sheets galvanized in higher Al level (0.24%) bath as compared to those sheets which were galvanized in lower Al level bath (0.12%).

Minimum spangle size of $\sim$2 mm was achieved in the coated sheet which was galvanized in 0.24% Al bath at a bath temperature of 743 K and dipped for 1.5 s (minimum possible residence time in the zinc bath) followed by wiping at a highest possible wiping gas flow rate of 450 lpm (leading to higher post-dipping cooling rate: $\sim$25 K/s) and least possible wiping

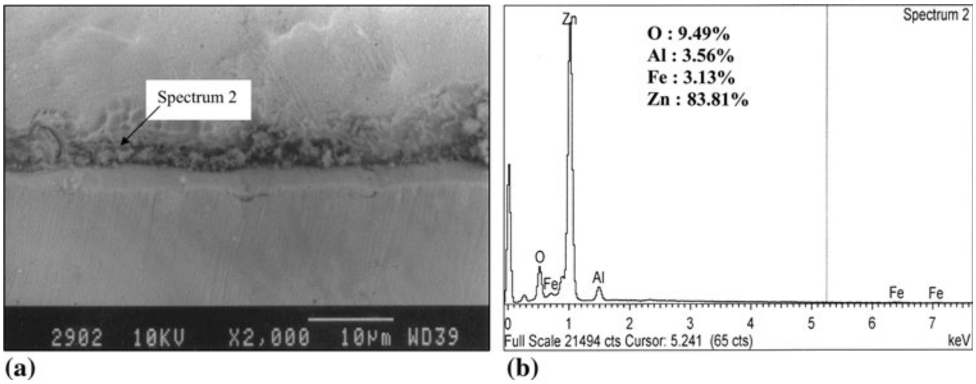


Fig. 5 (a) SEM micrograph of GI sheet galvanized in 0.20% Al-Zn bath; (b) EDAX analysis of spectrum 2 (a)

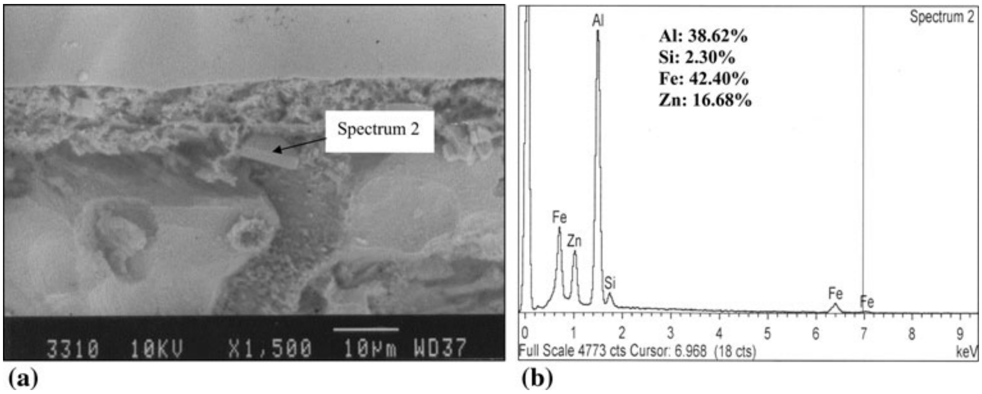


Fig. 6 (a) SEM micrograph of GI sheet galvanized in 0.28% Al-Zn bath; (b) EDAX analysis of spectrum 2 (a)

delay time (0.1 s) All the above factors lead to lower coating mass (16 μm). Since lower coating mass leads to less heat content of the composite (per unit length) (Ref 9), hence, faster will be the cooling rate under similar operating conditions, leading to the possibility of very small spangle size of the GI sheet.

In Fig. 8, variation of spangle size with post-dipping cooling rate has been shown for the galvanized sheets of 0.20-24% Al bath and bath temperature of 733-743 K. It can be seen that spangle size decreases sharply with increase in post-dipping cooling rate, as it leads to increase in the nucleation density of solidifying zinc crystals which results in smaller spangle size of the galvanized sheets (Ref 10).

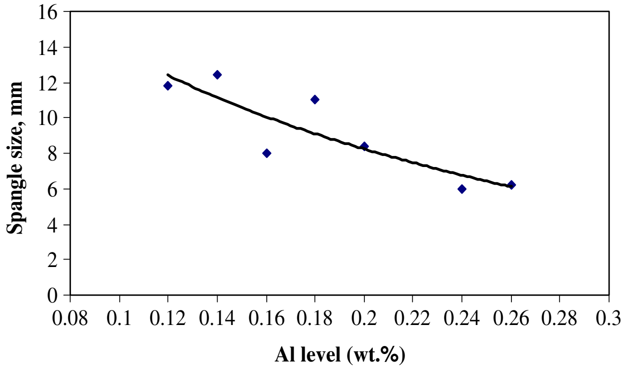


Fig. 7 Variation of GI sheet spangle size with zinc bath Al level

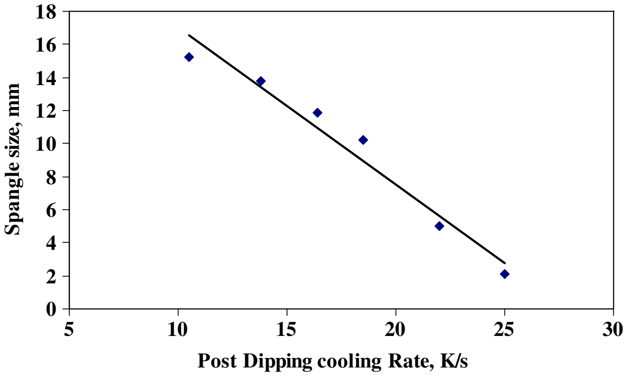


Fig. 8 Variation of GI sheet spangle size with post-dipping cooling rate

Maximum spangle size of 17.4 mm was observed for sample which was coated in 0.10% Al bath at 723 K temperature and dipped for 3.5 s in the bath followed by wiping delay time of 2.1 s and wiped with gas flow rate 200 lpm. All the above galvanizing parameters lead to thicker coating thickness of 30 μm in this GI sheet, which is responsible for the slow cooling rate of the sheet subsequent to dipping. Further, since the wiping gas flow used in this case was also on the lower side (200 lpm), it was not sufficient to enhance the nucleation rate of the zinc crystals. All these factors led to formation of very big spangles on the GI sheet.

3.3 Corrosion Characteristics of Simulated GI Sheets

The corrosion rate of some of the selected simulated GI sheets was evaluated to examine the effect of spangle size on the corrosion characteristics of the GI sheets. Samples which manifested either lowest/largest spangle size, maximum/minimum Erichsen cupping value or combination of above attributes were subjected to Linear Polarization Tests to assess their corrosion rate. These results are shown in Table 2.

It can be seen from the table that as the spangle size decreases (from 17.4 to 2 mm), corrosion rate increases (from 4.9 to 11.5 mpy) sharply, as shown in Fig. 9 also. This is because higher is the spangle size, the better is the corrosion resistance, as it lowers the quantum of grain boundaries, which being at higher energy level are more active than the matrix proper. However, the corrosion resistance of the mini-spangle galvanized sheets can also be enhanced by maintaining proper

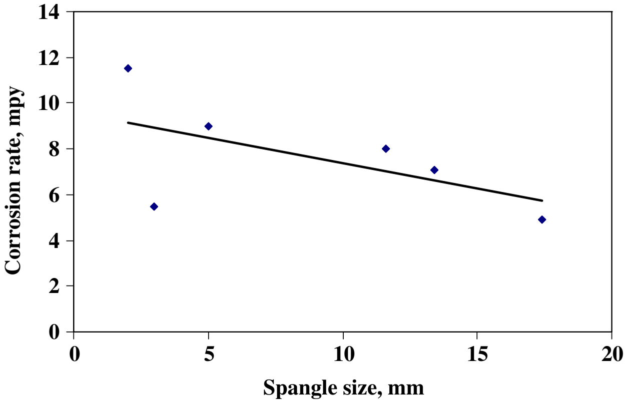


Fig. 9 Effect of spangle size on corrosion characteristics of simulated GI sheets

Table 2 Corrosion characteristics of some selected simulated GI sheets

	Processing parameters									
No.	AL	BT	NZ	WDT	DT	WFR	E_{cv}, mm	Spangle size, mm	Corrosion rate, mpy	Remarks
1	0.10	738	15	0.10	1.5	200	5.6	5 ± 0.71	9	Min E_{cv}
2	0.10	723	17	2.10	3.5	200	8.4	17.4 ± 1.67	4.9	Max SS
3	0.24	743	17	0.10	1.5	450	7.9	2 ± 0.53	11.5	Min SS
4	0.20	733	17	2.10	1.5	400	9.0	3 ± 0.83	5.5	Min SS Max E_{cv}
5	0.14	738	15	1.10	2.5	300	7.5	11.6 ± 1.14	8	Max SS Min E_{cv}
6	0.20	728	16	1.10	1.5	300	9.3	13.4 ± 2.28	7.08	Max E_{cv}

amount of Al (~0.20%) in the molten zinc bath and bath temperature (733 K).

The best combination of formability properties (E_{cv}: 9.0 mm) and minimum spangle size (3.0 mm) was attained in a sample which was galvanized in 0.20% Al bath at a bath temperature of 733 K, dipped for 1.5 s and wiped with a gas flow rate of 400 lpm while maintaining wiping delay time 2.1 s. Due to formation of a very thick and uniform inhibition later at the coating-steel interface, its formability property was very good and due to proper amount of Al (~0.20%) in the molten zinc bath and bath temperature (733 K), the Al level (~1.42%) in the zinc coating was also adequate, which led to its superior corrosion resistance property (corrosion rate: 5.5 mpy) in spite of having very small spangle size of 3.0 mm.

4. Conclusions

Based on the above work, the following conclusions can be drawn:

- Zinc bath Al level, bath temperature and dipping time of the strip have a pronounced effect on the formability characteristics of the composite. Superior formability property (E_{cv}: ~9.3 mm) in the galvanized sheet (t: 0.8 mm) can be achieved by maintaining bath Al level: 0.18-0.24%; bath temperature: 718-733 K; and dipping time: ~1.5 s.
- Post-dipping cooling rate of ~25 K/s or more in association higher zinc bath Al level ~0.24% facilitates suppression of spangle growth. Minimum spangle size of ~2 mm can be achieved by maintaining high wiping gas flow rate of 450 lpm and 0.1 s wiping delay time in a zinc bath containing 0.24% Al and at bath temperature of 743 K.
- Best combination of spangle size (~3.0 mm) and formability property (E_{cv}: 9.0 mm) was established for bath chemistry containing 0.20% Al, maintaining bath temperature at 733 K, dipping time for 1.5 s and wiping gas flow rate at 400 lpm.
- Spangle size of the GI sheets significantly influences its corrosion characteristics. Lower spangle size leads to enhanced corrosion rate of GI sheets. However, the corrosion resistance of the mini-spangle galvanized sheets can also be enhanced by maintaining proper amount of Al (~0.20%) in the molten zinc bath and at bath temperature of ~733 K.

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