Solution Minispangling Of Hot Dip Galvanized Sheet Steel

By Jong-Sang Kim and Jeong-Real Park

Minispangling of a regular hot dip galvanized sheet steel by the spraying of atomized water and 2.0 wt percent $NH_4H_2PO_4$ solution has been investigated in the laboratory and its coating properties have been evaluated. Spraying the water onto a molten galvanized layer does not develop sufficient cooling for the minispangling unless the spray pressure is very high. Such high pressure results in damage to the layer. Spraying the solution causes fast cooling of the layer through endothermic decomposition reactions and forms numerous nuclei for minispangling, leading to microstructurally characteristic flowery minispangles. The temperature of a molten galvanized layer at the onset of spraying is critical for the best minispangling under limited spray conditions.

On a galvanized steel surface, zinc crystals, referred to as “frost flowers” or “spangles,” are usually formed because of their dendritic mode of solidification.[1,2] Their sizes are in the range of 5 mm or more (*i.e.*, clearly discernible to the naked eye), and in industry, they may be called “regular spangles” (RS) or, simply, “spangles.” If they are small enough to be hardly visible (*i.e.*, in the range of 1.5 to 0.5 mm or smaller), they may be called “minimized spangles” (MS) and “zero spangles” (ZS), respectively. Minimized and zero spangles are not generally differentiated, however, because both are not actually discernible to the naked eye. They may be, on the whole, called minispangles, or simply, spangle-free surfaces.

A regular spangled surface of galvanized sheet steel has been deemed unsuitable for painted applications, as in the automotive, appliance and precoated sheet steel industries, because spangles not only show (or print) through the paint, but also cause poor coating and paint adherence to the steel.[3] Many minispangling techniques have been proposed and practically applied in a continuous galvanizing line (CGL) of steel strip:

(1) Heavy temper rolling after galvanizing[3]
(2) Galvanizing in the zinc bath, free from spangle-forming alloying elements[4]
(3) Reheating the galvanized strip[5]
(4) Application of cooling rolls[6]
(5) Zinc dust impingement (Heurtey process)[7]
(6) Aqueous solution spray[8]

Spangles can be erased superficially by the first technique, but they eventually show up after subsequent stamping and painting. In the second technique, mostly Pb, Sb and Bi concentrations are maintained at about 0.02 wt percent or less. This technique has been adopted in many CGLs. It is not good for a line, however, where both the regular spangled and minispangled steels are produced in one molten zinc pot because of the change of zinc bath chemistry, and the total concentration of the contaminating elements must be restricted to less than 0.01 wt percent for complete minispangling all over the strip. In the reheating technique, the galvanized surface loses brightness and anti-powdering property by alloying with the steel substrate. The application of cooling rolls on the molten zinc coating just before solidification has not been sufficient for minispangling a thick coating in a high-speed (*e.g.*, 100 m/min or more) galvanizing line because of the limited cooling power of the rolls. In the Heurtey process, although the application of zinc dust particles (~5 μm diam.) as nuclei of MSs and heat sinks on the molten zinc coating has been well established and popularly adopted in many CGLs, minispangling of a thick galvanized layer on thick strip is difficult because of the very slow cooling of the layer, caused by the large amount of latent heat of the substrate and the layer itself. Additionally, the partially fused zinc dust particles on the galvanized strip tend to accumulate on the work rolls during subsequent temper rolling, resulting in surface defects on the strip. They may also dissolve excessively in the subsequent chromate conversion coating process, causing a bad chromated surface and rapid contamination of the chromating solution.

Galvanized hot-rolled steel strip has been mostly minispangled by spraying a mist of an aqueous solution of inorganic compounds onto the molten zinc coating surface.

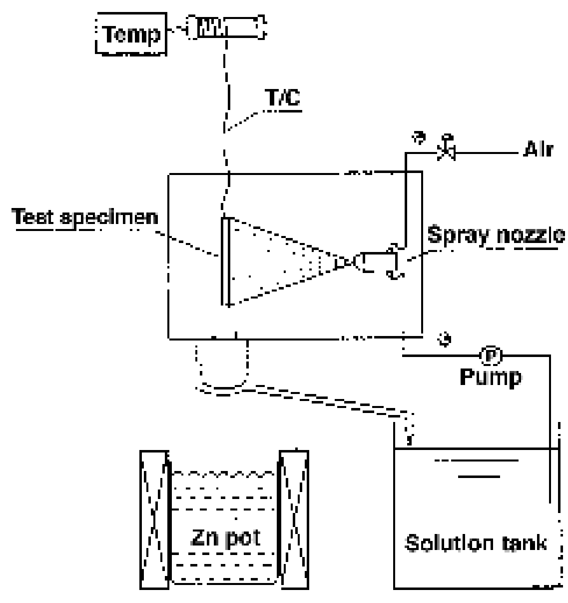

Fig. 1—Schematic diagram of a minispangling experimental apparatus for a spray cooling method. T/C: thermocouple.

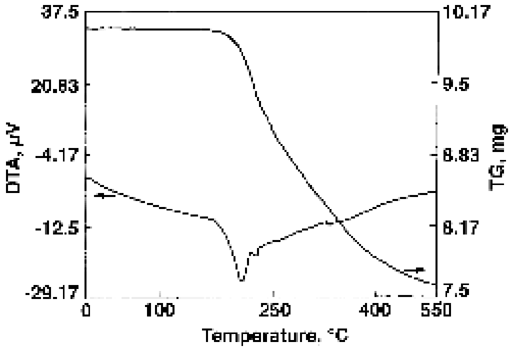

Fig. 2—DTA/TGA analysis data of MAP ($NH_4H_2PO_4$) powder.

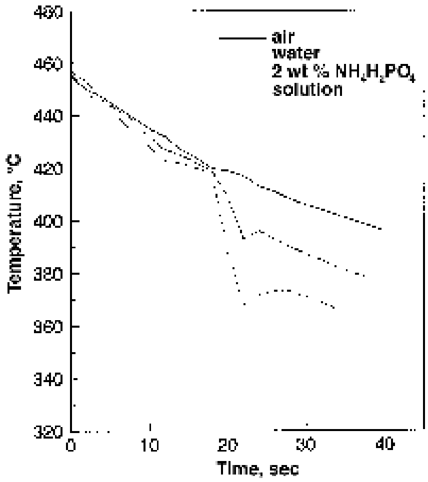

Fig. 3—Cooling curves of specimens galvanized at 460 °C and continuously air-cooled, and sprayed with low pressure water and 2.0 wt % MAP solution at 420 °C for one second.

Table 1
Spangle Size Index of a Hot Dip Galvanized Coating

Index	1	2	3	4	5
Spangle	completely RS	RS + MS	completely MS	MS + ZS	completely ZS

RS: Regular spangle (dia. >5 mm); MS: Minimized spangle (0.5 mm < dia. <1.5 mm); ZS: Zero spangle (dia. <0.5 mm).

Table 2
Surface Roughness & Gloss
Of Hot Dip Galvanized Coatings Solidified by Air Cooling
Or Spraying 2.0 wt % MAP Solution & Water

Classification	Air cooling	2.0 wt % MAP solution	Low-pressure water	High-pressure water
Spangle	RS	minispangle	RS + MS	minispangle
Surface roughness (Ra, mm)	0.8–1.2	0.4–1.0	0.7–1.1	0.8–4.5
Gloss (at 20°)	150–250	80–120	70–100	5–50

RS: Regular spangle; MS: Minimized spangle

Table 3
Texture Coefficients of Hot Dip Galvanized Coatings
Solidified by Air Cooling or Spraying MAP Solution & Water

Lattice plane of HCP Zn	Air cooling RS	MAP solution minispangle	Low-pressure water RS + MS	High-pressure water minispangle
(0002)	3.14	3.42	3.16	2.3
(1010)	0.6	0.07	0.35	0.39
(1011)	1.0	—	1.11	2.42
(1012)	0.1	—	0.22	0.31
(1013)	0.16	—	0.14	0.31

RS: Regular spangle; MS: Minimized spangle

The chemical composition of the proprietary solution has been determined to contain proper salts and ingredients that are helpful for the formation of minispangles as soon as the solution is sprayed on the galvanized layer; also for the improvement of properties of the galvanized surface other than minispangling.[9,10] In the application of this minispangling solution to a CGL, surface appearances of the minispangled coating have been known to depend greatly on the spray conditions, such as the solution pressure and the air atomizing pressure in the spray nozzle, the spray time and the temperature of the galvanized strip just before the spray, in addition to the galvanizing conditions (*e.g.*, zinc bath chemistry and temperature, strip gauge and temperature, line speed, and coating weight). The minispangling mechanism and characteristics of the galvanized coating using this technique have not been systematically investigated, although its adoption has sharply increased lately because of the shortcomings of other techniques, as stated earlier.

In this study, the effects of one of the most popular sprayed solutes (mono ammonium phosphate, MAP: $NH_4H_2PO_4$) on the minispangling and properties of a galvanized coating have been investigated via laboratory minispangling experiments on galvanized steel panels. The effects of the spray conditions have been examined for the best minispangling.

Experimental Procedure

Thermal analysis data of MAP, which was added as the only solute in the spray solution, were rare, so thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of 10 mg of reagent grade MAP were performed at a heating rate of 10 °C/min from room temperature up to 500 °C. An aqueous solution of 2.0 wt percent MAP and water were tested as minispangling agents. Spangling by air cooling of a molten galvanized layer was conducted as a control.

All the minispangling experiments were carried out using a laboratory minispangling simulator, as shown in Fig. 1. Panels (200 x 100 x 0.6 mm, l wt) of mill-galvanized steel strip in a zinc bath nearly free of Pb and Sb (less than 0.01 wt percent), which already had MS appearance, were used as specimens in the minispangling experiments because the cleaned and reduced bare surface of a steel panel for galvanizing, as in the entry step of steel strip into the zinc bath of a CGL, was very difficult to prepare in the simulator. They were thoroughly degreased with acetone in an ultrasonic cleaner. A thermocouple was spot-welded on one side of a panel. It was hot-dipped for 30 sec in a zinc bath at 460 °C. The mill-galvanized layer was remelted and a new zinc layer formed on the panel. The bath contained 0.1 wt percent Pb, 0.2 wt percent Al, 0.1 wt percent Fe and the balance Zn, and this was a typical composition for a regular galvanizing. The

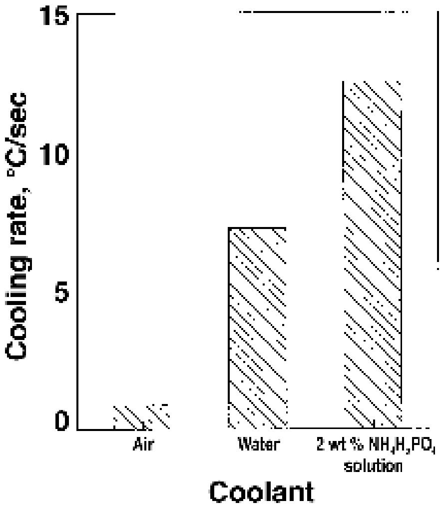

Fig. 4—Maximum cooling rates of specimens galvanized at 460 °C, continuously air-cooled, and sprayed with low-pressure water and 2.0 wt % MAP solution at 420 °C for one sec.

new galvanized panel was lifted from the bath and allowed to cool to the temperature of the solution containing the minispangling agent to be sprayed, as shown in Fig. 1. The agent, at a pressure of 1.0 kgf/cm^2, was introduced into the nozzle, atomized with air at 4.0 kgf/cm^2, and sprayed onto the thermocouple-welded surface of the regalvanized specimen for one sec. In the case of water as an agent, it was sprayed at the high pressure of 50 kgf/cm^2, as well as at 1.0 kgf/cm^2. The temperature of a specimen was monitored, using the welded thermocouple throughout the experiment.

Observations of spangles, surface appearance (roughness and gloss), preferred orientation, scanning electron microscope (SEM) surface morphologies and energy-dispersive spectroscopic (EDS) analyses, and optical microstructures of the cross section of a specimen were conducted as a function of the minispangling agent and the temperature of the specimen. Spangle sizes were graded from one to five in the order of increasing fineness, as shown in Table 1. Ten measurements of the surface roughness and ten measurements of the surface gloss of a specimen along its longitudinal center line were averaged to obtain the average surface roughness value (Ra) and gloss value, respectively. Surface gloss was measured at an angle of 20° with respect to the surface, using a gloss meter. Preferred orientations of the minispangled surface were determined by XRD and converted to texture coefficients of HCP crystalline planes by the Harris method.[11]

Results

Thermal Analyses of MAP

Measured DTA and TGA data of MAP powder as a function of temperature are shown in Fig. 2. In the TGA data, the weight loss began at 178.6 °C, continued with increasing temperature and became 23 percent of the initial weight at 500 °C. The largest rate of weight loss occurred near 200 °C. According to the DTA data, at least one strong endothermic reaction occurred in the temperature range of 178.6 to 210 °C and reached a peak at about 200 °C. Weak endothermic reactions were detected at 217, 222 and 330 °C, as revealed by small peaks in the DTA data.

Cooling of Galvanized Layers By Minispangling Agents

Figure 3 shows cooling curves of specimens that were regalvanized at 460 °C, cooled to 420 °C in air, then sprayed with the 2.0 wt percent MAP solution or water. These curves are shown together with the continuous air cooling curve of a specimen. The water and solution sprays caused rapid cooling by about 30 and 50° below 420 °C, respectively. The cooling rates of specimens during this rapid cooling were calculated from Fig. 3 and are shown in Fig. 4. The amount and rate of cooling by the presence of 2.0 wt percent MAP in the solution were clearly larger than by water alone. The spangles developed by the solution spray were complete minispangles, while the spangles from the water spray at low pressure were mixed with MSs and RSs. Only regular spangles formed on the air-cooled surface.

Effects of Specimen Temperature on Minispangling

Because of the limited amount and time of the solution spray for a CGL adopting a solution minispangling method, it is very important to determine the temperature of the galvanized strip. Spangle size of a solution-minispangled specimen was measured as a function of the temperature of the specimen under the spraying conditions described in the experimental procedure; its results are presented in Fig. 5, using the spangle size index, according to Table 1. Minispangles could be formed by the solution spray only in the very narrow temperature range 420 ± 2 °C of a galvanized specimen.

Characteristics of Minispangled Surfaces

Figure 6 shows SEM surface morphologies of an air-cooled galvanized specimen and minispangled specimens tested with 2.0 wt percent MAP solution and water at the specimen temperature, 420 °C. In Fig. 6a, a large, regular-spangled (5–10 mm dia.) galvanized and air-cooled surface is seen; shiny, frosty and feathery spangles are shown clockwise from the left top corner. Small white particles in the frosty spangle and smaller particles in the feathery spangle were identified as Pb particles by EDS analysis. They were insoluble in the solid Zn and precipitated along the dendritic boundaries and interdendritic sites in the last stage of the solidification of a galvanized coating. A typical minispangle (~0.5 mm dia.) made by the solution spray is shown in Fig. 6b. The spangle looks like a flower. Its central circular spot was identified by EDS to consist of Zn matrix, Pb particles and phosphorus residues. A black spot close to the center spot in Fig. 6b was proved to be phosphorus by EDS analysis, indicating a mark produced by impingement of the solution. The same small marks were observed all over the surface in Fig. 6b. Figure 6c shows a RS formed on the specimen by the water spray at the low pressure. Mossy minispangles were built up, however, on the specimen by the water spray at the high water pressure (50 kgf/cm^2), as illustrated in Fig. 6d.

Figures 7a and 7b show typical cross-sectional micrographs of minispangled layers at the low spray pressure and at the high pressure, respectively. The galvanized surface and layer were not damaged by the impinging particles of a minispangling agent at the low pressure. The freezing surface was indented, however, by the impinging water particles at the high pressure, forming the rough and cracked surface.

Table 2 indicates measured values of the surface roughness and gloss of minispangled specimens, as shown in Fig. 6. The

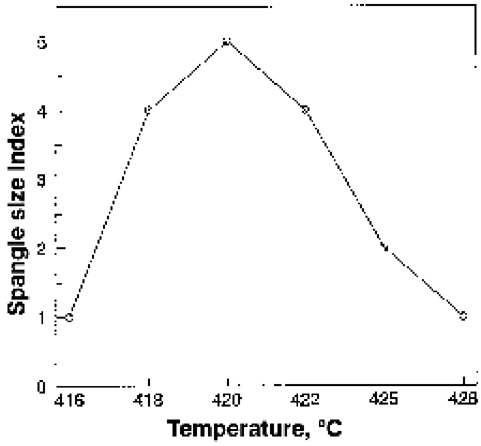

Fig. 5—Spangle size index vs. the temperature of a hot dip galvanized coating just prior to spraying the 2.0 wt % MAP solution. See Table 1 for the size index.

surface roughness was very high when minispangled by the high-pressure water particles and decreased by solution minispangling at the low spray pressure. The surface gloss was high on the air-cooled RS surface, but became low when sprayed with the solution and the water, and was very low on the roughest surface.

The preferred orientation of a galvanized coating was the basal plane of an HCP lattice parallel to the steel substrate when minispangled with the solution. However, two preferred orientations (the basal and pyramidal planes of an HCP lattice) developed on the minispangled coating with the high pressure water particles, as shown in Table 3.

Discussion

Spangle formation in an air-cooled galvanized sheet steel coating has been considered to result from the fast dendritic solidification of a thin, liquid zinc alloy layer.[3,12,13] If alloying elements, such as Pb, Sb and Bi, are dissolved in the molten galvanized layer, solute segregation and constituent undercooling at the solid/liquid interface, during solidification of the layer, result because of their limited solid solubilities in Zn, and the interface becomes dendritic.[14] The dendrite tip curvature becomes smaller because of lower values of the surface tensions of the segregated solutes than Zn, resulting in a higher growth velocity of the dendrite along the layer/substrate or the layer/air interfaces and larger grains (spangles). Regular spangles have been known to form by air cooling of a molten galvanized layer when 0.04 wt percent or more of Pb, Sb and Bi is normally added in the galvanizing bath. The spangle size increases with increasing concentration of the spangle-producing solutes, leveling off at higher concentrations (*e.g.*, 0.10 wt percent Pb).[13] An amount of 0.02 wt percent or less of the spangle-producing solutes in a galvanizing bath is suggested for this minispangling.[12] In many CGLs adopting this minispangling process, however, the concentration level has been restricted to less than 0.01 wt percent (*i.e.*, in the range of 0.005 wt percent).

The thermal undercooling in the air-cooled solidification of a galvanized layer containing Pb was reported to be less than 1 °C, according to an accurate measurement.[13] The current result shows the same negligible undercooling, as indicated by the air cooling curve of Fig. 3, where the point at which discernible spangles appeared is 418 °C. As soon as the temperature of the thin molten zinc layer reaches 418 °C,

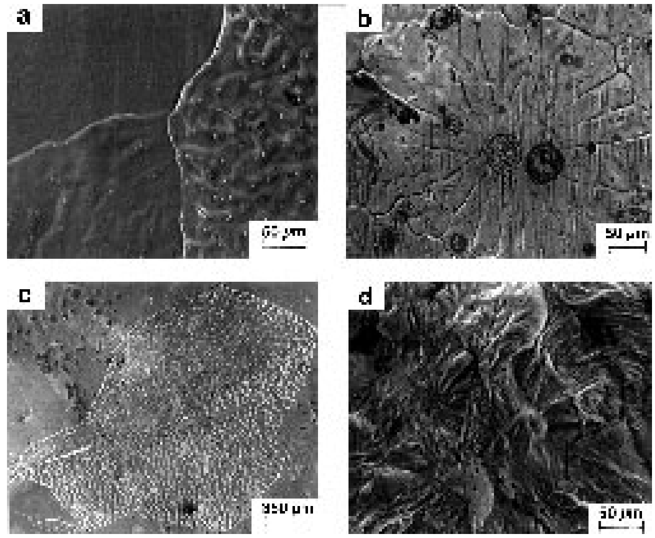

Fig. 6—SEM micrographs of the surfaces of hot dip galvanized (at 460 °C) and minispangling tested (at 420 °C) specimens by: (a) air cooling; (b) spraying 2.0 wt % MAP solution; (c) spraying low-pressure water; (d) spraying high-pressure (50 kgf/cm^2) water.

a small number of nuclei form and grow rapidly near that temperature. If zinc dust (~5 µm) particles impinge and stick uniformly on the molten galvanized layer, just prior to solidification, as in the Heurtey process, they act as cooling agents (by heating and melting), like heat sinks.[3,12] If the cooling effect is strong on a thin layer on a thin substrate, at the temperature just above the solidification temperature, the numerous spots impinged by the dust are solidified by nucleation, resulting in minispangling.

When water particles at the low pressure are sprayed onto the molten galvanized layer at 420 °C, the layer is cooled to 391 °C at the rate of 7.4 °C/sec. The layer solidifies just below 418 °C because of its low undercooling characteristics, but the solidification temperature cannot be well defined in the cooling curve, as shown in Fig. 3. This is a result of a small amount of heat loss in the thin layer and dissipation of the heat by the sprayed water. After the layer is cooled to 391 °C, its temperature increases slightly from the latent heat of the substrate, then decreases again by air cooling. The sprayed water particles do not act sufficiently as cooling agents for the nucleation necessary for minispangling (*i.e.*, one nucleus or more per area having diameter 1.5 mm or less). Insufficient minispangles (relatively small RS mixed with some MS), therefore, are formed by the water spray. Cooling of the molten galvanized layer is faster when sprayed under the high pressure because of the greater quantity of water sprayed. More nucleation and more restricted growth of spangles occurs, leading to the formation of very irregular, mossy and microstructurally unsound minispangles. This dull and rough surface, containing craters and cracks, has been found very sensitive to corrosion at high humidity, and easy delamination of the galvanized layer has been frequently observed. Details will be reported later.

When the MAP solution is sprayed on the molten galvanized layer at 420 °C, the layer is solidified/cooled down to the lower temperature, 368 °C, at a greater cooling rate (12.5 °C/sec) than with the water spray and flowery minispangles (~0.35 mm in size) are formed. The increase of cooling power

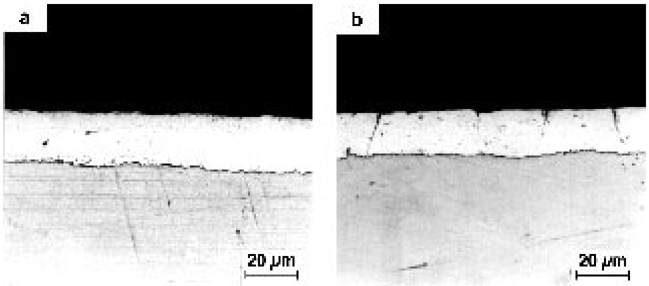

Fig. 7—Optical microscope photographs of the cross sections of hot dip galvanized (at 460 °C and minispangling tested (at 420 °C) specimens by: (a) air cooling, or spraying low-pressure water or 2.0 wt % MAP solution; (b) spraying high-pressure (50 kgf/cm^2) water.

of the solution by the presence of 2.0 wt percent MAP proceeds from endothermic decomposition reactions like those of the thermal analysis data (Fig. 2). As soon as the solution is sprayed on the molten layer, the MAP component is heated to about 200 °C or more and endothermic reactions may occur: Decomposition of MAP into ammonia, water and glassy phosphatic hydride may occur.[15] The layer, therefore, is cooled rapidly and covered with small particles of decomposed residues, such as glassy phosphatic hydride or incompletely decomposed phosphoric compound residues. According to SEM and EDS analyses of the minispangles by this solution spray, phosphorus is indeed detected on the impinged marks of the solution particles on the minispangled surface. Lead particles are observed in addition to phosphorus on the central circular spot of a flowery minispangle (Fig. 6b) as in the interdendritic sites of an air-cooled RS (Fig. 6a). The spot is thought to be the first dendritically solidified (*i.e.*, nucleated) area of the minispangle. It serves as a nucleation site from which the different spangle facets radiate, and this flowery surface morphology is characteristic of minispangles produced by the solution spray. If the solution is sprayed more finely, using a fine nozzle, and as long as droplets of the solution are large enough to impart sufficient cooling to the impinged spot for nucleation, more nuclei and smaller spangles will be formed.

To investigate effects of inorganic salts other than MAP in solution minispangling, solutions containing general salts that do not exhibit considerable endothermic reactions in the temperature range well below the freezing point of Zn were prepared and sprayed on the molten galvanized layer. The strong cooling effects and minispangling, as with the MAP solution spray, did not appear, although the component salts were detected all over the layer surface. Large cooling power of a spray solution is therefore a necessary condition for solution minispangling of a galvanized layer.

The spray conditions for the MAP solution for good minispangling are quite strict because of easy regular spangling by a very small undercooling for a short time. The usable temperature range of the molten galvanized layer just prior to spraying the solution is very narrow, 422 to 418 °C, under the existing minispangling conditions. The higher temperatures, 422 to 420 °C, and a minimum amount of the solution for the minispangling are recommended, to secure a safe cooling allowance and high gloss of a minispangled surface, respectively.

Regular spangled and high-pressure water-minispangled surfaces are rougher than a MAP solution-minispangled surface because of the spangle relief and cratering, respectively, so the latter surface is recommended for heavy deformation, in addition to applications requiring paint. The gloss of the painted surface is proportional, however, to the gloss of the substrate; modifications of the minispangling solution and the spray conditions are thus needed to improve the gloss of a solution-minispangled surface compared with the high gloss of a regular spangled surface, as listed in Table 2. The texture of a MAP solution-minispangled layer is confined to the basal plane. This texture is expected to be industrially desirable, considering that shiny spangles with the basal plane texture[16] have better corrosion resistance and formability than others.[17,18]

Conclusions

1. It is difficult to secure a sound, minispangled surface by water-minispangling of a galvanized layer containing spangle-producing alloying elements.
2. Useful minispangling by spraying 2.0 wt percent MAP solution on a molten galvanized layer is obtained because of the greater cooling resulting from the endothermic decomposition of MAP components on the layer and the numerous nucleations.
3. The temperature range of a molten galvanized layer for MAP solution-minispangling is very narrow; the range, 422 to 420 °C, is recommended for spraying the solution under the given conditions.
4. Microstructurally flowery minispangles, where different spangle facets radiate from a center nucleus, are characteristic of the MAP solution-minispangled morphology.
5. Modifications of the minispangling solution and spray conditions are needed to obtain better surface properties, such as gloss, corrosion resistance and post-treatability.

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