Development of Lubricating Coated Galvannealed Steel for Automobiles

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The high degree of automation within the automotive industry has generated a significant demand for thin-coated steel sheets that exhibit superior weldability, formability, paintability, and corrosion resistance. Initially, steel manufacturers addressed this demand by electroplating a Fe-rich-Zn alloy layer onto the galvannealed (GA) surface to enhance formability. However, the elevated cost associated with the electroplating process prompted the development of more cost-effective lubricating film treatments for GA steel sheets.
This study aimed to improve surface hardness and reduce the friction coefficient by forming a hard protrusion film on the GA surface. The fine groove structure of the film aids in retaining lubricating oil during processing, thereby enhancing formability. Through production trails, we successfully developed a one-coat lubricating film reagent and production technology tailored for automotive lubricating GA steel coils, offering the advantages of low manufacturing costs and a simplified process. Test pieces from the trial production GA steel coils demonstrated significantly improved formability while maintaining the adhesive properties, chemical treatment compatibility, and paint adhesion of the original bare GA steel sheets, thus meeting automotive industry standards.

Keywords: Hot dip galvannealed steel, Automotive lubricating film treatment, Formability, Sealer adhesion

1. INTRODUCTION

Zn-Fe alloy-coated steel (hot dip galvannealed steel, GA) is extensively utilized in the automotive industry due to its superior corrosion resistance. For automotive applications, GA steel sheets must demonstrate excellent formability, weldability, and paintability (including chemical pretreatment and electrodeposition painting) to meet the rigorous demands of highly automated production processes(1).

The formability of GA steel sheets is significantly influenced by the properties of the alloy layer. During the alloying (annealing) treatment, the zinc coating undergoes an alloying reaction, sequentially forming ζ phase ($FeZn_{13}$), δ phase ($FeZn_7$), and Γ phase (Fe_3Zn_{10}). A high degree of alloying renders the GA coating harder and more brittle, reducing the friction coefficient, which is beneficial for processing and forming. However, this high alloying can cause the GA layer to pulverize or peel off during forming. Conversely, a low degree of alloying results in better plastic deformation ability and adhesion, preventing the pulverization or peeling of the GA layer. Nonetheless, the friction coefficient becomes too high, which can cause the workpiece to seize on the mold and rupture during the forming process.

An optimal GA layer should possess a thin Γ layer and a δ layer with low Fe content, ideally forming a uniform single-phase surface structure. These characteristics can be controlled by adjusting the aluminum content and temperature of the zinc bath, as well as the alloying temperature and time. However, the optimal conditions are often very narrow and difficult to maintain. Historically, most Japanese steel mills addressed this by electroplating a layer of Fe-Zn alloy onto the GA surface to increase the surface layer's hardness (thus reducing the friction coefficient) while controlling the degree of alloying in the GA layer to achieve excellent processing formability. Notable examples include Nippon Steel Corporation's GA-E and Nippon Kokan Corporation's PZB.

Recently, steel manufacturers have developed more cost-effective GA inorganic lubricating films to replace the electroplated Fe-Zn alloy treatment(1-2), as shown in Table 1. For instance, Nippon Steel Corporation's GA-L

Table 1 High lubricity GA products from Japanese steel mills.

Company	Name	Lubrication Treatment/Process
Prev High-Lubricity GA Products		
Nippon Steel	GA-E	3 g/m^2 Fe-rich Fe-Zn alloy layer / Electroplating
Nippon Kokan	PZB	Fe-rich Fe-Zn alloy layer / Electroplating
Current High Lubricity GA Products		
Nippon Steel	GA-L	10nm Mn-P oxide film / Dipping, Electrolytic
Nippon Kokan	PZA-N	50 nm Nickel compound inorganic layer / Electrolytic
Sumitomo Metal	GA-V	Phosphate film / Dipping, Spraying, Roll coating

* Nippon Kokan and Kawasaki have merged to form JFE; Nippon Steel and Sumitomo Metal have merged to form Nippon Steel Corporation.

employs dipping and electrolytic processes to form a 10 nm manganese-phosphate oxide film on the Fe-Zn alloy layer's surface. Nippon Kokan Corporation (NKK) applies a cathodic electrolytic treatment to deposit a Fe-Ni-Zn-O film (approximately 50 nm thick) over the galvanized layer, known as PZA-N, despite the high cost of electrolytic equipment(3). Sumitomo Metal Industries uses a two-step process involving dipping, spraying, or roll coating to form a phosphate film forming lubricity on the GA surface(4). However, although this process is advantageous due to its low reagent cost, it still requires two sets of equipment and more operators.

For steel mill production processes, forming an inorganic film on the GA steel sheet surface using a one-coat process is the simplest and most cost-effective method. Although current commercial film technology meets most characteristics required for automotive applications, such as formability, lubricity, phosphatability, adhesion, and corrosion resistance after electrodeposition painting, it falls short of the adhesion criteria set by car manufacturers. Specifically, the percentage of cohesive failure of the fracture surface must exceed 90%. Therefore, it is necessary to develop reagents and technologies for producing automotive lubricating filmed GA steel coils using a one-coat process.

2. EXPERIMENTAL METHOD

2.1 Formulation Design of Lubricating Film Reagent

Currently, the prevalent commercial lubricating film reagents are primarily phosphate-based aqueous solutions. When these reagents are applied to the surface of GA steel sheets via roll coating, the water rapidly evaporates, resulting in the formation of a film. Due to the brief duration of film formation, the resultant phosphate film is predominantly amorphous with a loose structure. Consequently, in adhesive bond strength tests, failure often occurs within the loose phosphate film rather than within the sealant adhesive.

To mitigate this issue, a film modifier was incorporated into the previously developed phosphate film formulation(5-6). The objective was to form a hard and particle-rippled film on the GA surface, ensuring that the failure surface occurs within the adhesive layer.

2.2 Assessment Method

In this study, specimens were prepared by coating the surfaces of GA steel sheets (Zn coating weight per side: 45 g/m^2) provided by China Steel Corporation (CSC) with a lubricating inorganic film, resulting in a coating weight ranging from 0.1 to 0.3 g/m^2. The performance specifications of the GA lubricating film adhere to the specifications set by the automobile manufacturer, as shown in Table 2. The detailed assessment methods are described below:

(1)Lubricity (surface friction coefficient measurement)

The friction coefficient was measured using a friction wear tester with a 5 mm diameter steel ball under a load of 200 g. The measurement speed was set to 5 mm/sec, with a back-and-forth motion of 4.2 cm considered as one cycle. The friction coefficients were recorded at the 4th and 20th cycles. Measurements were conducted under both room temperature and high temperature (100°C) conditions.

(2)Formability (safe range of blank holding force, BHF)

Test specimens were cut into 100 mm diameter blanks and subjected to a cupping test using a 50 mm diameter punch. The BHF was varied for each specimen to evaluate the stamping operating window of the steel sheet, defined as the range between the occurrence of wrinkling and stamping fracture. The minimum and maximum holding force ranges that allowed successful stamping were identified.

Table 2 Specifications of GA lubricating film for automobile.

Specification Item	Standard or Description
Workability & Formability	
Friction coefficient, 25°C	4th/20th, ≤ 0.15/≤ 0.15
Friction coefficient, 100°C	4th/20th, ≤ 0.15/≤ 0.15
Minimum holding force for successful stamping	≤ GA without lubricating film
Maximum holding force for successful stamping	> GA without lubricating film
Adhesion	
Structural edge adhesion strength (T-Peel test)	≥ 27 kPa
	Cohesive failure ≥ 90%
Vibration damping adhesion strength (Shear Tension test)	≥ 0.20 MPa
	Cohesive failure ≥ 90%
After Chemical Treatment	
Appearance of phosphate film	No scars or uneven shades
Phosphate coating weight	Based on the automobile manufacturer
After Electrodeposition Painting	
Appearance after electrodeposition painting	No scars or uneven shades
Water-resistance adhesion test	Retention rate 100%
SST, 840h	Peeling width ≤ 4mm or equivalent to GA without lubricating film

(3)Surface adhesion performance

Two types of adhesives were applied to specific areas on the specimens, with thickness controlled by spacers, and the specimens were overlapped and bonded. Pre-curing was performed by heating to 180°C for 30 minutes. A tensile test was conducted to measure the failure strength, and the failure mode was observed.

(a) Structural adhesive for edge bonding: Evaluated using a T-peel test. The edge bonding adhesive was SUNDINE #2301-8HH. Test specimens measured 200 mm×25 mm with a bonding area of 25 mm×140 mm and a spacer thickness of 0.15 mm. The tensile speed was set to 200 mm/min.

(b) Vibration damping adhesive: Evaluated using a shear tension test. The vibration-damping adhesive was SUNDINE #1155. Test specimens measured 100 mm×25 mm with a bonding area of 25 mm×25 mm and a spacer thickness of 1.0 mm. The tensile speed was set to 50 mm/min.

(4) Chemical treatment properties

The specimens were subjected to an immersion-type phosphate treatment. The surface appearance of the phosphate film was observed, and its deposition amount was measured using an X-ray fluorescence spectrometer (XRF).

(5) Water resistance and corrosion resistance after paint coating

Test pieces for the water-resistance adhesion test and salt spray test were prepared by applying a phosphate pretreatment to the specimen steel sheets, followed by an epoxy paint coating using electrodeposition. The electrodeposition coating surface had to be free of scars, uneven shades, and other defects.

(a) Water-resistance adhesion test: The test pieces were immersed in distilled water at 40oC for 480 h (20 days). The paint coating was then cross-cut into 1 mm × 1 mm grids, and the area percentage of the coating remaining after peeling with adhesive tape was measured.

(b) Salt spray test (JIS Z 2371): The paint coating was cross-cut in an X pattern, and the test pieces were subjected to salt spray for 600 h and 840 h, respectively. The maximum blister width on one side of a cross-cut line was measured.

2.3 Microstructure Analysis

The surface morphologies of the lubricating film and the crystal structure of the phosphate film were analyzed using scanning electron microscope (SEM) observation.

3. RESULTS AND DISCUSSION

3.1 Effect of Film Modifier

The incorporation of a film modifier into the previously developed phosphate reagent formulation was investigated to enhance the adhesive properties of the vibration-damping adhesive(6), aiming for a cohesive failure ratio greater than 90% in the shear tensile test. Table 3 summarizes the experimental results for reagents with film modifier dosages of 3 and 2, alongside a comparative test using the commercial reagent G0. Fig.1 depicts the test specimens after the shear tensile test. The results indicate that reagents containing the film modifier achieved a cohesive failure ratio exceeding 90%, thereby confirming that the addition of a film modifier significantly enhances the adhesive properties of the vibration-damping adhesive. In contrast, the commercial reagent G0 failed to meet the required standards.

Subsequent experiments involved reducing the film modifier dosage to ascertain the minimum required amount for the lubricating film to meet the specifications for vibration-damping adhesive adhesion. Table 4 presents the performance of GA lubricating films with film

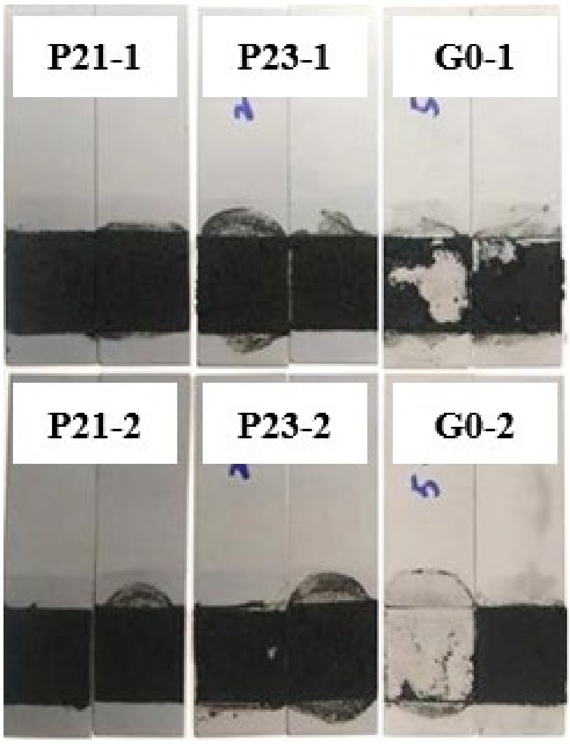


Fig.1. Test specimens (No. P21, P23, G0) after shear tension test using vibration damping adhesive.

Table 3 Results of the adhesive test for GA lubricating film with varying film modifier content compared to commercial reagent.

Film Reagent (Specimen number)		P21	P23	G0
Film modifier dosage		3	2	—
Vibration damping adhesion strength (shear tension test)	MPa	1.15	1.14	0.80
	Cf %	100/100	100/100	5/40

* G0: Commercial reagent. Cf %: Percentage of cohesive failure.

Table 4 Lubricating and adhesive performance of GA lubricating film with optimal modifier content compared to commercial reagent.

Film reagent (Specimen number)		P6	PX	P0	L2	G0
Film modifier dosage		0.8	0.6	0	—	—
Friction coefficient	4^{th}	0.083	0.078	0.095	0.100	0.099
	20^{th}	0.105	0.073	0.117	0.111	0.114
Vibration damping adhesion strength (shear tension test)	MPa	0.978	0.877	0.948	0.907	0.945
	Cf %	99/99	80/95	85/88	9/2	65/70

* L2, G0: Commercial reagent. Cf %: Percentage of cohesive failure.

modifier dosages of 0.8, 0.6, and 0, including their friction coefficient and adhesive feature. The performance of commercial reagents was also re-evaluated for comparison. Fig.2 shows photographs of the test specimens after the shear tension test with the vibration-damping adhesive. The results demonstrate that when the film modifier dosage was below 0.8, the adhesive performance did not meet the requirements, with a cohesive failure rate of less than 90%. Similarly, the commercial reagents L2 and G0 also failed to meet the standards. The experiments confirmed that a film modifier dosage of 0.8 or higher is essential to provide a qualified inorganic lubricating film for vibration-damping adhesive adhesion.

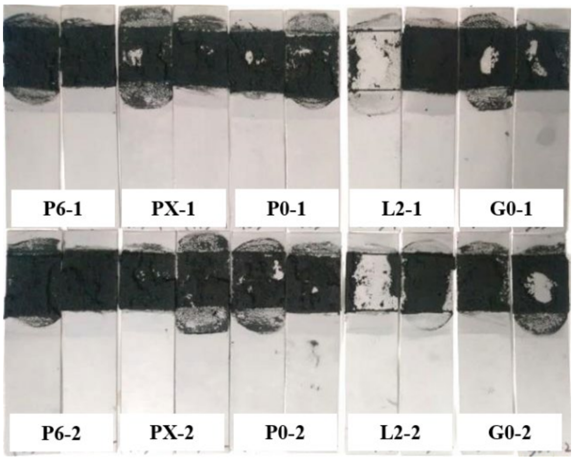


Fig.2. Test specimens (No. P6, PX, P0, L2, G0) after shear tension test using vibration damping adhesive.

3.2 Performance of Lubricating Film Coated GA Steel Sheet

After determining the minimum required dosage of the film modifier, P23 and P33 reagents with dosages of 2 and 1.5, respectively, were selected. Laboratory-prepared GA specimens coated with these lubricating films underwent various performance evaluations specified by the automotive industry. The results are summarized in Table 5 and described as follows:

(1) Friction coefficients: The friction coefficients of the P23 and P33 filmed GA specimens were significantly lower than those of the bare GA sheet, confirming that the film enhances the lubricating properties of the GA specimens.

(2) Adhesion tests: The P23 and P33 film-coated GA specimens exhibited 100% cohesive failure. Fig.3. shows photographs of the test specimens after the shear tension test with the vibration-damping adhesive.

(3) Chemical treatment: The application of the lubricating film did not affect the crystal structure or the deposition amount of the phosphate film, as shown in the SEM photomicrographs in Fig.4.

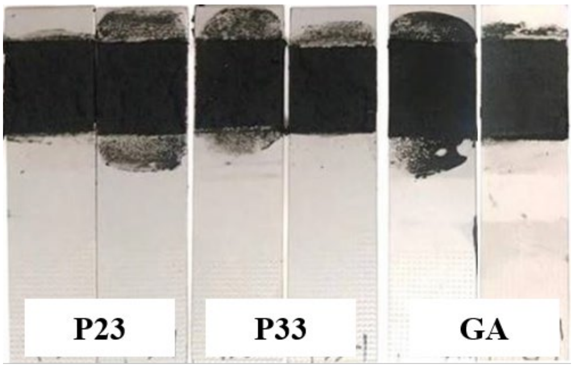


Fig.3. Test specimens (No. P23, P33, and bare GA) after shear tension test using vibration damping adhesive.

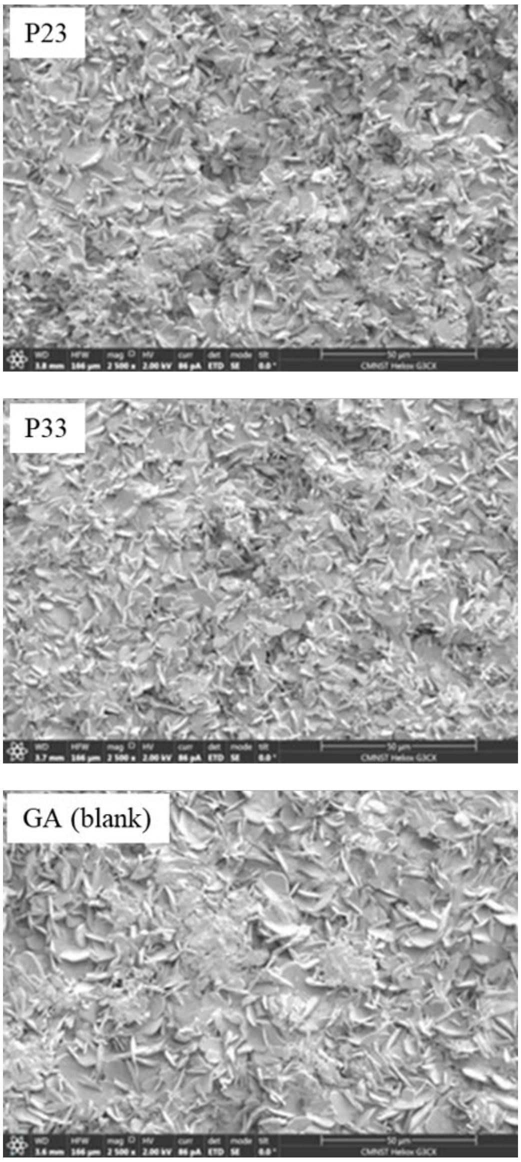


Fig.4. SEM images of chemical treatment film.

Table 5 Performance evaluation of GA steel sheets with application of P23 and P33 lubricating films.

Film reagent (specimen number)		P23	P33	GA
Film modifier dosage		2	1.5	blank
Friction coefficient	4^{th}	0.13	0.12	0.27
	20^{th}	0.15	0.10	0.28
Structural adhesion strength (T-peel test)	KPa	40.9	93.6	107.6
	Cf %	100	100	100
Vibration damping adhesion strength (shear tension test)	MPa	1.07	0.91	0.85
	Cf %	100	100	100
After Chemical Treatment				
Appearance of phosphate film		Normal	Normal	Normal
Phosphate coating weight	g/m^2	5.1	5.1	5.2
After Electrodeposition Painting				
Appearance of ED paint		Normal	Normal	Normal
Water-resistance adhesion	%	100	100	100
SST，600 hrs	mm	5.0	5.0	6.5
SST，840 hrs	mm	6.0	5.0	6.0

* Cf %: Percentage of cohesive failure.

(4) Water resistance and corrosion resistance: No significant paint exfoliation was observed in the water-resistance adhesion test, regardless of the presence of the P23 and P33 lubricating films. The remaining paint coatings were 100% intact. After 600h and 840h of salt spray tests (Fig.5), no significant change in paint blister width from a cross-cut line was observed, indicating that the P23 and P33 lubricating films do not affect the corrosion resistance after paint coating.

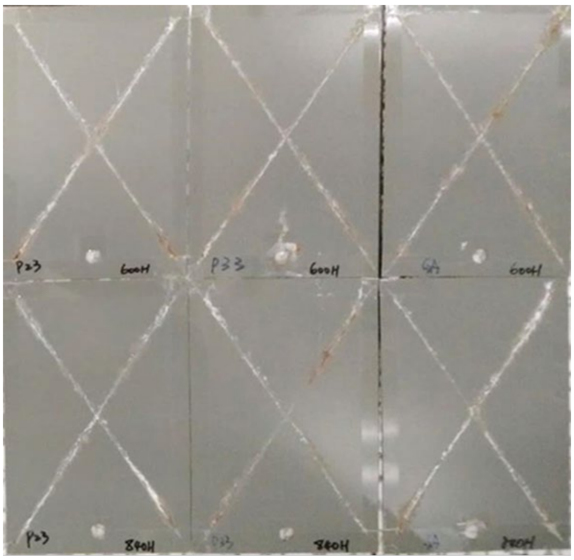
These findings demonstrate that GA steel sheets coated with P23 and P33 lubricating films meet the performance requirements for automotive applications.

3.3 Lubricated GA Steel Coil Production Trial

Following laboratory evaluations confirming that P23 and P33 coated GA steel sheets met performance criteria for automotive lubrication films, the P33 reagent was selected for a lubricated GA steel coil trial on the CGL production line. The performance evaluation results are summarized in Table 6, with Fig.6, Fig.7, and Fig.8 depicting the blank holding force (BHF) test, the adhesion test, and the 840h cross-cut salt spray test after paint coating.

(1)Friction coefficient and BHF: The steel coils showed significant improvement in formability, with an increase in stamping BHF of over 60%.

(2)Adhesion tests: The adhesion tests for structural edge adhesive and vibration-damping sealer met the specifications.



P23 P33 GA

Fig.5. Cross-cut salt spray test results at 600 hours (upper row) and 840 hours (lower row).

Table 6 Performance evaluation of the lubricated GA steel coils.

Steel coil number		71	72	GA
Successful stamping holding force	KN	2 ~ 45	2 ~ 45	2 ~ 25
Friction coefficient	4th	0.108	0.107	0.155
(25°C)	20th	0.108	0.105	0.160
Friction coefficient	4th	0.110	0.106	0.154
(100°C)	20th	0.114	0.103	0.162
Structural adhesion strength (T-peel test)	KPa	28.7	35.0	25.6
	Cf %	100	100	100
Vibration damping adhesion strength (shear tension test)	MPa	0.89	0.91	0.97
	Cf %	100	100	100
Appearance of phosphate film		Normal	Normal	Normal
Phosphate coating weight	g/m^2	5.1	5.0	5.0
Appearance of ED paint		Normal	Normal	Normal
Water-resistance adhesion	%	100	100	100
SST，840 hrs.	mm	5.0	6.0	7.0

* Cf %: Percentage of cohesive failure.

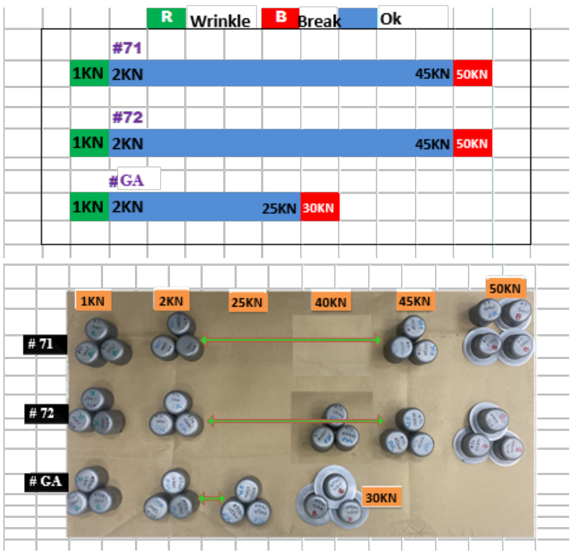


Fig.6. Results of blank holding force (BHF) test of CGL trial steel coil, ls 71, 72, and GA sheet.

(3)Appearance after paint coating: The chemical treatment and electrodeposition coating results were normal, and the water resistance adhesion tests met the specifications.

(4)Salt spray test: The results of the 840h cross-cut salt spray test after paint coating (chemical treatment and electrodeposition coating) were comparable to, or slightly better than, those of the original GA bare material.

These results indicate that the lubrication film reagent developed in this study can produce lubricated GA steel coils suitable for automotive use through a one-coat process on the hot-dip galvanizing production line.

3.4 Lubrication Mechanism of Film-Coated GA Steel Sheets

The application of an inorganic film treatment on GA steel sheets to enhance formability during processing is based on two theoretical principles. First, forming a hard, thin layer on the GA surface reduces the friction coefficient. Second, creating a surface microstructure with numerous fine grooves or protrusions retains lubricating oil during processing, ensuring effective lubrication when the steel sheet contacts the mold (see Fig.9 for a schematic diagram).

The inorganic lubricating film treatment technology developed in this study employs these principles. A one-coat process is used to form a hard, thin layer with a specific microstructure containing hard protrusions on the

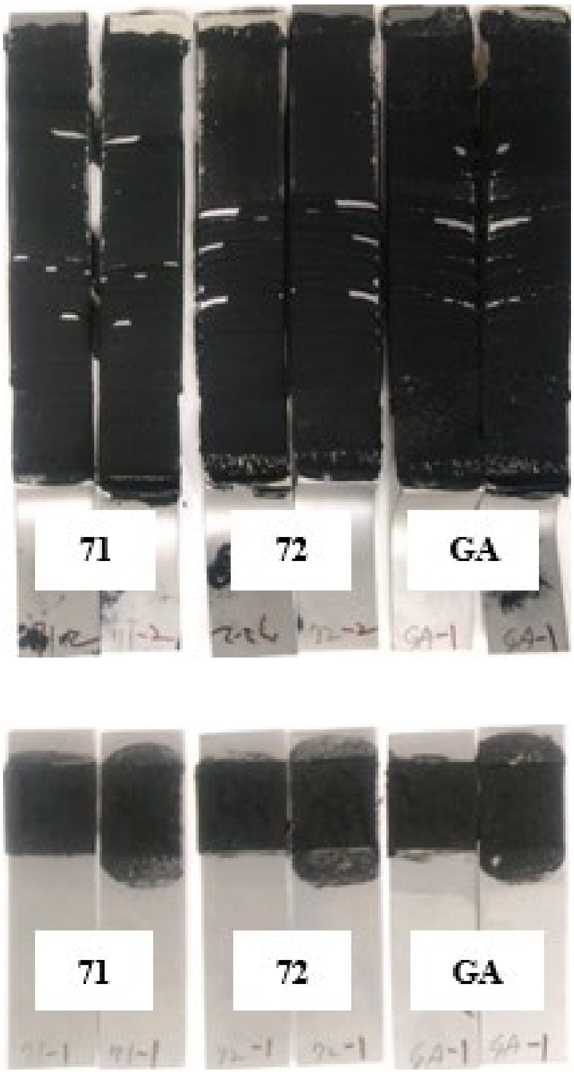


Fig.7. Photographs of test specimens after the structural adhesive peeling test (top) and vibration damping adhesive tensile test (bottom) for CGL trial steel coils,71, 72, and GA sheet.

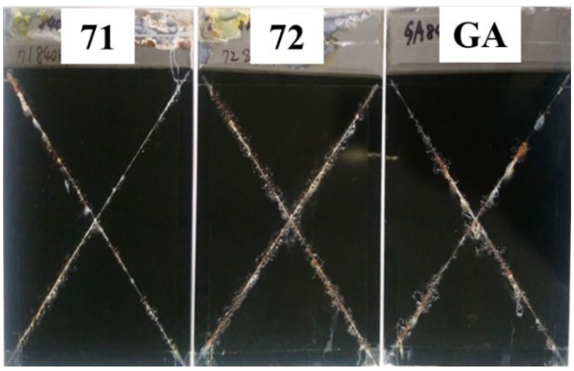


Fig.8. Cross-cut salt spray test results at 840 hours for the CGL trial steel coils, 71, 72, and GA sheet after chemical treatment and electrodeposition paint coating.

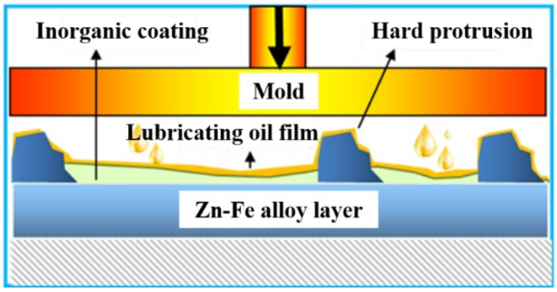


Fig.9. Schematic diagram of the lubrication mechanism during the forming process of inorganic film-coated GA steel sheet.

surface of GA steel sheets. Experimental results confirm that this method effectively improves formability. The film morphology on the GA surface was observed using SEM. Fig.10 shows SEM photomicrographs of the GA sheets before and after applying the lubrication films, including the P33 reagent film and a commercial one-coat reagent film. The P33 reagent film surface exhibits significantly more protrusions compared to the bare GA sheet and the commercial one-coat reagent film. These protrusions are likely hard compounds formed by the reaction of the reagent components with the GA surface, supporting the theoretical mechanism proposed above.

4. CONCLUSIONS

This study successfully developed a water-based lubricating film reagent that forms an inorganic film with granular protrusions on GA steel sheets, enhancing both the adhesion of vibration-damping adhesives and processing formability. This reagent can produce lubricated GA steel coils through a one-coat process on a hot-dip galvanizing line. Production trials confirmed that the self-developed lubricating filmed GA steel sheets meet the requirements for automotive lubricating steel, significantly enhancing processing and forming lubrication while retaining the adhesive properties, chemical treatment compatibility, and paint-coating adhesion of the original bare GA steel sheets, thereby meeting stringent automotive specifications.

In commercial production of lubricated GA steel coils using roll-coating methods, only a two-coat reagent technology has fully met the requirements for automotive lubricating steel sheets. Compared to the two-coat process, which requires two sets of roll-coating equipment and ovens, the one-coat process adopted in this study requires only one set of equipment, significantly reducing production costs and labor requirements. This approach offers the advantages of lower manufacturing costs and a simplified production process.

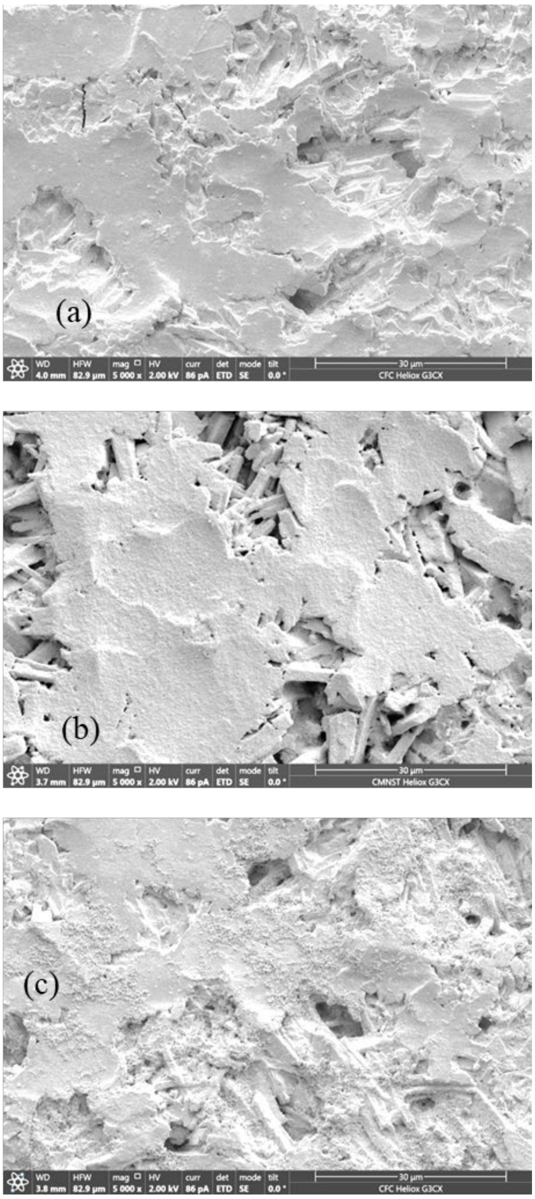


Fig.10. Microscopic morphology (SEM 5,000X): (a) surface of GA, (b) surface of commercial one-coat lubricating reagent film, (c) surface of P33 reagent film.

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