

# Effect of Annealing Atmosphere Control on Phosphating of High Strength Cold-Rolled Steel Sheet

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To clarify the annealing atmosphere effect on high strength cold-rolled steel phosphating, a reduction of the protection environment was enhanced by raising the mixed Hydrogen-Nitrogen (HN) gas flow. The surface condition of cold-rolled steel sheet should be maintained as iron fresh or oxidation free as this would result in better phosphating quality. To compare with phosphating quality of the original and modified mixed Hydrogen-Nitrogen (HN) gas flow in annealing, the surface condition of raw materials and electrochemical behavior while phosphating were analyzed. Phosphating weight gain was also measured to clarify the differences between the original and modified annealing atmosphere process. As mixed HN gas flow increased, a wider distribution of the Fe element near the surface existed compared to that of the original process. Phosphating crystalline with more compaction and better coverage could be observed after the manufacturing modification compared to the original annealing process. Phosphating weight gain also increased by 42% obviously after rising annealing HN mixed gas flow. Furthermore, the corrosion resistance after electro-deposition painting, resulted in less paint peeling after a 240 hours warm-salt-water dip test.

**Keywords:** High strength cold-rolled steel sheets, Phosphating, Corrosion resistance

## 1. INTRODUCTION

To enhance the adhesion and corrosion resistance of vehicle cosmetics, conversion phosphating is treated as a pretreatment to the electro-deposited paint (ED-paint) process<sup>[1]</sup> in the automotive industry. For cold-rolled or galvanized steels, zinc phosphating conversion coating can create a rough surface on substrate physically and inorganic/organic interface chemically for the subsequent paint application. Therefore, the adhesion and corrosion resistance ability on further electro-deposition paint will be improved.

The quality of phosphating coatings on steels are affected by several manufacturing factors. Alloying-design, such as chromium, nickel, molybdenum or vanadium, would induce oxidation on the surface resulting in acting as an obstacle layer for zinc phosphating<sup>(2, 3, 4)</sup>. Carbon and silicon elements also influence the coating generated by carbides and silicates precipitation. To increase cold-rolled steels formability, the annealing process is applied before coiling. However, steels exposed in a lesser reduced atmosphere, various oxides

would generate and degrade the following zinc phosphating reaction<sup>(5)</sup>.

To upgrade the mechanical properties of sheet steel, noble alloying elements would be considered metallurgically for a higher strength of sheet. A more sensitive reaction of oxidation, however, would occur during the cold-rolled steel sheets annealing process. Therefore, a more reductive environment is necessary for high strength steel manufacture.

The aim of this investigation is to clarify the effect of reduction atmosphere protection in the annealing process on conversion phosphating properties and corrosion resistance of the subsequent ED painting application.

## 2. EXPERIMENTAL METHOD

Major chemical compositions of high strength cold-rolled steel are listed in table 1, and marked as JSC780Y, this was used to evidence for the HN modification effect on phosphate coating. To assess the evidence for the effect of manufacturing processes and control of high strength cold-rolled steel sheets for phosphating ability, the annealing parameters were modified

**Table 1** Major chemical compositions of cold-rolled steels (in wt%)

	C	Si	Mn	P	Cr
JSC780Y	0.12	0.10	1.99	0.01	0.51

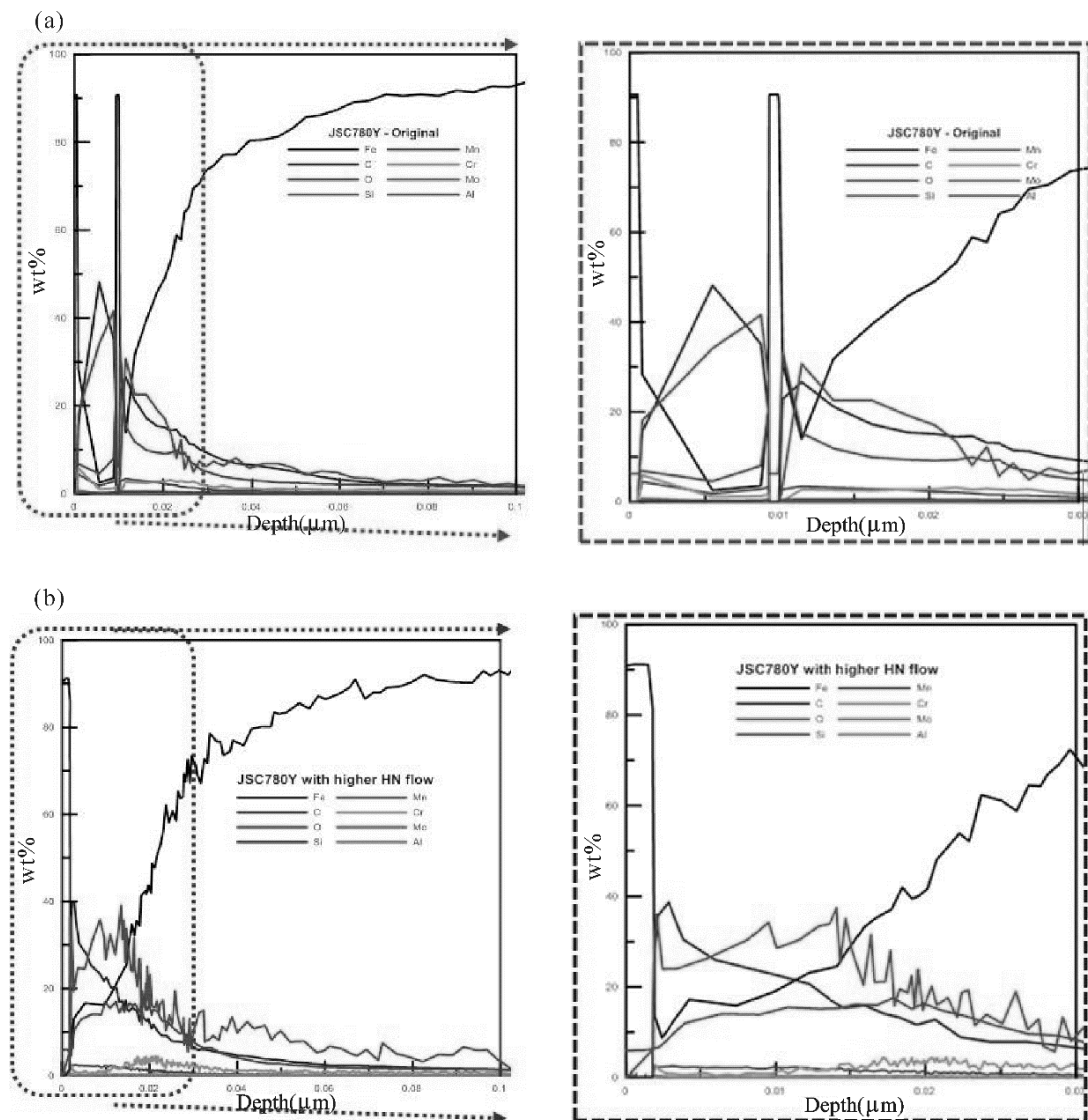
to enhance the reduction environment by increasing hydrogen-nitrogen (HN) mixed air flow in GJ area of CAL.

A glow discharge spectrometer (GDS) was used to examine the depth profile of the constitute elements content to realize the environment control effect. An electrochemical open circuit potential (OCP) measurement was employed to identify the potential fluctuation while phosphating. The phosphating weight gain was measured by dipping a phosphated-sample in 75°C CrO<sub>3</sub> aqueous solution for 15 minutes to confirm phosphating quality. Scanning electron microscope (SEM) was used to observe the crystalline and coverage ability of phosphating on substrate. Electronic-deposition (ED) painting, with scratch X-cut, corrosion resistance was checked by using a 5% NaCl warm-salt-water dipping

test at 55°C for 240 hours, then identified by the taped off method to observe the ED peel-off condition from the X-cut edge.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the GDS results of raw materials with original and manufacturing modified JSC780Y. As compared with the original and modified JSC780Y substrate, shown in Fig.1 (a) and (b) respectively, the Fe content width from surface toward bulk of the modified sample became wider than the original did. Besides, the original sample possesses an obvious oxidation and high C content region between 0.005 to 0.01 μm depth from the substrate surface. In phosphating processes, Fe and Mn were beneficial elements to assist phosphating<sup>(3)</sup>, and the distribution of these elements were enhanced



**Fig.1.** Element depth profile of raw materials with different HN flow. (a) JSC780Y with lower HN flow (b) JSC780Y with higher HN flow

near the surface of the modified manufacturing JSC780Y.

Dipping samples in colloid titanium solution were conducted before phosphating to enhance the subsequent phosphating reaction. Figure 2 shows the 600 seconds OCP measurement of JSC780Y to realize potential changes during phosphating. Potential fluctuation was detected in each sample, including both original and modified manufacturing. OCP results of the original JSC780Y, marked as a blue solid-line, indicated the surface reaction trend to be stable. On the contrary, the more drastic potential fluctuation, marked as a red solid-line, occurred while modified JSC780Y was being phosphated. Therefore, the manufacturing modification created more apparent active sites on the substrate surface and assisted the phosphating reaction effectively.

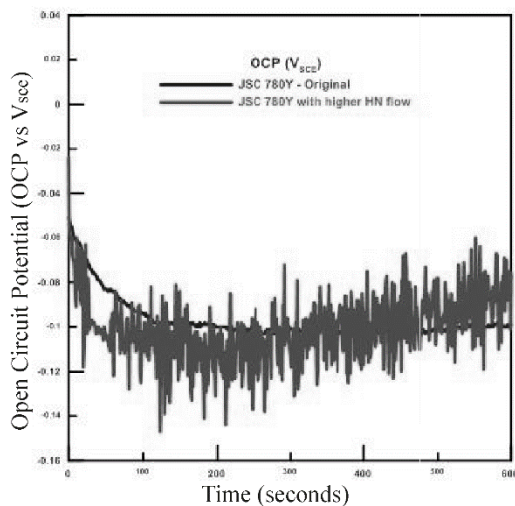


Fig.2. OCP measurement in phosphating

Figure 3 illustrates the phosphating weight gain measured at six interrupted phosphating times. The weight gain of original JSC780Y increased with phosphating time, but more outstanding weight gain occurred on the manufacturing modified sample. As compared with the OCP results in Fig.2., original and modified samples both had a potential drop in the beginning, but a more obvious potential fluctuation phenomena occurred on the modified sample resulting in a more efficient phosphating reaction. Normally, the phosphating inhibitors of alloy content, such as carbon, oxide and chromium especially<sup>(3)</sup> as indicated by the GDS result, would act as obstacles to phosphating. Due to mechanical strength concerns of JSC780Y, adding higher phosphating inhibitor elements would induce less weight gain of phosphating. Compared with the original and modified steels, the phosphating weight gain of modified substrate would be more apparent to increasing than the original one by 42% after 150 seconds reaction.

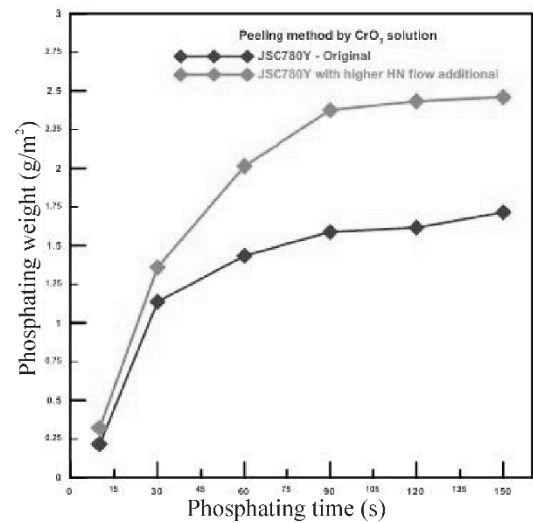
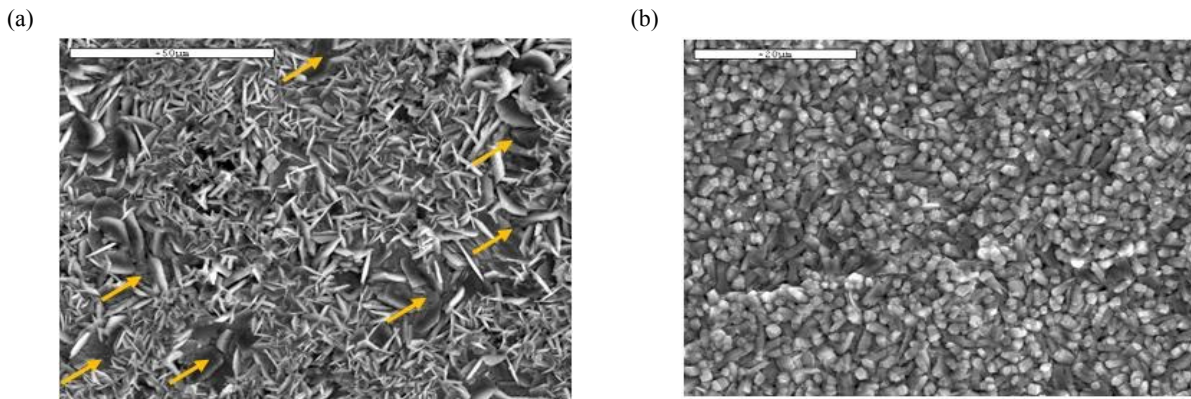


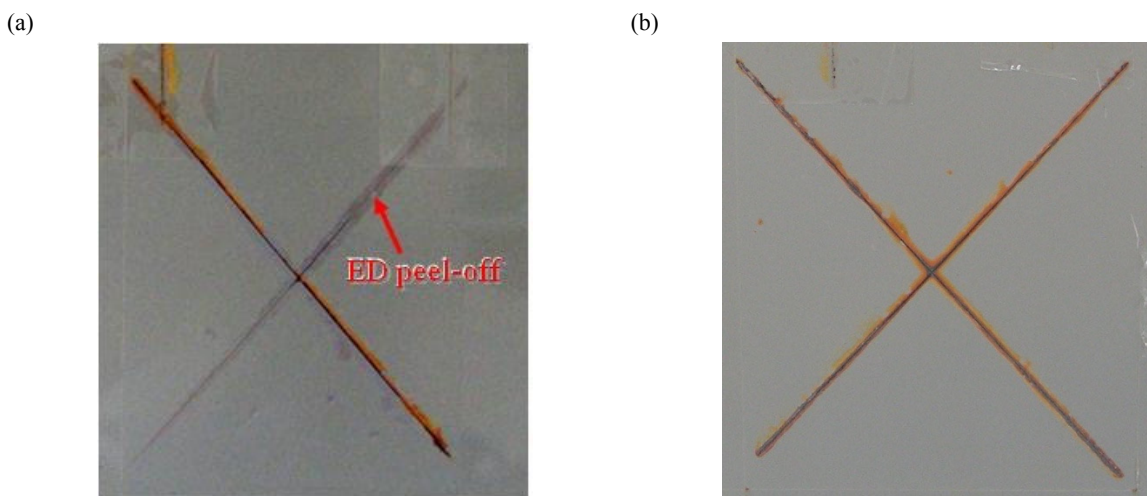
Fig.3. Phosphating weight measurement.

SEM was applied to observe phosphating morphology including crystalline and coverage ability after 150 seconds reaction of JSC780Y. In Fig.4. (a), phosphating of the original sample revealed the inconsistent crystalline size and lesser coverage ability with substrate exposed as pointed out by the arrows. On the contrary, the crystalline qualities of the modified sample became more uniform in grain size with compact crystalline without substrate exposure compared with the original JSC780Y. Furthermore, the columnar-like phosphating coating was observed on the modified surface, which means more  $Zn_2Fe(PO_4)_2 \cdot 4H_2O$  product (Phosphophlyte) formed as shown in Fig.4. (b). The plate-like coating formed of the original sample, showed in Fig.4. (a), indicated more  $Zn_3(PO_4)_2 \cdot 4H_2O$  phosphating product (Hopeite) existed. Consequently, more Fe element dissolved from the substrate surface and participated with the phosphating reaction in conversion solution of the modified substrates than the original types. Therefore, the modifications of manufacturing could provide a friendlier metallic surface and assist more  $Zn_2Fe(PO_4)_2 \cdot 4H_2O$  to crystallize during phosphating. According to research,  $Zn_2Fe(PO_4)_2 \cdot 4H_2O$  would be more corrosion resistant than  $Zn_3(PO_4)_2 \cdot 4H_2O$ , especially in thermal<sup>(6)</sup> and alkaline<sup>(7)</sup> environments. Thus,  $Zn_2Fe(PO_4)_2 \cdot 4H_2O$  would be more sustainable during ED painting (pH = 12~13) and afterward ED curing (180°C).

Figure 5 shows the corrosion resistance test by dipping ED samples in warm-salt-water. Apparent ED paint peel-off occurred on the original JSC780Y ED painting sample as shown in figure 5(a). Modified JSC780Y, however, showed better corrosion resistance and no obvious ED paint peeling occurred as figure 5(b) showed.



**Fig.4.** SEM observation after phosphating. (a) Original JSC780Y. (b) JSC780Y with higher HN flow.



**Fig.5.** Effect of manufacture modification on corrosion resistance of ED samples. (a) Original JSC780Y. (b) JSC780Y with higher HN flow

#### 4. CONCLUSIONS

Manufacturing modifications improve the surface quality of raw JSC780Y and enhance further phosphating reaction. According to additional HN mixed gas flow modification in annealing, the following phosphating reaction would be more effective with better crystalline and a more compact coating than the original manufacturing annealing parameter. Meanwhile, obvious phosphating weight gains of modified JSC780Y increased from the original types by 42%. Furthermore, the apparent improvement on corrosion resistance after ED painting was enhanced with no obvious peel-off of ED paint being observed after warm-salt-water dipping test.

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