Performance Characteristics of Zinc Nickel Alloys and Dip Spin Coatings for Fastener Applications

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As the performance criteria for plated fasteners have increased, directives to meet strict environmental considerations has forced sweeping changes to surface finishes. The resulting field performance has been as varied as the alternatives. This paper will compare Zinc Nickel Alloy Plating and Dip Spin Coating Technology in regards to various critical performance characteristics for automotive fastener applications. Corrosion resistance, total friction co efficient and contact with dissimilar metals among other key properties will be discussed.

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Comparison between Zn-Ni electro plating and dip spin

In today's competitive market place, consumers require higher quality products than ever before. The automobiles are used under severe conditions, especially in regions such as North America and Europe. During the winter, people spread salt with gravel for prevention of road ice. In the summer, sand particles causes erosion, which plays a role in initiating cavities. Dipsol of America provides several zinc-alloy plating processes for fastener application which offers better performance against high corrosive environments. At this time we will try to compare performance between Zn-Ni alloy electro plating and dip spin application.

General Alloy Plating Mechanism for corrosion performance.

More than 100 types of electroplated alloy processes have been invented since zinc-copper alloy was developed in 1841. The merits of alloy plating are as follows:

1. We can achieve new phases that do not exist on metallography phase diagrams.

2. We can get the alloy which we can never get by melting method, as between high melting point metal and low melting point metal, because low melting point metal vaporizes as a high melting point temperature.

3. We can get a high performance deposit film while using a thin coating.

Feature

- Corrodes sacrificially to steel.
- Stability of its corrosive products.
- Adherent chromate conversion film.
- Low dissolution rate of chromate film against salt solution.

Corrosion of Steel Plated with Zn and Zn Alloy

By plating deposits of zinc and zinc alloys on steel substrate, steel substrate will be protected. Because of their poor ionization tendency, zinc and zinc alloys sacrificially dissolve prior to the iron.

Fig-1) Corrosion performance NSS

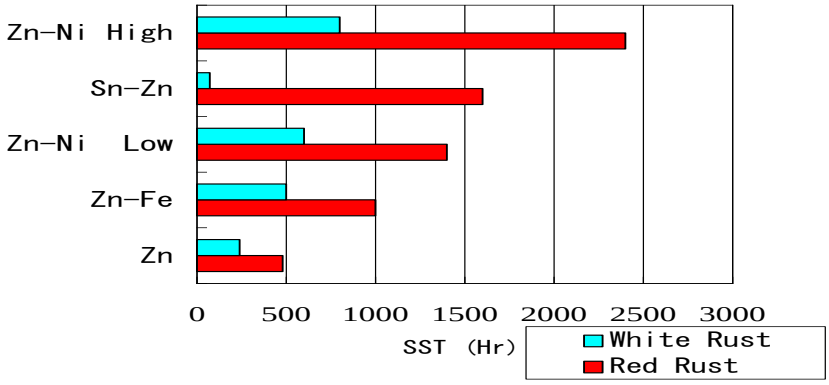


Fig-2) Corrosion performance and Ni co-deposition rate NSS

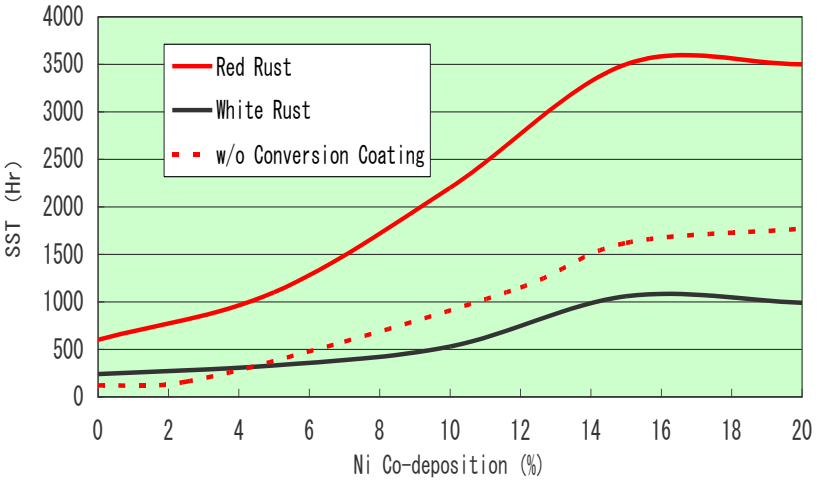


Fig-3) Corrosion Potential (in 5% NaCl Solution)

Base → Noble

Zn < Zn-Ni (6 - 7%) < **Zn-Ni (10 - 16%)** < Cd < **Fe** < Ni

-1.1V -1.0V～ -0.9V -0.6V

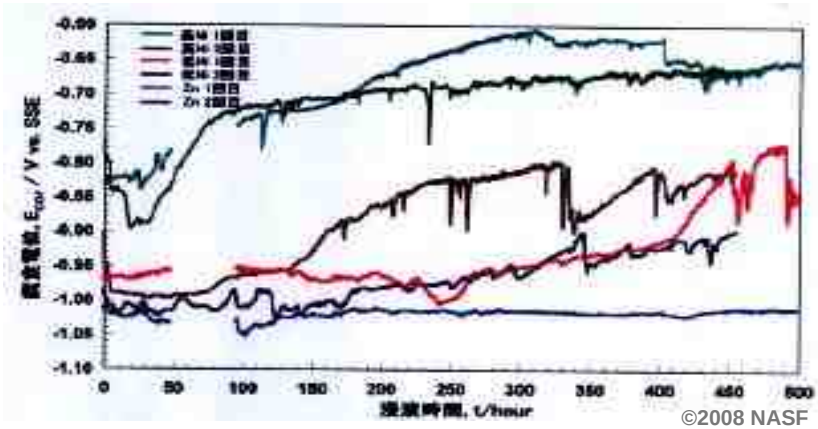


Fig-4) Crystal Structure of Plating deposit (XRD)

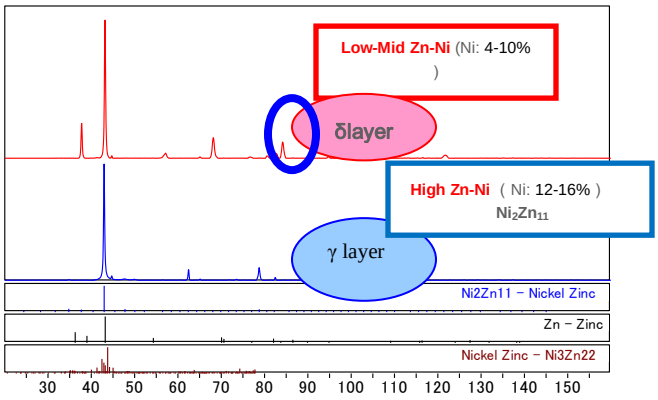
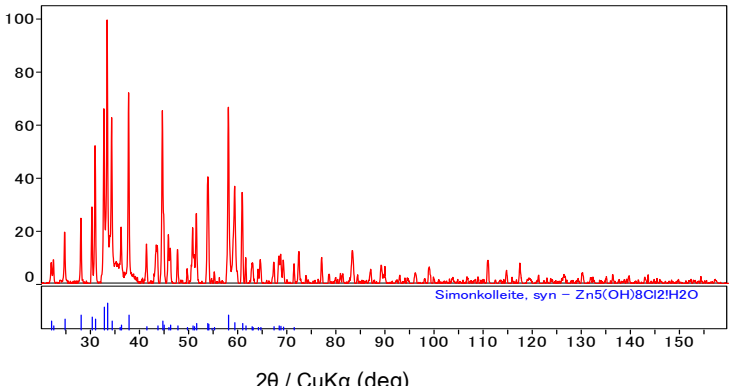


Table-1) Corrosion Speed

	Zn	Zn-7%Ni	Zn-15%Ni
Metal Density (ρ)	7.14	7.26	7.40
Nyquist Prot Charge Transfer Resistance (Ω)	500	5000	21300
Corrosion Current Density (A)	4.2×10-05	4.2×10-06	9.8×10-07
Corroding Speed (μ m/month)	51	5.0	1.2

5% NaCl solution, Immersion Time: 10min, Reference Electrode: Ag/AgCl, Sub Electrode: Pt

Fig-5) Corrosive production



$Zn_5(OH)_8Cl_2 \cdot H_2O$

As we see at Fig-1) Corrosion performance NSS(Neutral Salt Spray). We could get very stable corrosion performance finish from Zinc alloy electro plating deposit.

The reason of high corrosion performance

1. Corrosion potential is getting closer to steel substrate (Fe) according to increase of Ni content in Zn-alloy deposit. Refer Fig-2), Corrosion performance is going better according to Ni co-deposit percentage. Previously we thought that at 15% Ni co-deposition rate we have the maximum peek for corrosion performance due to corrosion potential becomes noble. Fortunately our newest conversion coating technologies improvement provides still better sacrificial protection even over 16% of Ni, and we could get higher corrosion performance. At Fig-3) we could see corrosion potential difference between conventional zinc, low Zn-Ni and high Zn-Ni. Zn is -1.1V and this is too much for sacrificial protection. So addition of Ni provides control of excess of sacrificial protection.
2. Crystal structure of deposit is uniform and single structure. In case of low Zn-Ni, Zn-Ni has 2 phases crystal structure in its deposit. And it provides galvanic cell corrosion. Refer Fig-4. low Zn-Ni has Zn, Ni_3Zn_{22}, δ + γ as dual phases. High Zn-Ni has only Ni_2Zn_{11} γ phase.
3. Corrosive production is very stable against corrosive atmosphere. Refer Fig-5) Zn-Ni alloy creates Basic Zinc Chloride on the top of its deposit layer , and it provides barrier film which has high electric resistance and lower dissolution rate . We could see corrosion speed of Zn, low Zn-Ni and high Zn-Ni alloy deposit at Table-1). High Zn-Ni corrosion speed is 1/50 of conventional Zn.

Corrosion resistance performance

Refer Fig-6), we could see comparison between Zn, low Zn-Ni and high Zn-Ni.
Even bending area which was executed 8mm Erichsen test, has good corrosion performance.

Fig-6) Corrosion performance test NSS with bending

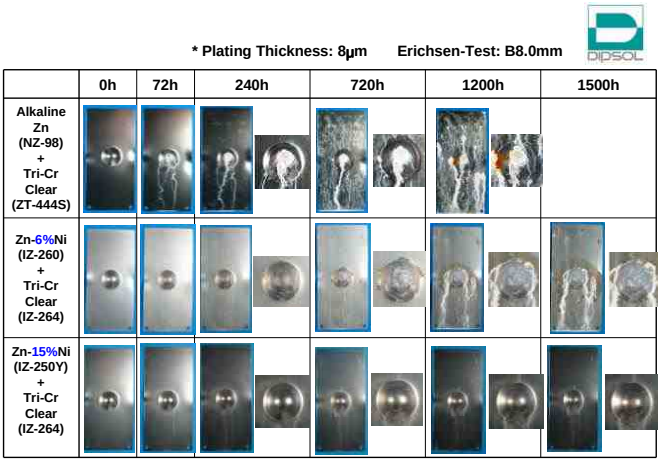


Fig-7) Bend test 3000hours after NSS

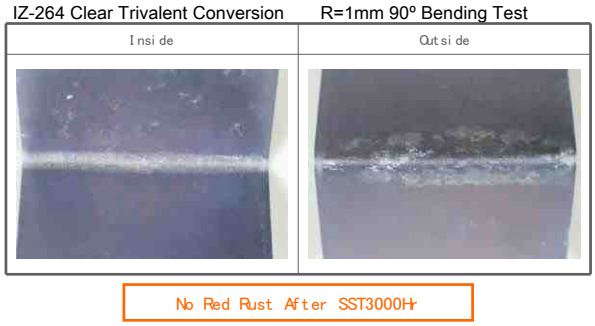
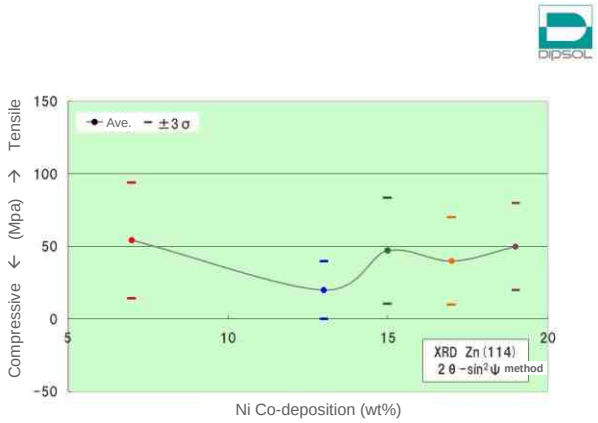


Fig-8) Deposit hardness

Non-Cyanide Zinc	100	-	140	Vickers
Acid Chloride Zinc	60	-	80	Vickers
Zinc Cobalt (Acid)	180	-	210	Vickers
Acid Zinc Nickel	140	-	180	Vickers
Alkaline Zinc-Nickel	250	-	310	Vickers
High Zn-Ni	350	-	450	Vickers
Zinc Iron (Alkaline)	100	-	150	Vickers
Tin Zinc	13	-	17	Vickers

Fig-9) Stress test



Bending property/ Ductility
Due to existence of Ni metal in deposit, Zn-Ni has higher hardness. Refer Fig-8)
This higher hardness property is positive for anti-scratch performance.
Also we could pass corrosion performance requirement even after Sevier bending test. Refer Fig-6,7,
Also High Nick system showed very minor Tensile stress which does not provide serious stress trouble.

Performance Comparison between Zn-Ni alloy and dip spin

Fig-10) CCT comparison (finished fastener itself)

JASO Mode "Cyclic Corrosion Test" (Salt Spray 35°C-4Hr ⇒ Dry 60°C-2Hr ⇒ Humidity 95%-50°C-2Hr)

		0 cycle	10 cycle	30 cycle	60 cycle	100 cycle	200 cycle
High Nick Process (Ni: 15%) + Tri-Cr Conversion IZ-264	Plating 5μm						 Red Rust
	Plating 8μm						 Red Rust
Geomet 720	2Coat 2Bake		 Red Rust				

Fig-11) Comparison table between Zn-Ni and dip spin (Description)

	Film Forming	Post Treatment	Film Structure	Corrosion Resistance Mechanism
High Ni% Zn-Ni Alloy Plating (High Nick Process)	Electroplating in Aqueous Solution (Room Temperature Operation)	Tri-Cr Conversion Coating	Alloy – Zn, Ni distributed uniformly Zn · Ni_2Zn_{11}(γ)	Zn's sacrificial protection & anti-rust compound made of Zn·Ni
Geomet 720	Dip Coat Paint Bake to dry (Over 200°C)	Organic Polymer Top Coat Or Friction Modifier	A type of Paint made of metal flake and silicon- series inorganic binder	Coating film works as a barrier layer

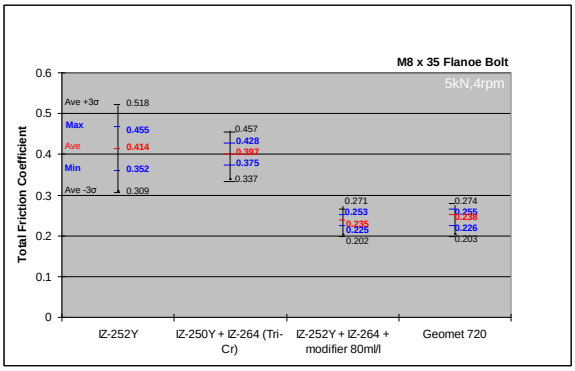
Both Alkaline High Alloy Zinc Nickel and Geomet 720 provide a higher level of corrosion protection in terms of Salt spray protection. As shown in figure 10, the zinc nickel performance advantage really becomes evident when subjected to Cyclic Corrosion Testing. Many consider cyclic testing to be most representative of field performance.

The corrosion resistance advantage of zinc nickel is founded on its fundamental electro potential difference to steel. This results in a coating that is sacrificial to steel thus protecting the functional performance of the part, which is paramount for fastener applications (figure 11).

Dip – Spin type coatings as indicated in figure 11, work as a barrier film to protect the base part or substrate. As with all barrier coatings, performance can be excellent, however their performance relies heavily on that barrier layer not being damaged or breeched. Much has been done to try and improve the coatings susceptibility to reduced corrosion resistance whenever the barrier layer is damaged but this issue remains as a significant problem particularly with field or production scale parts.

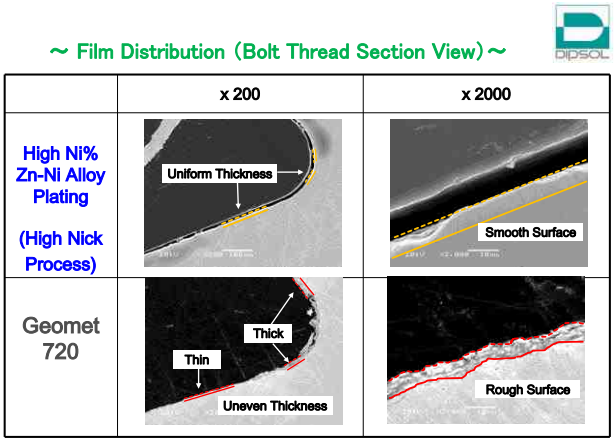
Torque values for both zinc nickel alloy plating and Dip spin type finishes are achievable for most desired requirements. (Fig-12)

Fig-12) Torque tension comparison



The rapid advancement of Organic polymer or friction modifying topcoats enable them to be applied and bonded to either finish. Zinc Nickel Alloy plating in field or production scale provides a more consistent torque and corrosion resistant result. This is largely due to the smooth, consistent finish over the entire part and especially threaded areas when compared to dip spin applications, which can suffer from significant variances Figure 13. Zinc nickel is free from the head and thread fill issues of dip spin coatings.

Fig-13) Zn-Ni plating and dip spin comparison Cross section



Conclusion

There is a long track record of performance for both alkaline zinc nickel alloy plating and dip spin coating technology. Alkaline zinc nickel coatings are an electro chemical process and therefore provide a smooth, more uniform finish when compared to dip spin coatings. High Alloy Alkaline Zinc Nickel coatings maintain stable performance even after aging and can use conventional plating equipment. The above attributes, combined with zinc nickel being a truly sacrificial coating, make it an ideal choice for peak performance fastener plating.