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**A Comparative Study of Gamma-Phase Zinc-Nickel Deposits
Electroplated from Various Alkaline and Acid Systems**

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ABSTRACT

Sacrificial, anodic coatings, specifically zinc deposits, have provided corrosion protection to components and parts across many industries with an increasing demand in the automotive and industrial sectors. Today, typical sacrificial applications for fasteners, fuel systems, braking systems and drive assemblies require an increasing demand for higher corrosion performance from anodic coatings. Electrochemical alloys can be designed to provide the highest corrosion potentials to meet these increased demands. Today zinc-nickel alloy systems deposited from alkaline and acid chemistry types can provide excellent performance in many applications. However, comparing and contrasting these deposits and the systems that provide the zinc-nickel alloys will provide a good knowledge basis for selecting the best system for the required application.

Keywords: zinc-nickel deposits, alkaline chemistry, acid chemistry, fastener finishes, alloy plating, properties, sacrificial corrosion

Introduction

In the last decade, electroplated zinc-nickel deposits have become increasingly requested. The main reason for this is the ability of zinc-nickel to offer excellent corrosion protection when applied over ferrous substrates. Galvanic corrosion happens in an aqueous environment, such as a 5% neutral salt solution, when two metals with different electrode potentials come in contact with one another. When this happens, as shown in Fig. 1,¹ the sacrificial metal, which has a more negative potential, loses electrons and oxidizes to become an aqueous cation. The greater the difference in potential between the two metals, the faster this dissolution happens. As shown in Fig. 2,² reactive metals such as zinc and magnesium have a more negative potential compared to cast iron and steel, while noble metals like silver and platinum have a less negative potential.

In Fig. 2, highlighted in yellow, zinc-nickel is seen to be sacrificial to cast iron and steel, though not quite as sacrificial as pure zinc. In this way, a zinc-nickel layer over steel would corrode less quickly than a pure zinc layer of comparable thickness. It is also seen that cadmium has a very close sacrificial potential to steel, and would provide superior corrosion resistance in a salt water environment. However, due to the well-known toxicity of cadmium and its compounds, zinc-nickel deposits have been desired by industry as a more environmentally safe alternative to cadmium.

Of particular interest in the zinc-nickel alloy system is the gamma phase zinc-nickel (γ Zn-Ni). The reason for this is that it has been widely accepted that γ Zn-Ni provides better corrosion resistance and ductility than other phases when applied over cast iron or steel. The binary phase diagram in Fig. 3³ depicts how the majority of this γ phase is found when the nickel content ranges between 14 - 25 wt% in a temperature range of 0 - 700°C. In the electroplating industry, a deposit containing between 12 - 16 wt% nickel is usually what is specified and desired, although specification ranges may be opened to 10 - 18 wt%.

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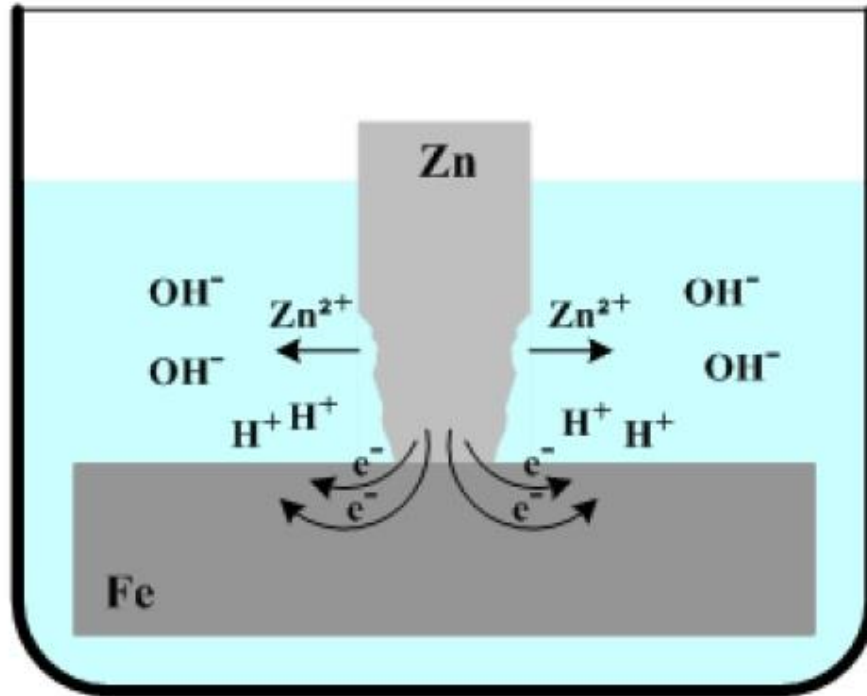


Figure 1 - Schematic representation of the corrosion of zinc deposited on a ferrous substrate.¹

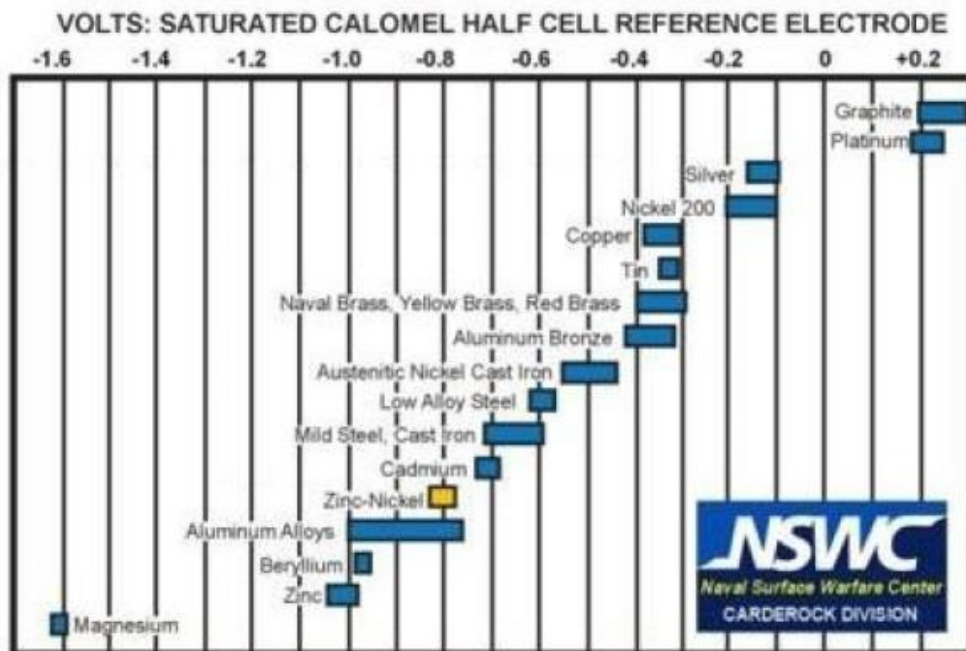


Figure 2 - Electrochemical potentials of various metals and alloys in salt water.²

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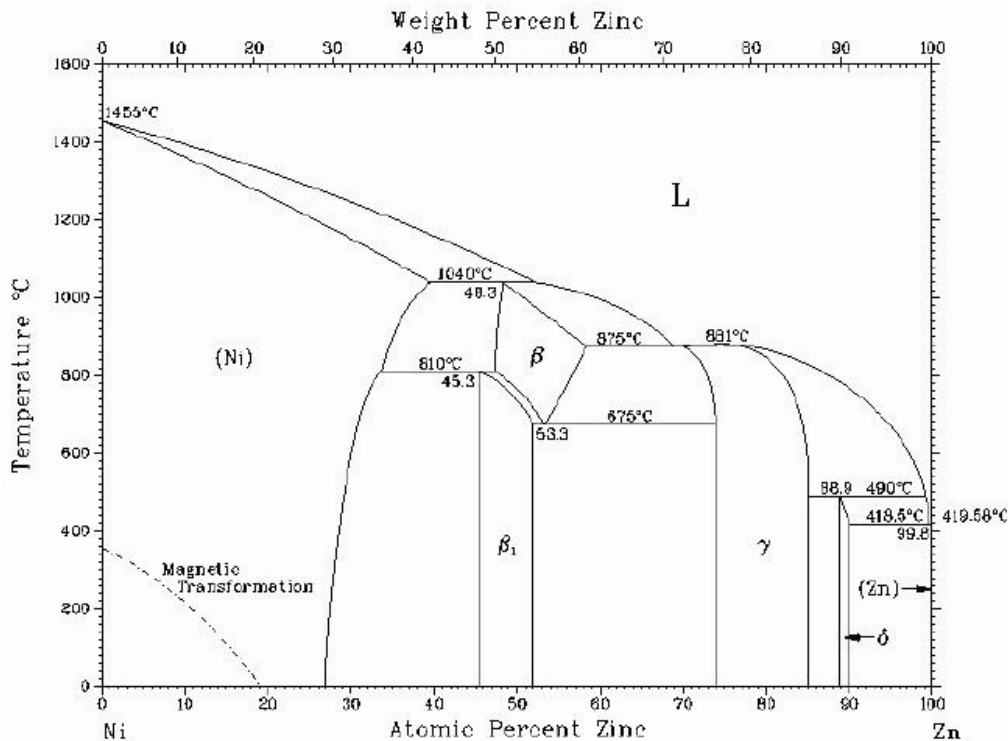


Figure 3 - Zinc-nickel phase diagram.³

In the mid-1980s, ammonium chloride-based acid zinc-nickel processes were the first commercially available systems that were able to provide a gamma zinc-nickel plated deposit. By the mid-1990s, there were patents issued for alkaline zinc-nickel systems that provided this desired deposit. Both systems have benefits and disadvantages, as well as similarities and differences in their operation and deposit characteristics.

Operational and deposit characteristics

Two very obvious differences between the alkaline and acid based systems are the plating speed and distribution. Like other alkaline plating systems, the alkaline zinc-nickel plates at a significantly lower plating speed than the acid system, but has a better distribution of thickness between the high current density (HCD) and low current density (LCD) areas. Typically, alkaline Zn-Ni systems plate with ~60% cathode efficiency upon fresh makeup, and often drop lower as carbonates and breakdown products form. By comparison, the acid systems plate in the 90 - 95% efficiency range, depending on metal levels in the bath. As shown in Fig. 4, to achieve an 8-μm minimum thickness in the LCD area (Point #2), the alkaline system will deposit ~1.5 times as much plate in the HCD (Point #1) while the acid system deposits twice as much thickness in the HCD. It is also seen how tightly the alloy range is maintained from the HCD to LCD in the alkaline compared with the acid system.

Figure 5 shows that, while the thickness distribution is better in the alkaline system, the plating speed is about double with the acid chemistry. Also seen to a lesser degree is the difference in deposit aspect. The alkaline deposits are typically less leveled, and appear as a brushed stainless steel. They also tend to have a frosted appearance in the HCD due to formation of dendrites of zinc-nickel metal. Acid Zn-Ni deposits, on the other hand, visually resemble a bright acid zinc deposit. The panels in Fig. 5 were photographed reflecting a black and white striped backdrop to show brightness of the deposit.

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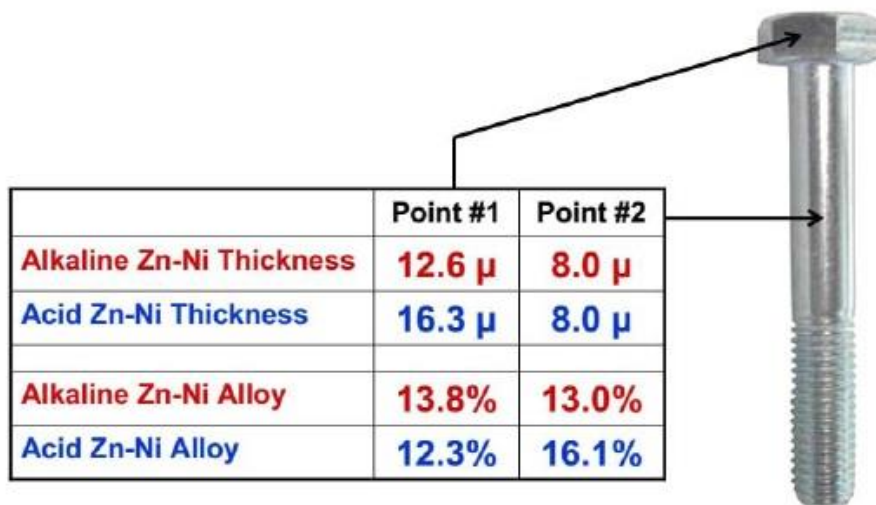


Figure 4 - Comparison of thickness and alloy composition in high and low current density areas between alkaline and acid zinc-nickel deposits.

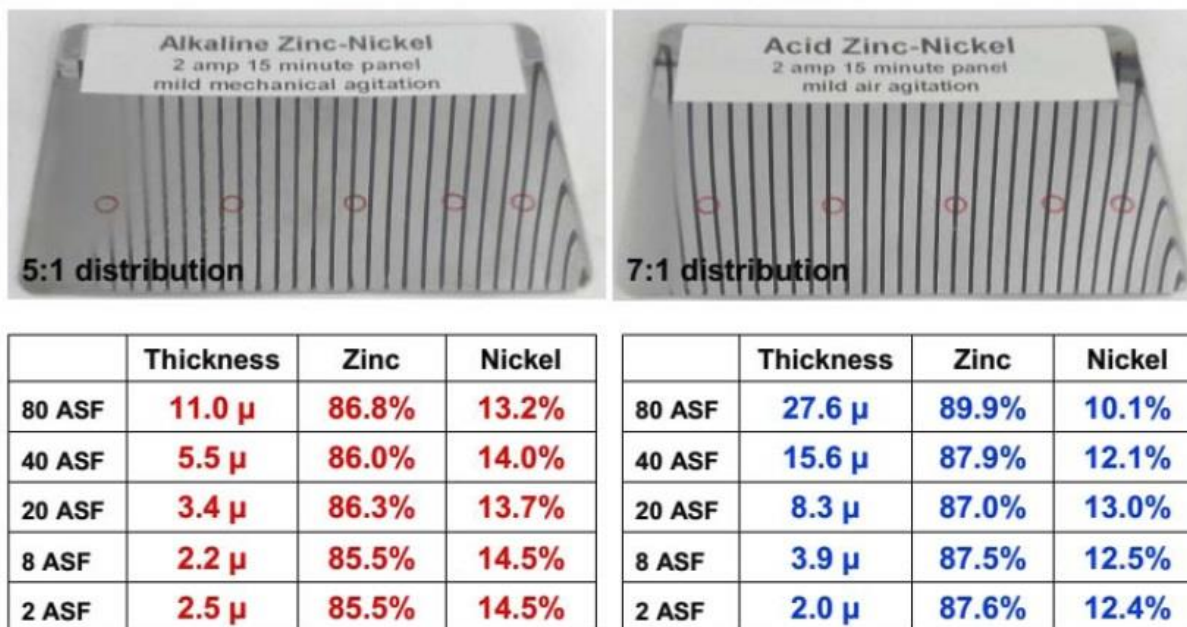


Figure 5 - Comparison of thickness distribution, plating speed and deposit appearance between alkaline and acid zinc-nickel deposits.

When comparing the different deposits of γ Zn-Ni, it is also important to look at the surface morphology and grain structure of the deposits. With the use of a scanning electron microscope, we are able to see in Fig. 6 how the alkaline Zn-Ni appears to have a slightly more globular morphology, especially in the HCD areas. This may explain why the acid Zn-Ni plated bolt that corresponds with these images has a higher luster than that of the alkaline Zn-Ni bolt.

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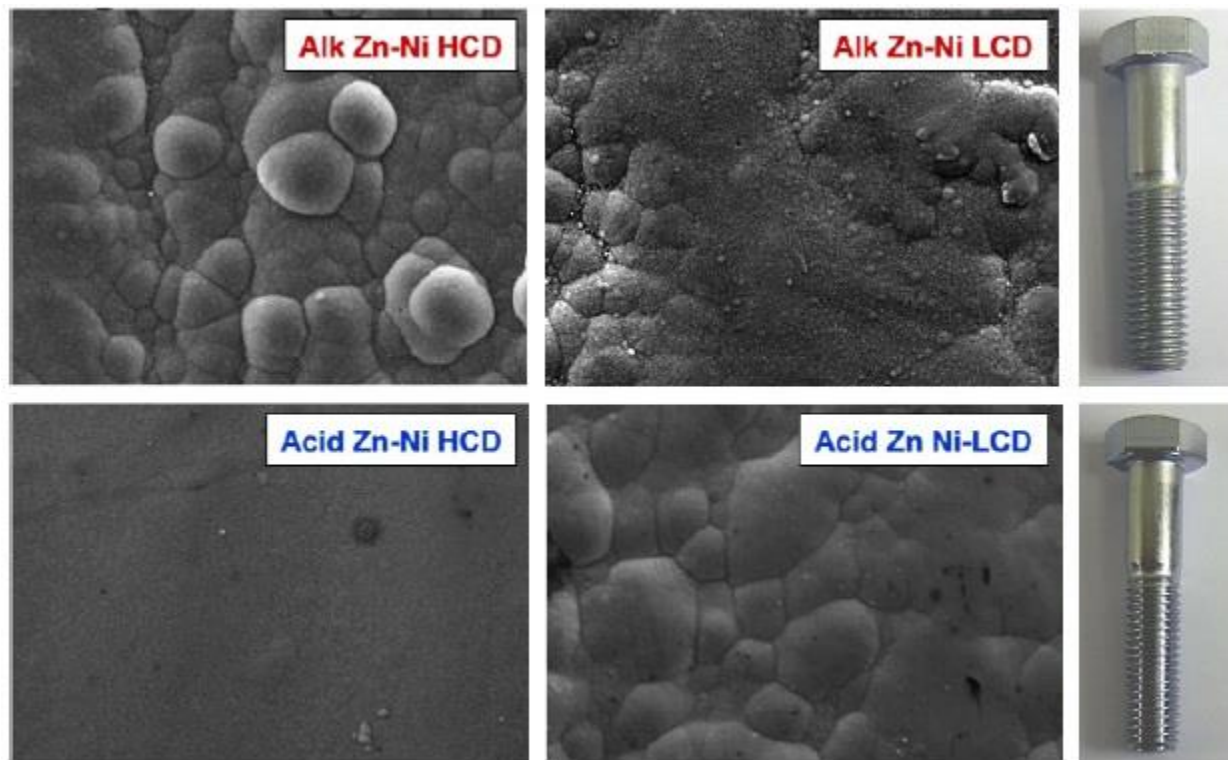


Figure 6 - Comparison of the surface morphology of alkaline and acid zinc-nickel deposits at high and low current density areas (SEM: 2000 $\times$).

In Fig. 7, different deposits were cross-sectioned, polished, and then etched to show grain boundaries. While all of the deposits show a columnar structure to some degree, the barrel-plated parts show some laminar tendencies as well. One possible explanation for this may have to do with the make-and-break contact occurring in a barrel. As a part breaks contact, the deposit may passivate before the part makes contact again, and another layer of plate is laid down. This possibility may be further supported by the appearance of this laminar layer being more prominent with the alkaline process, as a higher pH solution will not keep the zinc-nickel layer as active as with an acidic solution.

One major advantage of the acid zinc nickel system is its ability to plate difficult substrates such as cast iron. Some products that might be constructed from cast iron would include black iron pipe, check valves, couplings and automotive brake calipers. With an alkaline process, the plated layer tends to trap solution in the pores of the substrate, which leads to latent bleed-out of trapped solution and premature corrosion. Also, because of the high carbon content of cast iron (between 2.1 - 4.0 wt% carbon), plating initiation is extremely difficult with the less efficient alkaline system. If an alkaline zinc-nickel finish were desired, it would require the extra step of an acid zinc strike. Since the introduction of the acid Zn-Ni processes, castings can be plated directly after pretreatment.

Figure 8 shows an automotive brake caliper bracket that was plated with a commercially available acid zinc-nickel bath. The deposit not only contains nickel alloy within the desired 12 - 16 wt% nickel, but also shows a bright and visually desirable appearance. Consistent with acid processes, the HCD areas contain nearly three times the amount of plating thickness as the LCD.

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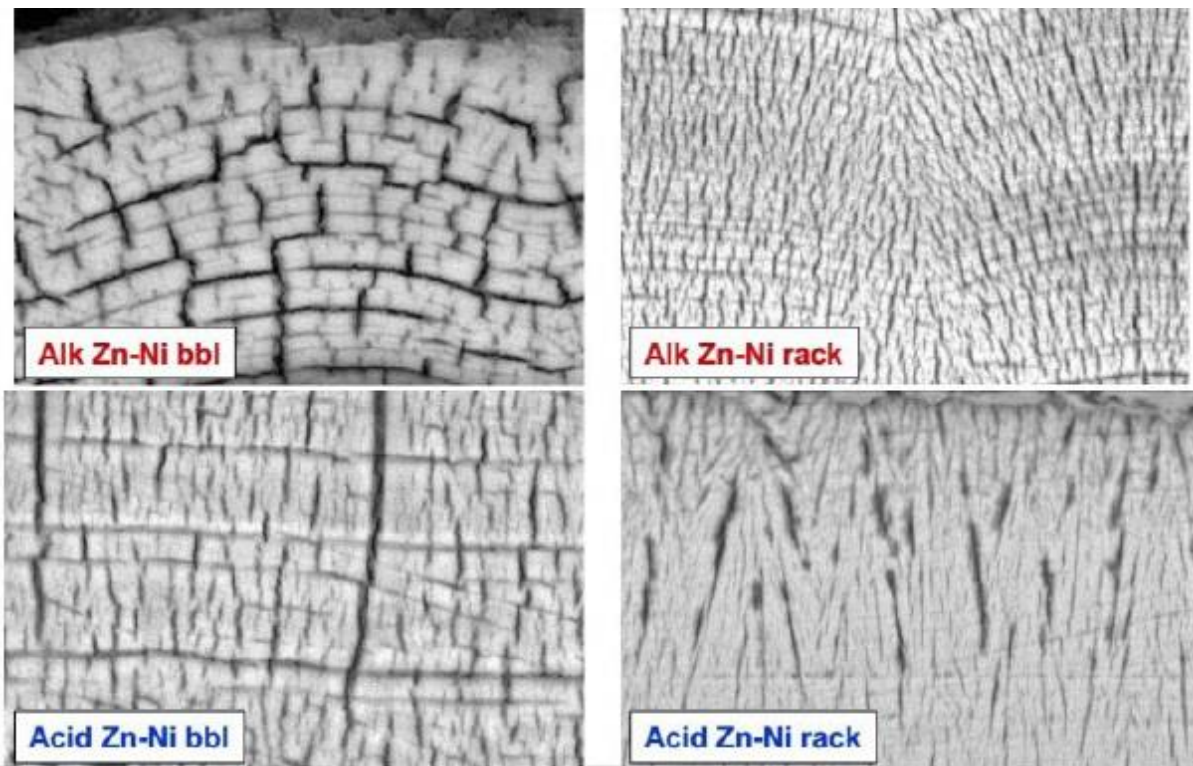


Figure 7 - Comparison of the cross-sections of alkaline and acid zinc-nickel deposits produced by rack versus barrel plating (SEM: 10,000 $\times$).

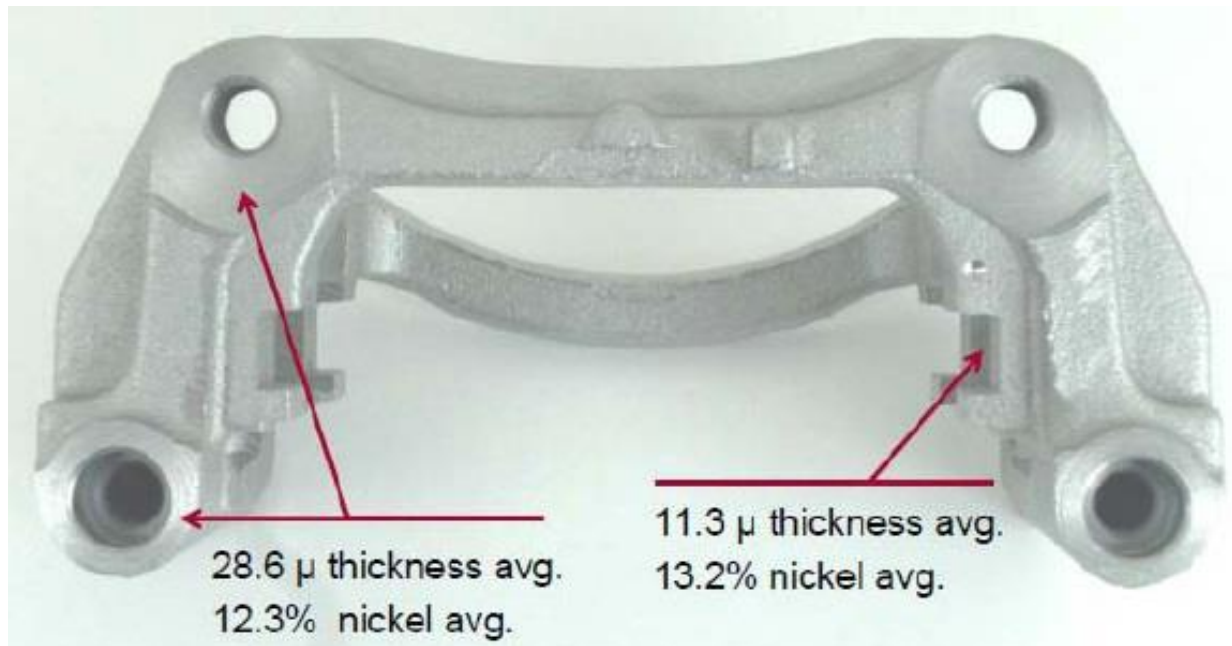


Figure 8 - Appearance, composition and thickness distribution on an automotive brake caliper bracket plated with a commercially available acid zinc-nickel bath.

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Corrosion performance

As stated previously, zinc nickel's coveted property is its ability to withstand corrosion protection. Not only is corrosion protection important for material integrity, but also aesthetics. In the case of brake calipers for instance, many of today's sporty automobiles have wheel rims that display the braking mechanism (Fig. 9). Of increasing importance to end users is a brake caliper that not only has a bright and uniform deposit, but displays no unsightly red rust.



Figure 9 - Modern wheel rim style with exposed brake calipers.

For automotive corrosion specifications, two very frequently used standard tests are the neutral salt spray test, and the cyclic test. Specifications vary, but at the higher end demand 25 cycles in a cyclic chamber, or 1000 hr of neutral salt spray with no signs of red corrosion. In Fig. 10, we can see that these corrosion resistance specifications are met easily with an acid zinc nickel deposit.

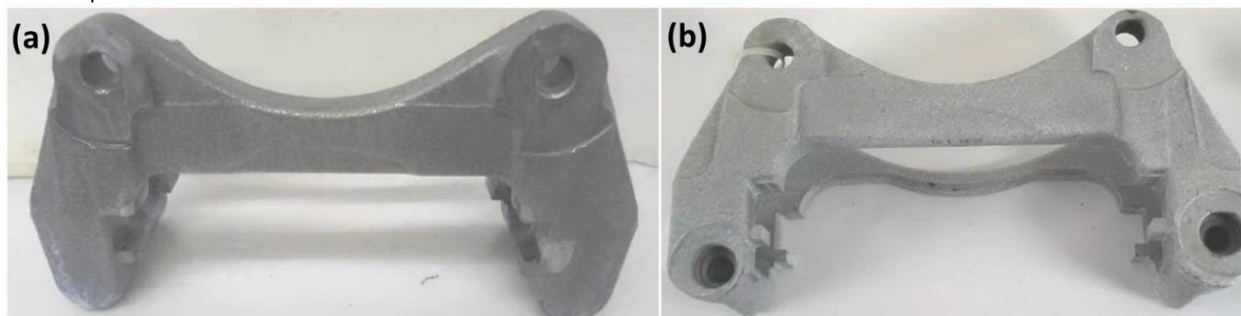


Figure 10 - Automotive corrosion test results on acid-zinc-nickel plated brake calipers after (a) 2480 hr of neutral salt spray testing per ASTM B-117 and (b) 25 cycles of GMW 14872 cyclic testing.

Electrochemical studies

Salt spray and cyclic chambers provide a reasonable comparison of corrosion protection, but if a more scientific approach is desired, a potentiostat / galvanostat can offer more numeric precision. Below are some graphs that show a conventional alkaline Zn-Ni versus acid Zn-Ni run through several tests using this method. In all cases, the steel test panels had 9 μm of thickness, with 12.5 wt% nickel in the deposit.

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Since the open circuit potential (E_{OC}) is the starting point for potentiostatic corrosion experiments, we began with the experiment shown in Fig. 11(a). The value of the open circuit potential was determined to establish relative electrode potentials. The figure shows an open circuit potential versus a silver chloride reference electrode. The test pieces were immersed for 30 min in a 5% neutral sodium chloride solution with no current applied. After the test pieces were allowed to stabilize, the electrode potential of each sample was calculated and plotted on a graph. The acid Zn-Ni deposit exhibited a more negative electrode potential than the alkaline Zn-Ni deposit, indicating that the acid deposit would be more anodic to the steel substrate than the alkaline deposit and thus would corrode more quickly.

Figure 11(b) shows an anodic polarization sweep. In this experiment, there was a constant upward sweep of potential, while measurements of current density on the surface of the test pieces were measured. The voltage was increased at a rate of 2.5 mV/sec versus a silver chloride reference electrode for 400 sec. Although very similar, the acid Zn-Ni deposit had a slightly higher activity at a given applied voltage than the alkaline. This would again suggest a more rapid corrosion rate, which is in fact proven. The acid zinc nickel, though identical in thickness, failed to the base substrate slightly before the alkaline process.

Figure 11(c) shows a very similar trend. In a galvanostatic corrosion test, a constant current (10 mA/cm²; 9 A/ft²) was applied for 30 min. Again, the acid Zn-Ni process failed slightly before the alkaline Zn-Ni deposit of similar thickness and alloy content.

Physical properties

Gamma phase zinc-nickel exhibits relatively high hardness values. This can be valuable when wear resistance is needed. As shown in Fig. 12, not only does gamma phase Zn-Ni have a higher Vickers hardness value than either pure electroplated metal, but it is also harder than 8.8 steel. The first five values on the left side of the chart are accepted literature values.⁴ The last three values on the right were ones that were actually observed during micro-hardness tests using a 100-g load. Note that just as alkaline zinc is harder than acid zinc, so alkaline zinc-nickel is also harder than acid zinc-nickel. All test specimens were plated from commercially available systems, and all proprietary chemistry was kept in accordance with an optimized technical data sheet.

With increased hardness of deposits comes the likelihood of reduced ductility. In the case of hardware or brake calipers, ductility is not so crucial, as parts are not bent. However, zinc-nickel may be desired over a part requiring post-finish bending, such as a fuel rail. Because of the complex three-dimensional configurations of such a part, it is more economical to plate the part while straight, and then bend after finishing. The issue that could arise from this type of processing is deformation of the zinc nickel deposit, causing fissures in the plate that extend to the basis metal layer, simultaneously setting up a galvanic cell, and leading to corrosion sites. Figure 13 is a depiction of the conical mandrel that was used in several experiments to observe the ductility of three zinc-nickel systems. The substrate was a mild steel panel with thickness of 0.021 in. (534 μ m). The panels were plated to a thickness of 10 - 14 μ m with 12 - 13 wt% nickel in the deposit, and then bent over the mandrel.

Figure 14 shows how cracks propagate across the zinc-nickel layer when bent. The images were taken using the SEM at 250 $\times$ magnification. Tensile bending, in which the deposit was stretched on the outside of the substrate, was compared to compressive bending, where the deposit was compressed on the inside bend of the substrate. Tensile bending (Fig. 14(a)) did show a little difference between the systems, inasmuch as the ductile zinc nickel appeared to have more of a micro-discontinuously cracked surface, especially at the tighter 4.2-mm diameter bend area. One might expect that this micro-cracked surface would offer more corrosion protection than the acid Zn-Ni deposit, where the cracks were less numerous, but seemingly deeper and wider. The theory behind this is twofold. First, shallow and narrow cracks would limit the pathways of solution to the substrate, preventing the set-up of a galvanic corrosion battery. Secondly, if there was any current generated from galvanic corrosion between the dissimilar metals, the current would be on many sites and spread over a greater area, therefore reducing the current density on any one site, and decreasing the rate of corrosion on those sites. Compressive bending (Fig. 14(b)) seemed to show an even greater contrast between the systems. Clearly, deposits from the conventional alkaline process seemed to produce much larger cracks in the deposit than those from the ductile alkaline system, which was expected. What was not expected was how small and discontinuous the cracks were in the acid process, especially at the wider diameter compressive bend.

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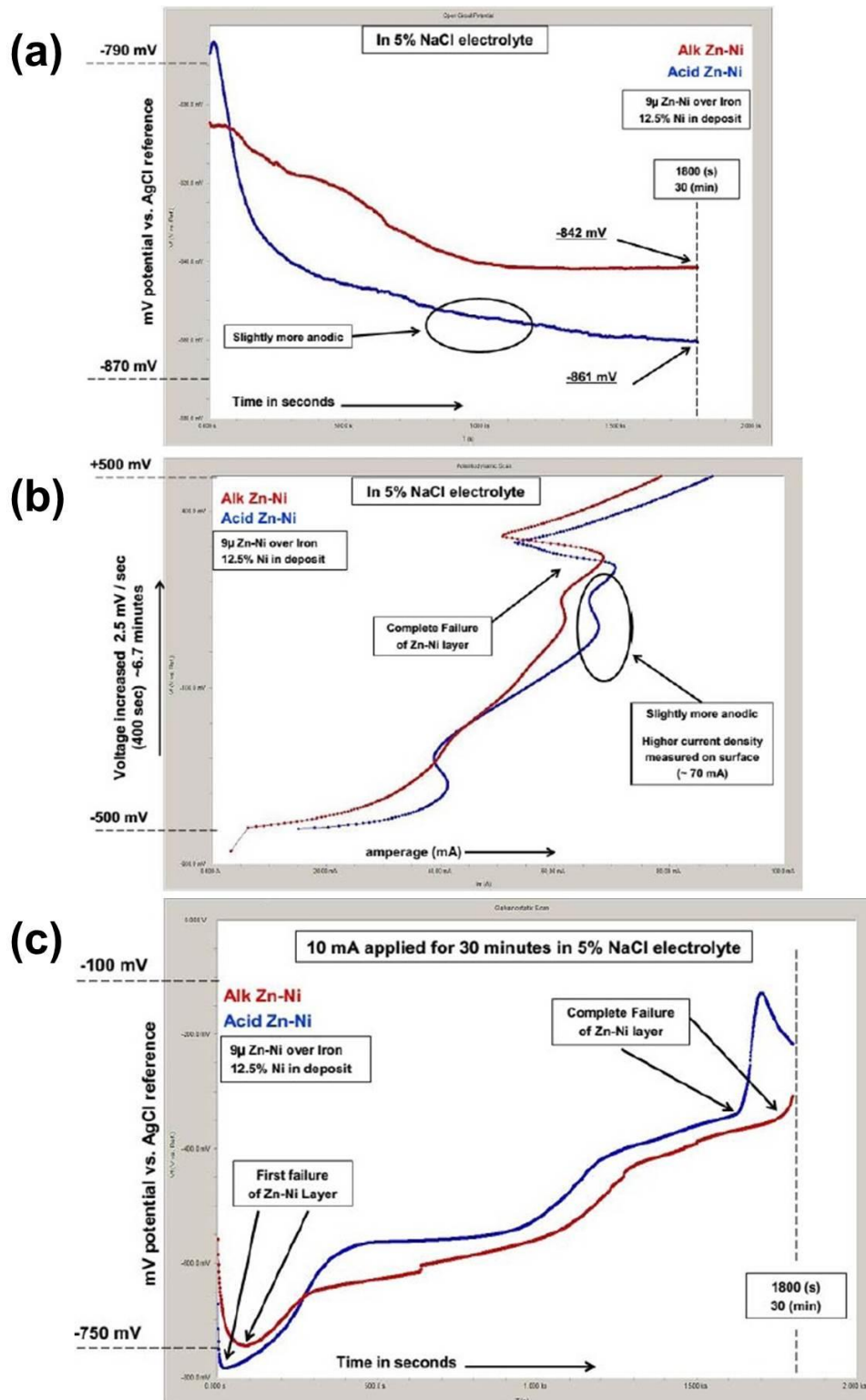


Figure 11 - Electrochemical test results: (a) Open circuit potential measurement; (b) anodic polarization study and (c) galvanostatic corrosion study.

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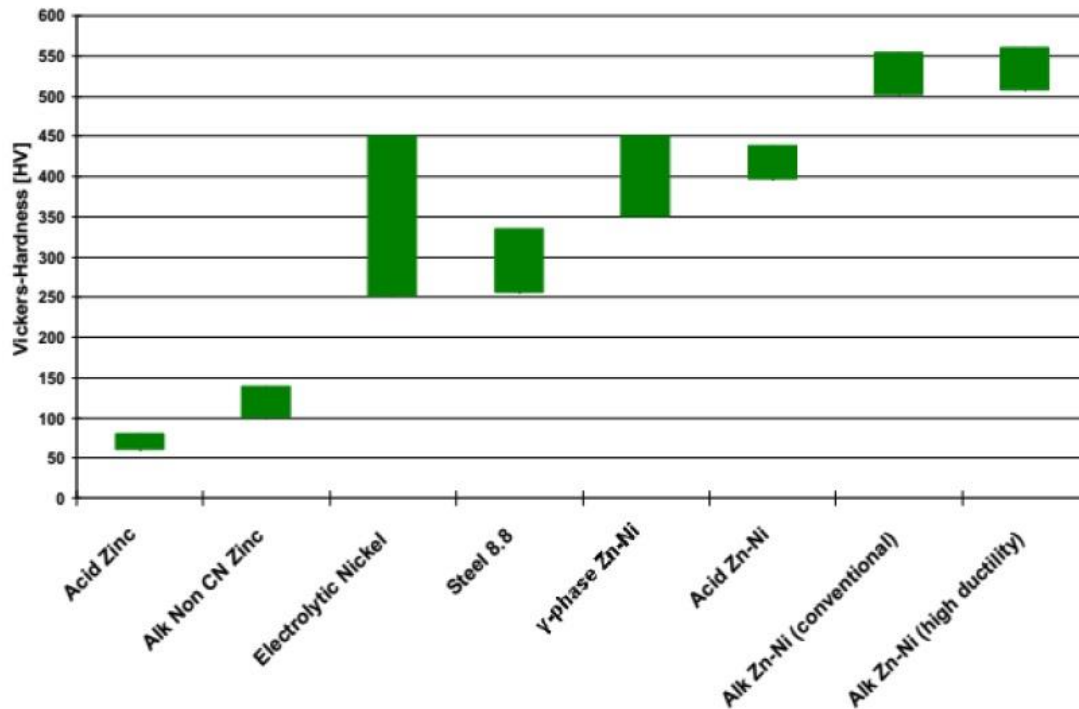


Figure 12 - Vickers hardness values of various zinc, nickel and various zinc-nickel alloy electrodeposits (8.8 steel used as a reference).⁴

Theoretical 3 mm diameter at the edge

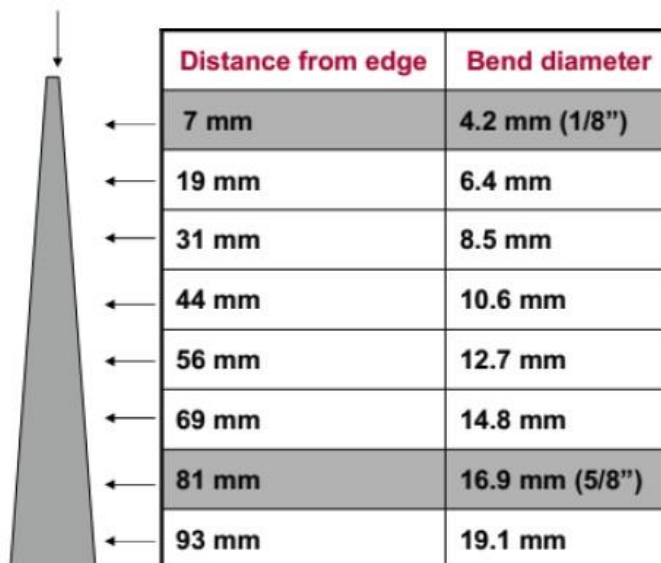


Figure 13 - Geometry of the conical mandrel used in the bend test for deposit ductility.

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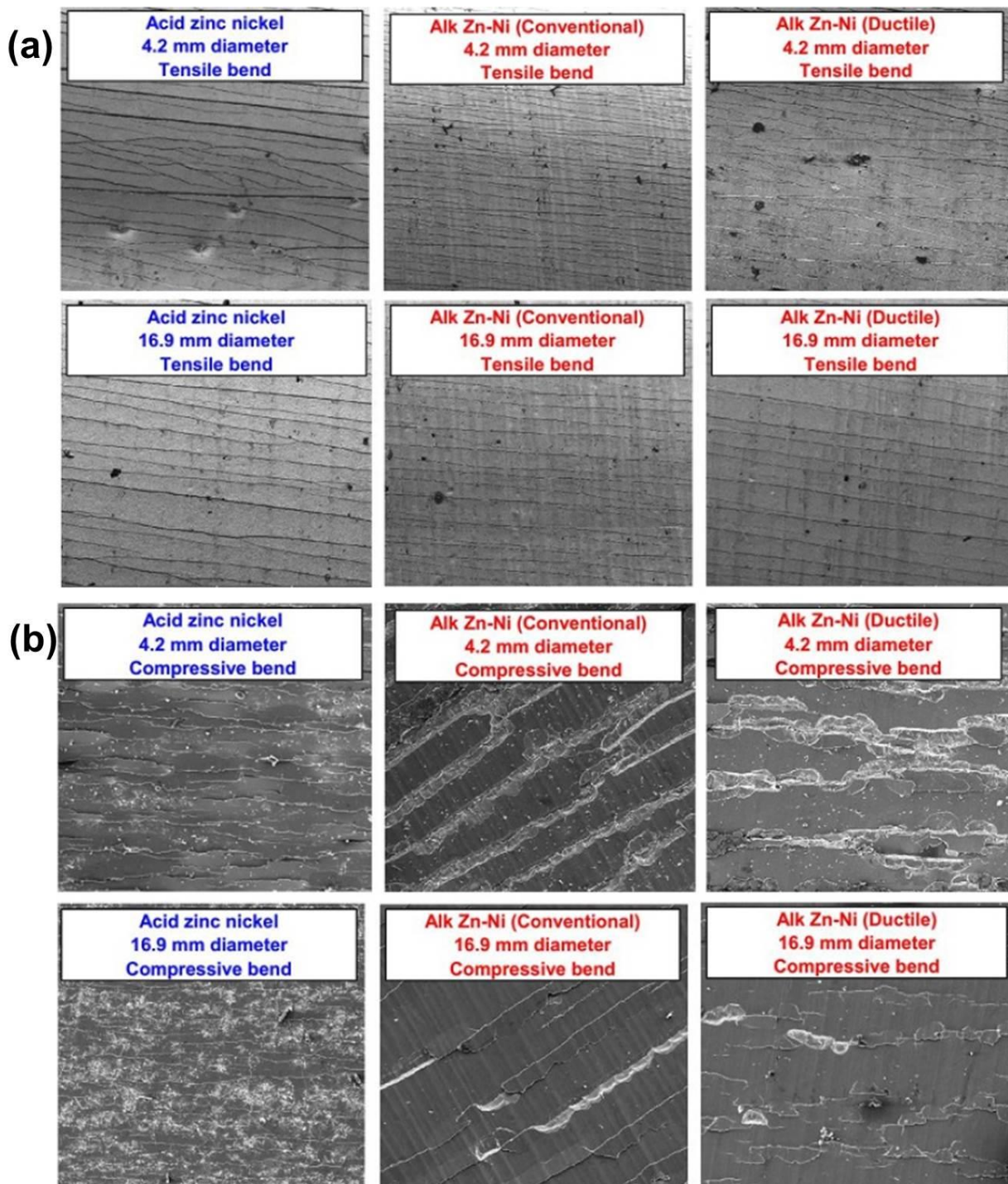


Figure 14 - Crack propagation during bend testing with the conical mandrel shown in Fig. 13: (a) tensile bend and (b) compressive bend (SEM @ 250×).

Another factor that may lead to poor deposit quality is the intrinsic stress (also called residual stress) of the deposit. Typically, both zinc and bright nickel baths have compressive intrinsic stress. Excessive stress can lead to problems like latent blistering or

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delamination of the deposit. To analyze the deposit stress, we used test strips which had two legs that were bare metal on one side, and coated with a resistive film on the other (Fig. 15⁵). When these strips were plated, the deposit, which was only on one side of the thin substrate, would either compress or elongate the substrate. The distance between the ends of the two legs could then be checked against a calibrated scale, and the distance could then be used in an equation involving thickness of the deposit to give a numerical value for the stress of the deposit in lb./in.². All strips were plated with the typical 9- μ m zinc-nickel at a current density of about 20 A/ft². To keep consistent with conventional nomenclature, in the figures to follow, compressive stress is represented by a negative value, while tensile is shown as a positive value.

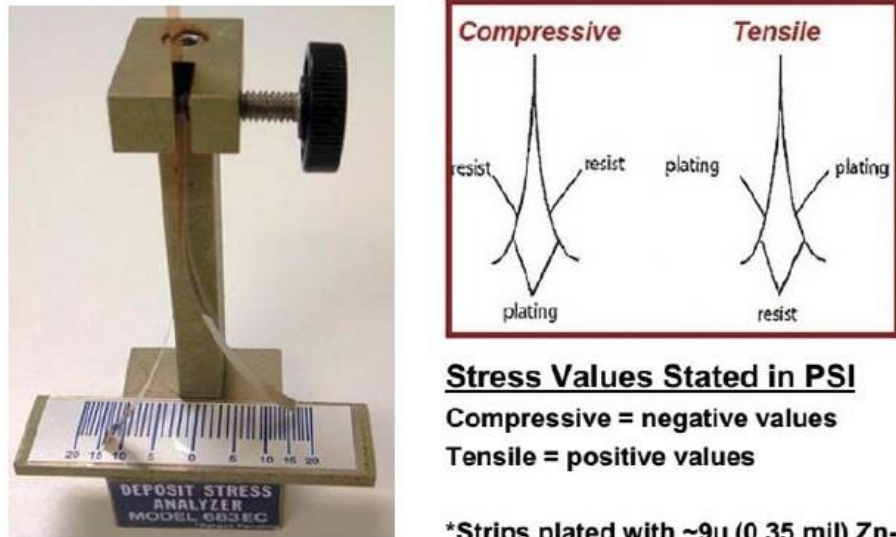


Figure 15 - Measurement of residual stress.

Again, the same three systems were compared (Fig. 16). Regarding the alkaline processes, the trends follow what we might expect, with the ductile process having less compressive stress than the conventional system. The acid system however acted very differently than expected. Not only was the deposit from the acid system less compressively stressed than the alkaline, on first analysis, it appeared to decrease over time. It is not uncommon for a deposit to relieve stress by up to 20%, but the acid system seemed to completely relax within 100 hr of sitting at room temperature. This was repeated several times with the same observations. However, subsequent analysis showed that there was more to this phenomenon.

Because acid zinc-nickel technologies are becoming increasingly important to certain applications, we decided to delve more comprehensively into the acid process. Because of the importance of bath temperature to deposit alloy composition in the acid process, the next study involved altering only the temperature of the plating bath. As shown in Fig. 17, the deposit nickel content increased with increasing temperature. The corresponding pictures show that the tensile stress also increased with this increase of temperature and nickel content.

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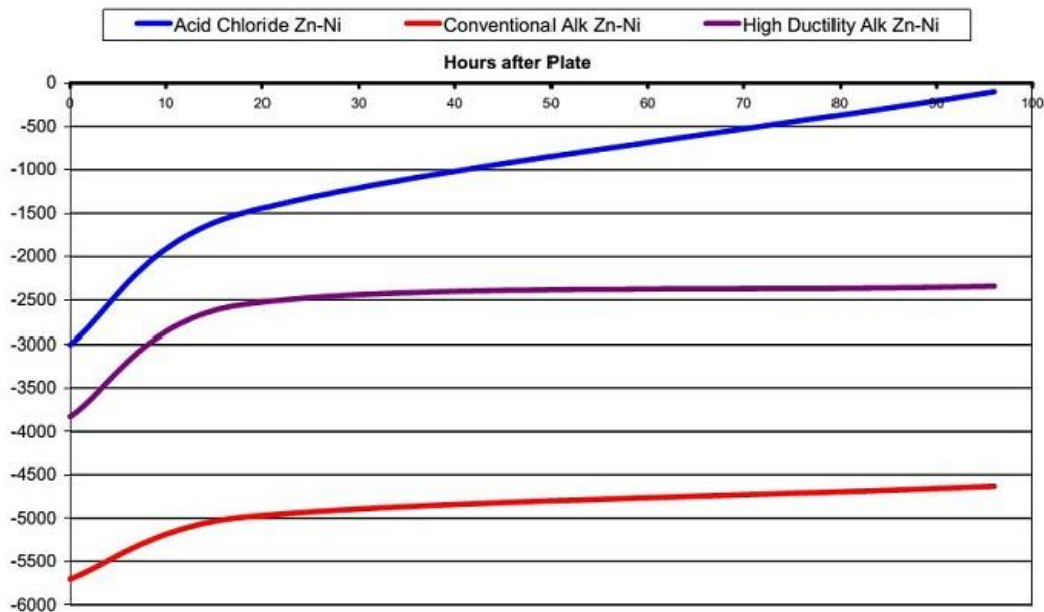
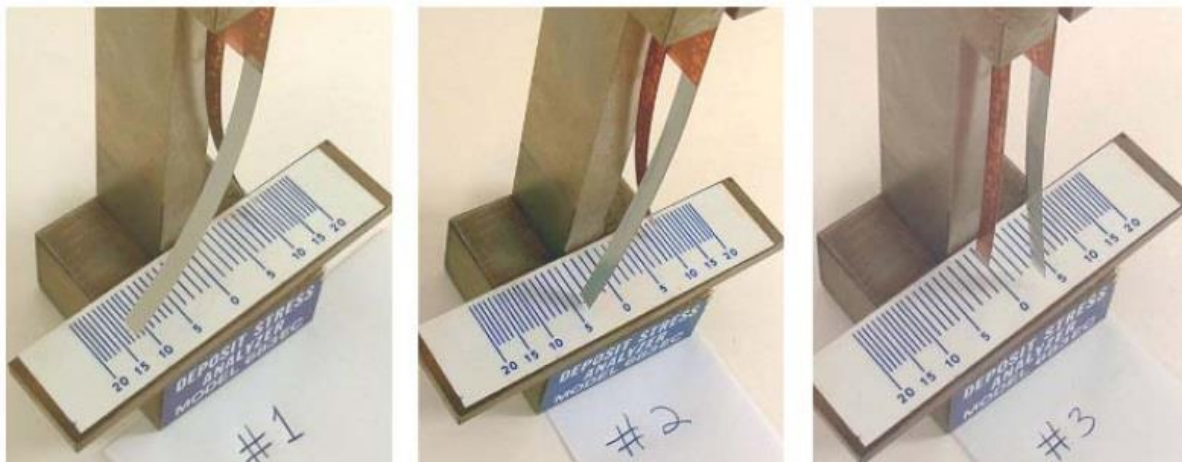


Figure 16 - Change in stress over time for deposits from various zinc-nickel processes.



	Current Density	Time	Temperature	Thickness	Nickel in deposit
# 1	20 ASF	20 min	37 °C	8 μ	17.6 %
# 2	20 ASF	20 min	35 °C	8 μ	16.5 %
# 3	20 ASF	20 min	33 °C	8 μ	13.0 %

Figure 17 - Effect of temperature on nickel content and internal stress.

The strips were again allowed to sit for 100 hr at ambient temperature. What is shown in Fig. 18 is that what was previously mistaken for relaxation of the deposit was actually a stress change in the tensile direction. A deposit that exhibits a slight compressive stress will, after 100 hr of sitting, exhibit a slight tensile stress, just as a deposit that exhibits a slight tensile stress

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will exhibit, after 100 hr of sitting, a larger tensile stress. This test shows conclusively that with this particular acid Zn-Ni system, the tensile stress in the deposit will increase approximately 4500 psi (31.0 MPa) over the course of several days.

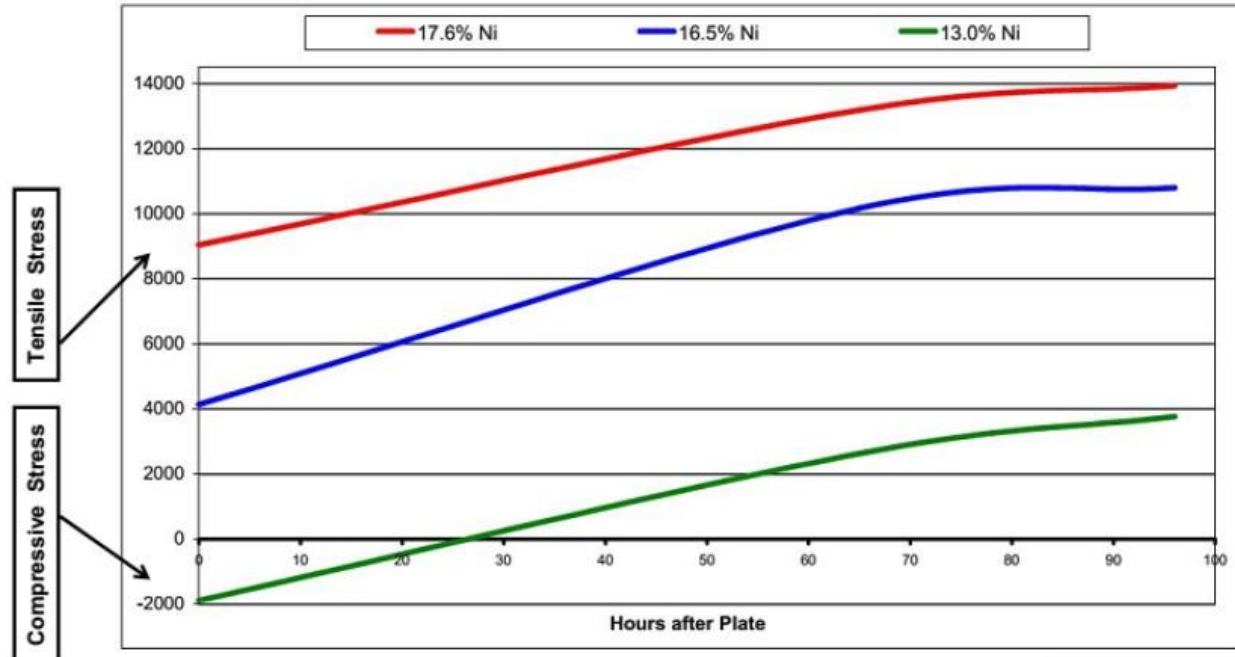


Figure 18 - Change in stress over time for acid zinc-nickel deposits with varying nickel content.

It appears that electroplated zinc nickel deposits, even when containing identical percentages of nickel, are quite different from each other depending on the electrolyte from which they are plated.

Summary

In summary, the deposits plated from alkaline electrolytes have advantageous tendencies such as:

- More uniform thickness distribution
- More uniform alloy distribution
- Slightly better corrosion resistance in a saltwater medium
- Slightly harder deposits
- More ductility on a tensile bend
- Not subject to as much tensile stress

Deposits plated from acid electrolytes have advantageous tendencies such as:

- Higher efficiencies
- Faster plating speeds
- Brighter and more leveled deposits
- Ability to be plated directly over cast iron substrates
- Better ductility on a compressive bend
- Ability to be plated with low compressive and tensile stress

Acknowledgement

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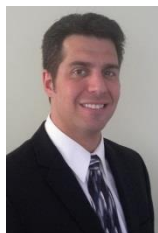
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About the author



During his 15 year career in the metal finishing industry, **Tony Oriti** has spent the last five as a research chemist for Coventya Inc. Tony has given several presentations pertaining to protective finishes at Sur/Fin trade shows. His main area of focus within the protective product lines is development of alloy plating systems, and trivalent passivates. Tony, a native Clevelander, received his bachelors of science in chemistry from Cleveland State University. He currently resides in the greater Cleveland area.