Zinc Nickel Electroplating in the New Millennium

Paul C. Wynn, Atotech UK Limited, United Kingdom

Reviewing the Production Performance of Zinc Nickel

Nickel has made an important comeback in the automotive sector as an alloy with zinc. In a move to offer increased vehicle warranty and component service life, major European automotive manufacturers are changing specification requirements for improved performance from electrodeposits. A growing importance is being placed on the ZnNi alloy to meet these demanding needs. This paper will bring the ZnNi story up to date, reviewing current achievements with the latest 12-15 percent nickel alloy systems. The latest performance benefits offered by this technology and its practical production operation will be established. A number of current automotive specifications for ZnNi will be reviewed.

For more information, contact: Mr Paul C. Wynn European Product Marketing Manager Corrosion Resistant Coatings Atotech UK Limited William Street West Bromwich West Midlands United Kingdom B70 0BE

Tel: +44 (0) 121 606 7109 Fax: +44 (0) 121 606 7224 E-mail: pwynn@atotech.co.uk

Introduction

The application of zinc based coatings to protect ferrous substrates from the effects of corrosion are well established in the surface coatings industry. This metal can be readily deposited through a number of cost-effective, bulk production techniques such as electrodeposition, mechanical plating and hot dip galvanising. The resultant coatings are anodic to iron and steel, providing sacrificial protection; this means that the zinc corrodes preferentially to the substrate. The application of conversion coatings onto the zinc deposit extends the time to oxide formation (white or zinc corrosion products) which greatly enhances the overall corrosion protection. Such benefits have found the metal diverse global market acceptance, with the automotive sector being one important high-profile user.

Significant research and product development interest in electrodeposited zinc, has been focused onto the development of alloy coatings that contain small amounts of other elements, such as Fe, Co, Sn and Ni^{1,2,3,4}. (Manganese a potentially intriguing alloy with zinc has also been proposed, but at present the technology has not matured into an acceptable medium for commercial utilisation). The inclusion of another element into zinc modifies corrosion potentials. Alloys that are compositionally high in zinc will retain their anodic potential to steel. Since these alloys are more electrochemically noble than zinc, sacrificial protection will be maintained and they will corrode at a lower rate (Figure 1).

The provision of a zinc nickel alloy generates many end user benefits that are particularly attractive to the automotive sector.



Zinc Nickel Interest

Zinc alloyed with nickel offers the greatest all round performance of the current market technologies. Introduction has been driven forward by the demands of the automotive industry to offer extended vehicle warranties to meet increasing expectations of consumers. This has pressured the coatings industry to improve the performance of traditional zinc and chromated electrodeposits.

Improvements in corrosion protection are becoming increasingly important for higher temperature areas, such as underhood "hot zone" applications, where traditional zinc has limited performance due to the inability of chromate's to function in such environments. There is also pressure to overcome the volumious white oxide products generated from zinc, which reduces the ability of assemblies to be dismantled during their serviceable life. Extended wear resistance is another consideration to improve in-service life, so increased deposit hardness is a desirable characteristic for a number of automotive applications.

Manufacturers needing to extend component service life are increasingly turning to a zinc nickel alloy to realize the desired technology improvements.

Technology Developments

The early commercialization of the UK zinc nickel market occurred in the mid-1980's, with the installation of the first acidic based technology⁵. This was chloride based^{1,2,3,4} using ammonia as the nickel complexing agent, and operated with a dual anode system having separate anodes and rectifiers for the zinc and nickel metals. The electrolyte produced high plating efficiency with excellent deposition rates. Although the deposit was highly decorative in nature, poor alloy current density distribution led to premature low current density (LCD) corrosion failures. These nickel rich LCD areas were extremely difficult to passivate which lead to further processing and performance issues (Figure 2). The technology did not gain widespread adoption.

Figure 1: Corrosion potential comparisons.



Figure 2: Zinc nickel alloy distribution as a function of current density.

The first major UK commercial development of the electrodeposited alkaline zinc nickel alloy occurred during 1992^6 with the installation of a large production volume of low alloy having a typical deposit composition of 5-7% nickel. This installation was established to service the needs of the growing Japanese automotive presence within Europe. The electrolyte based upon sodium hydroxide and zinc, contains proprietary amine polymers as the complexing agents, the chemistry having being patented in 1989^{7,8}. The alkaline nature of this chemistry produced superior deposit throw and alloy distribution compared to that of the earlier acidic chloride based systems, which helped to improve the overall neutral salt spray (NSS^9) corrosion performance of the electrodeposits. However, this improvement was sacrificed at the expense of lower efficiency and therefore longer processing times. These new systems were production user friendly, and the deposits were more receptive to chromate there appearance is passivation. However, "technical", i.e. matt to semi-bright in nature (the highly lustrous finish from acidic formulations is not realised). There were also concerns raised at the quality of colored chromate's, particularly black, and the high cost of process operation.

High Alloy Zinc Nickel

The next major advancement in zinc nickel technology occurred with the development of the alkaline high alloy, i.e. 12-15% nickel. This was patented in 1995¹⁰, the formulation produces very stable and reliable chemistry, which is not based upon traditional alkaline zinc technology and so does not blister or burn. Developed through

research into alternative strategies for CrVI passivation replacement, the new alloy has proven to be the most suitable medium for accepting these alternatives¹¹.

It has become apparent that high alloy zinc nickel overcomes some of the shortcomings of the existing low alloy systems, offering reduced operating costs with easier process control and enhanced wear and corrosion resistance.

The first UK commissioned installation of this new system occurred in 1997⁶. By early 2001⁶, the total volume of electrolyte in production installations has exceeded that of the original low alloy zinc nickel systems.

Corrosion Performance

When other metals are alloyed with zinc, an increase in corrosion performance is realised^{1,2,3,4}. This is frequently evaluated by the 5% NSS⁹ test, which although recognised as having its limitations, is still to date the most widely accepted performance indicator¹¹.

When compared to the other sacrificial alloys, high alloy zinc nickel containing 12-15% nickel provides the highest degree of corrosion protection. Figure 3 shows the NSS⁹ comparisons of these alloys.

Corrosion potentials compared to hydrogen are more favourable for this alloy, as demonstrated in Figure 1. In addition, the metallurgical alloy phases of zinc nickel electrodeposits have been reported as a function of composition^{4,12} (Figure 4).

Above a 12% nickel content in the deposit, there is a notable change in the alloy properties; chromate passivation treatments become much more corrosion resistant which has been attributed to the formation of significant amounts of gamma phase zinc nickel. It was observed that much of early zinc nickel data was flawed because conversion coatings for high alloys were not well formulated. The formulation of the high alloy zinc nickel¹⁰, to produce a stable *gamma* rich electrodeposit and used in conjunction with specially developed CrVI passivations, has realised this increased NSS⁹ performance, as shown in Figure 5.

At this correct metallurgical phase, the as deposited high alloy zinc nickel produces a "columnar" field oriented crystalline metallographic structure, as demonstrated by the scanning electron microscopy cross-section in Figure 6.



Figure 3: NSS comparisons of commercially available zinc alloy electrodeposits.



*Figure 4: Zinc nickel alloy phases reported as a function of composition. Reproduced by kind permission of C. V. Bishop*¹²



Figure 5: NSS performance of high alloy zinc nickel electrodeposit with various topcoats.



Figure 6: SEM of high alloy zinc nickel structure. Reproduced by kind permission of C. V. Bishop.

Process Control

This new alkaline system uses a basic electrolyte of sodium hydroxide and zinc metal. Nickel is introduced into the solution through a proprietary liquid additive. Specialist proprietary *Carriers* are used to complex with the nickel for its in-solution activity, whilst others impart *grain refinement* and *brightness* characteristics to the deposit.

Operation and control of this electrolyte requires more attention than with the traditional zinc additive systems. Obtaining and controlling the alloy content is important if the additional performance benefits offered by the technology are to be realised. Table 1 details basic solution chemical parameters.

Zinc metal		10 – 1	ll g/L
Nickel metal		1.0 -	1.2 g/L
Sodium Hydr	oxide	130 -	140 g/L
Proprietary C	arriers	120 -	130 mL/L
Additive Dos	sage / KAH		
Additive C	Carrier	220	mL
	Brightener	190	mL
Additive B			
Additive B Additive Ni	Nickel	750	mL

Table 1 – Typical production operating parameters for high alloy alkaline zinc nickel installations.

Operating temperatures are important, 20-25^oC is the normal production range so provision for cooling and heating is vital, Teflon or titanium heat exchangers are generally specified. Variations in temperature influence alloy content, with excessively high temperatures destroying the chemistry.

Unlike alkaline zinc solutions, continuous filtration is required at three turnovers per hour through 10 μ m media. Independent solution circulation of two to three turnovers per hour is beneficial for the efficient operation of the electrolyte. This is particularly important when barrel plating to improve replenishment rate of fresh ions at the solution-substrate interface: This greatly improves deposition rates and reduces plating times, which can be lengthy at barrel current densities with electrolyte efficiency around 50%.

Operating cathode current densities are maintained at 0.2-0.8 Adm² for barrel application, whilst 1.5-2.5 Adm² is typical for rack. Preferred anode material in the plating electrolyte is pure nickel, but 25 μ m thick dull nickel plated steel sheet is acceptable. The zinc content in solution is maintained by the galvanic dissolution of zinc domes contained within steel baskets. This operation takes place in an off-line generator tank, as originally developed by J. Jackson of Rohco Chemicals in 1976. (Figure 7)



Figure 7: Schematic of electrolyte tank connected to off-line zinc generator systems.

Analysis and deposit measurement.

The basic solution parameters as detailed in Table 1, require regular monitoring to ensure efficient operation. Both zinc and nickel metal levels should be checked on-site each production shift as a minimum. Sodium Hydroxide requires daily analysis. The proprietary additives used are an

integral part of the zinc nickel electrolyte. Along with the nickel additive, they are consumed by electrolysis on an ampere hour basis. In anything other than laboratory-scale production, these additives must be dosed through an ampere hour meter.

Effective additive control in the laboratory is straight forward using the time honoured Hull Cell¹³. It remains the definitive way to monitor the condition and relationship of these proprietaries.

The metal finisher will need to demonstrate conformance of the electrodeposit with the relevant automotive specifications, which govern thickness and alloy composition. Daily checks for these can only realistically be achieved through the use of X-ray fluorescence measurement methods². The purchase of this instrument represents a significant financial investment to the finisher, but it can also be used to check zinc and nickel ions in the electrolyte. This technique is useful for quick solution checks, and can be performed by line operators throughout the shift due to its simplicity.

Table 2 confirms analysis methods.

Zinc metal :	Titration or XRF
Nickel metal :	Spectro-photometer,
	Atomic Absorption,
	or XRF
Sodium Hydroxide:	Titration
Proprietary additives:	Hull Cell
Chromate passivates:	Titration, pH
Plated Deposit:	XRF

Table 2: Analysis and measurement methods for the high alloy zinc nickel.

Since the chemistry is alkaline based, consideration should be made for carbonate removal. Carbonates are produced through atmospheric absorption of carbon dioxide and anodic oxidation. Removal can be achieved through freezing-out in a batch or continuos treatment system.

Weekly analysis of carbonates is recommended, and action to lower it should be taken when the level raises above 45gpl. Although the electrolyte will operate at much higher levels, it will further reduce efficiency resulting in increased plating times and reduced deposit throw.

Automotive Approvals

The high alloy zinc nickel technology has continued to gain acceptance amongst the automotive manufacturers and their tier one suppliers, as a functional finish onto components and assemblies over the last four years. It is now being specified to meet a diverse range of applications for a number of high profile companies onto such components as fasteners, fuel lines and brake calipers.

Its inclusion into automotive specifications has been driven forward principally through the European market. Volkswagen, through their specification TL244¹⁴, has made a significant contribution into this area. Volkswagen was one of the first to adopt the high alloy zinc nickel technology into the automotive sector. The specification details two specific points of interest: firstly, it requires a heat aging test prior to salt spray, a concept now being adopted by other companies. Secondly, it refers to the "grey veil" effect (also known as blanching) which can offer during the initial stages of corrosion testing, it has become accepted practice that this does not in itself, constitute a corrosion test failure. The general performance requirements of TL244 are detailed in Table 3. This version issued 1995 is believed to be under revision during 2001.

Alkaline electro Thickness – Mir	lyte – colourle 1 5 to 8 micron	ss/yellow/b s, Max 25.	lack conversion	coatings 12-15	5% N
Heat test 24hrs a	ut 115-125 ^o C,	then 1hr at	room temp 15-3	35 °C prior to 1	NSS.
Corrosion test to	DIN 50 021 S	SS	•		
		No zinc	Max 5% zinc	No base	
Colourless	Brl & Rack	120	240	720	
Yellow & Black	Brl	120	360	720	
Yellow & Black	Rack	240	48	720	

*Table 3: Basic performance requirements of TL244*¹⁴.

Other companies such as BMW have adopted general specifications that also include provision for high alloy zinc nickel. Their N $600 \ 00.0^{15}$ specification details a 5 micron deposit of 11-15% Ni alloy with black chromate; after heat age at

150[°]C for 2 hours, NSS¹⁶ test results of 120 hours with no zinc and 480 hours with no red corrosion products are required. Latest information is that a new draft revision of this specification is being prepared during February 2001, and red corrosion protection requirements will be increased to 720 hours.

Daimler-Chrysler issued the zinc nickel specification DBL 8451^{17} which details that a 10 to 15 micron deposit should provide NSS⁹ protection of 240 hours with no zinc and 360 hours with no red corrosion products. Latest information is that a revision is planned to this during 2001. Another document PS 8955¹⁸ calls for black and yellow chromate, with clear or leached colors being not acceptable. A 5 micron rack applied zinc nickel coating with yellow chromate has to meet 300 hours to 5% white, and 1000 hours with no red corrosion in NSS⁹ after 24 hour aging. The equivalent black chromated deposit to meet 240 hours to 5% white and 1000 hours with no red corrosion.

Ford¹⁹ has issued several of its own specifications governing the use of zinc nickel deposits; these are at present referenced against current UK production. WSS-M21IP25-A3 details a zinc nickel deposit with 4 to 15% nickel alloy, with a black chromate conversion coating of 5 microns minimum. NSS⁹ requirements are 48 hours with no white, 144 hours maximum 10% white and 500 hours no red corrosion products. WSS-MIP87-A1 is written for zinc nickel with chromate conversion coating, and details an 8 micron deposit to meet 768 hours NSS⁹ with no red corrosion.

The General Motors specification GME 00252²⁰ still referenced in the UK, is interesting in that it states a preference for a trivalent chromium conversion coating onto zinc and zinc alloy electrodeposits, with CrVI to be eliminated as soon as possible. Zinc nickel is detailed as a coating containing 10-14% nickel alloy.

Summary

The latest technology development with electrodeposition of zinc nickel has been through the commercialization of the high alloy 12-15% nickel containing deposit. This offers improved corrosion performance and a greater cost to benefit ratio than the other market specified sacrificial zinc based alloy coatings.

Process control requirements are more critical, but global experience has proven the reliability and cost-efficient operation of the electrolyte.

The automotive industry, its principal user, has realized performance benefits through its adoption, which is achieving extended in-service vehicle component life. Geographically, the market introduction for this technology has occurred principally within Europe, but has now spread throughout the Americas.

References

- 1 Zinc Alloy Plating for the Automotive Industry, David Crotty MacDermid, Inc *Metal Finishing* (September 1996)
- 2 Performance Characteristics of Zinc Alloys, David Crotty & Robert Griffin *Plating & Surface Finishing* (April 1997)
- 3 Zinc-Alloy Electrodeposits For Improved Corrosion Protection, Gary W. Loar, Klaus R. Romer and Tetuhiro J. Aoe *Plating and Surface Finishing* (March 1991)
- 4 Electrodeposited Zinc Alloy Coatings, G.D. Wilcox and D.R. Gabe *Corrosion Science* (1993)
- 5 Reference Graham Tonge, Tonge & Taylor Ltd, United Kingdom (Jan. 2000)
- 6 Paul C. Wynn Atotech UK Ltd, internal communication (January 2001)
- 7 Yanagawa et al. US Patent 4,877,496 (1989)
- 8 Oshima et al. US Patent 4,889,602 (1989)
- 9 Test Method ASTM B117 American Society for Testing and Materials
- 10 D.Block and C.V.Bishop US Patent 5,417,840 (1995)
- 11 Replacing Hexavalent Chromium in Passivations on Zinc Plated Parts,
 P.C. Wynn & C.V. Bishop, *Products Finishing* (February 2001) US publication.
- 12 Effects of Zinc Nickel Alloy Composition, Craig V. Bishop, Lawrence Emch, Dale Block of McGean-Rohco and Frank Freitas Central Metal Finishing *AESF SUR/FIN '98* (1998)
- 13 Cellular Approach Paul C. Wynn, *Product Finishing* (January 2000) UK publication.
- 14 Specification Volkswagen AG TL244 Zinc/Nickel – alloyed coatings (December 1995)
- 15 Specification BMW N600 00.0 *Types of Surface Preparation.*
- 16 Test Method DIN 50 021 SS
- 17 Specification Daimler-Chrysler DBL 8451 (August 1994)
- 18 Specification Daimler-Chrysler PS 8955 Zinc Alloy Electrodeposits (Change F)
- 19 Specification Ford Motor Company WSS-MIP87- A1 & A3.
- 20 Specification General Motors GME 00252 Electrolytically deposited coatings on iron and steel.