Performance Characteristics of Zinc Alloys

By David Crotty & Robert Griffin

Electroplated alloys of zinc with iron, cobalt or nickel are being used to improve the corrosion resistance of coatings, compared with normal zinc coatings. Acidic and basic plating solutions are being used to deposit these alloy coatings, resulting in a wide array of choices for the electroplater and the parts designer. This paper explores the characteristics of the plating baths used to deposit the zinc alloys and describes the properties of the resulting deposits.

Zinc alloy electroplated deposits are being used more frequently because they have the ability to provide improved corrosion protection for a wide range of items. While normal zinc electroplated deposits, with their associated post chromates, perform an important task that will certainly not be completely eliminated, the alloys with their chromates perform that job better.

The fundamental function of the iron, cobalt or nickel in the zinc alloy is to modify the corrosion potential of the deposit. The alloy becomes slightly more noble than zinc and, for this reason, the corrosion rate of the deposit is slowed. At the same time, the deposit is still sacrificial with respect to the steel substrate. Consequently, the same thickness of an alloy has the ability to protect the underlying steel for a longer time than conventional zinc.

In addition, some of the chromates used over alloys provide better corrosion protection than a similar chromate over conventional zinc. For example, with some of the alloys it is possible to form a black chromate that does not contain silver and provides much improved resistance to white corrosion.

The market demand for alloy deposits comes mostly from the automobile industry, which accounts for about 75 percent of the market. A smaller 20-percent portion comes from aerospace. The remaining five percent of the market includes a wide range of applications.

In the automotive market, alloys are used extensively in Europe and Asia, and use in North America is increasing. Most companies publish their own specifications for the alloys, as is the case for the major U.S. companies: General Motors,[1] Ford,[2] and Chrysler.[3] The Society of Automotive Engineers has published specifications as well.[4]

The aerospace industry has special concerns, which led Boeing to publish a specification for zinc/nickel alloy.[5] The major concern for the aerospace industry is to replace cadmium. In response to wider interests, the ASTM has also published specifications for zinc/cobalt, zinc/nickel, and zinc/iron alloy electrodeposits.[6]

Hydrogen embrittlement relief is important for some fastener applications, and specifications have been written[7,8] to address the plating, baking and testing of parts. While the alloys do not have the lubricity of cadmium, this is important for fasteners[9] and there are lubricants[10] that can be applied to provide predictable torque and clamping force.

In response to the demand for better corrosion protection, Both acid and alkaline alloy processes have been developed. Zinc-cobalt and zinc-nickel processes are available, both acid and alkaline, but zinc-iron is available only as an alkaline process. As with conventional zinc, both the acid and alkaline processes have advantages and disadvantages. In general, the acid processes exhibit higher cathode efficiency, but because of this, distribution of plated metal is poor. Alkaline processes tend to have lower cathode efficiency, but in return exhibit very good plate distribution over the normal current density range. The acid processes have the added advantage of being able to plate over hardened steels and cast iron.

Measurement Methods

It is difficult to overemphasize the importance of the correct use of analytical methods when determining the properties of any deposit. It is especially important in the case of alloys. The simple analysis of alloy content, or the measurement of thickness can be misleading if not performed with care. It is not within the scope of this paper to describe in detail the methods that are useful in alloy plating. We intend to list the methods found most useful, however, and point out a few obvious pitfalls. With every instrumental method, the best source of information should be the operating manual for the instrument itself, and the best training will be from the technicians who service the equipment. The instrument must be calibrated frequently and standards must be referenced along with the work to assure continual reliability. With every analytical method, the analyst must adhere to generally accepted procedures. The failure to use an instrument precisely, or to follow proper analytical procedures, will result in an erroneous measurement.

The thickness methods that have been used successfully for zinc alloy deposits in our laboratories are microscopic cross section,[11] magnetic measurement,[12] beta backscatter[13]

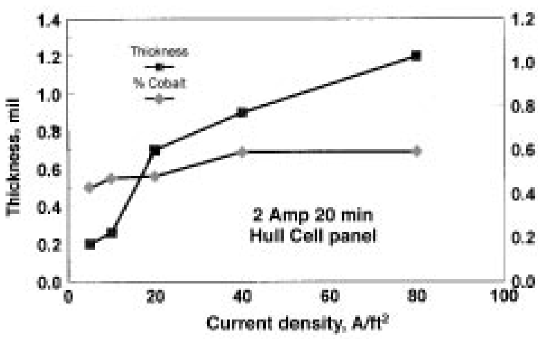

Fig. 1—Acid zinc-cobalt profile.

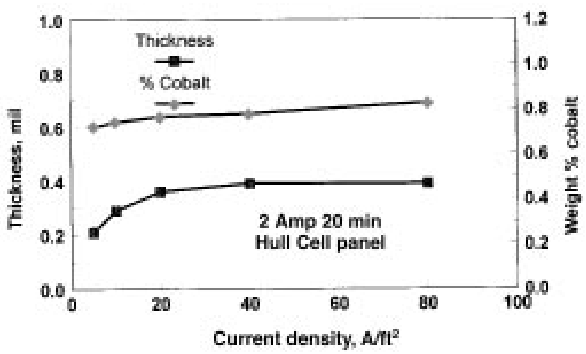

Fig. 2—Alkaline zinc-cobalt profile.

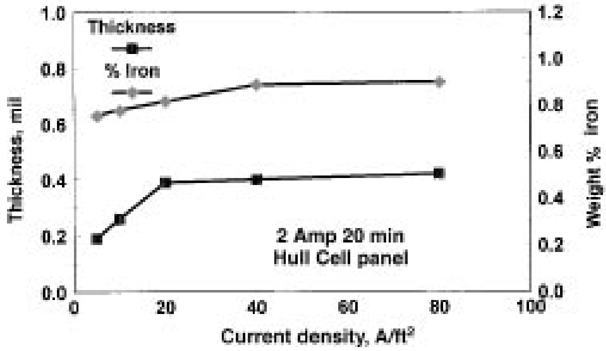

Fig. 3—Alkaline zinc-iron profile.

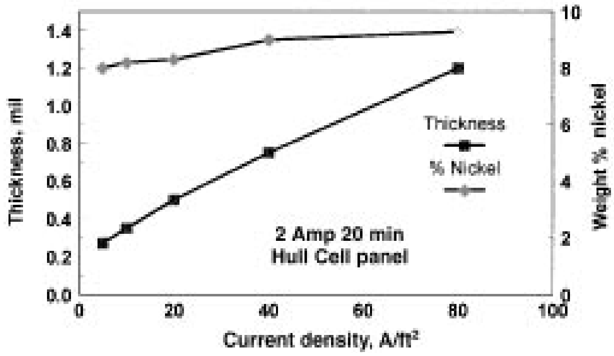

Fig. 4—Acid zinc-nickel profile.

and x-ray fluorescence (XRF).[14] Other methods may apply as well. The cross section method is generally considered the most reliable and is generally used to provide standards for other methods. This is, of course, destructive and very time-consuming. The magnetic method is generally the next best, but requires the deposit to be on steel that has not become magnetic itself during machining operations. X-ray fluorescence has found broad application because standards can be prepared for a wide range of deposits over a wide variety of substrates.

Determination of the alloy content of a zinc alloy is best done by atomic absorption, although Electron Dispersive X-ray (EDX) technique is useful for zinc-iron, zinc-cobalt and zinc-nickel alloys; X-ray fluorescence (XRF) is useful for zinc-nickel.

Some difficulties should be noted: If the thickness of a zinc-nickel deposit is below about 0.25 mil, the XRF readings will often show that the nickel content is high, but AA analysis shows the opposite. It appears that the XRF method has some difficulty in when the deposit is thin. Zinc-iron deposits present a special problem, because once the deposit is plated onto a steel substrate, it is impossible to strip the deposit without also stripping some of the part as well. In addition, the EDX method "sees" the iron from the substrate if the deposit is below about one mil. Consequently, for zinc-iron, the deposit must be prepared on a non-ferrous surface.

For atomic absorption work, the deposit must be dissolved completely from the substrate. If some smut remains on the substrate, it is likely some of the cobalt or nickel alloy. This will result in erroneous results. The use of 3-5 percent hydrogen peroxide with hydrochloric acid assists in dissolving the deposit completely. Also, when atomic absorption is used, it is very important to operate within the linear concentration range of the instrument. Best results are obtained if internal standards are used.

Corrosion protection is commonly measured by salt spray[15] or the Kesternich method[16] for quality control purposes. Obviously, the deposits must be tested in the expected environment before they can be certified for service in a particular application.

A comparison of the alloy processes requires a measure of thickness and alloy distribution of the various deposits. For this discussion, standard Hull Cell panels were plated from a 500-mL cell at 2 A for 20 min to build up enough deposit to measure thickness and alloy content. Thickness was measured by the magnetic method and XRF and alloy content were measured by EDX, XRF (for zinc-nickel) and by atomic absorption. The results are plotted to facilitate the comparisons.

Zinc-Cobalt Deposition Processes and Chromates

Zinc alloys with cobalt can be deposited from acid or alkaline plating baths. The processing baths are very similar to those used for normal zinc plating, but with the addition of cobalt and a complexor package designed to promote the deposition of cobalt with the zinc. The composition of the alloy that has been proven to provide the best corrosion protection is in the range of 0.4-1.0 wt percent of cobalt in the alloy. Lower cobalt content does not provide a significant improvement in corrosion protection. Cobalt content above about one percent also does not improve corrosion protection and makes chromating of the deposit difficult. If the cobalt content were in the range of 5-11 wt percent, the deposit would behave similarly to zinc-nickel.

Cobalt alloys will take yellow, olive drab and black chromate conversion coatings satisfactorily. These alloys also permit the development of a black chromate not based on silver. In conventional zinc plating, the black chromate obtains its color from metallic silver formed during the chromating process. With zinc-cobalt alloys, the black color can be developed from the cobalt that dissolves from the zinc-cobalt deposit; silver is not needed. The resulting black chromate film is more protective than traditional silver-based chromates. For a non-silver black chromate to work well, the zinc-cobalt alloy must generally contain at least 0.4 percent cobalt. Alloy deposits that contain cobalt in the range of 0.4-1.0 wt percent will generally not provide a good-looking blue-bright chromate conversion coating.

Acid zinc-cobalt deposition has the advantages of other acid zinc processes. The process is better at plating iron castings and hardened or heat treated steels than alkaline processes. The deposit distribution is not as good as with alkaline processes, but alloy content is fairly constant over the current density range, as shown in Fig. 1. The alloy content of the deposit depends on several factors, including the amount of cobalt metal in the plating bath, the temperature, and the concentrations of some of the additives.

The acid zinc-cobalt alloy process can be ammonia-free, low-ammonia, or high-ammonia. In general, the barrel and rack formulations are slightly different in composition, as are the conventional acid zinc plating baths and for many of the same reasons. Table 1 shows the typical composition of the ammonia-free acid zinc-cobalt bath. The anodes used are conventional zinc balls in a titanium basket.

Alkaline zinc-cobalt is similar to conventional alkaline zinc in composition and practice. Typical rack and barrel bath compositions are slightly different, as shown in Table 2. The anodes are generally steel and the zinc concentration is maintained using a side zinc dissolving tank. The advantages of using the alkaline process are that distribution is better over the current density ranges and that cobalt content is not greatly changed by current density variations (Fig. 2).

Zinc-Iron Deposition Process and Chromates

The zinc-iron alloy process is typically alkaline and has many of the properties of conventional alkaline zinc and alkaline zinc-cobalt. The thickness distribution is more uniform than with acid processes and the alloy distribution is very good over the current density range normally used. Like zinc-cobalt, the zinc-iron deposit accepts a non-silver black chromate because the alloy constituent becomes part of the chromate, forming a black color. Also, the corrosion resistance of this chromate is very good compared with typical silver black chromates. The zinc-iron deposits also readily accept yellow and olive drab chromates. As with zinc-cobalt, the zinc-iron deposit does not provide a good blue-bright chromate unless the alloy content of the deposit is very low. The best corrosion protection is obtained if the alloy is above 0.4 percent iron.

The alkaline zinc-iron plating bath composition is somewhat similar to that of conventional alkaline zinc, with the addition of iron ions and a complexor blend designed to promote the deposition of iron. The anodes are typically steel and the zinc metal concentration is maintained by the use of a side tank. Typical concentrations of the barrel and rack baths are given in Table 3. The profile for thickness and alloy distribution for the alkaline zinc-iron process is shown in Fig. 3.

Zinc-Nickel Deposition Processes and Chromates

Zinc-nickel alloy deposits are somewhat different from the cobalt and iron deposits discussed so far. First, the alloy content is significantly higher. Acid zinc-nickel deposits typically range from 7-13 percent nickel and the alkaline deposits typically range from 3-7 percent. In part, because of this, the corrosion protection is also considerably higher. Generally, the only types of chromates available for zinc-nickel alloys are yellow or olive drab. The very low zinc-nickel alloy deposits will take a silver or non-silver black chromate, but there is very little of this being done commercially. The zinc/nickel alloys provide the best salt spray corrosion resistance performance of all the zinc alloy processes, as well as the best performance for the cyclic heat/ corrosion tests.

The acid process is ammonium chloride-based. In earlier work, the dual anode system was often used, with zinc and nickel anode baskets being attached to different rectifiers. Today, the practice has changed to using zinc anode baskets with carbon auxiliary anodes. Table 4 lists the typical operating parameters for the acid zinc-nickel process. Figure 4 shows the thickness and alloy content profile for this process, revealing the high efficiency of the acid process, as well as good alloy distribution over the current density range.

There is a matte acid zinc-nickel process designed specifically for the aerospace industry.[5] It provides only a minimum of grain refinement, the purpose being to provide a porous matte deposit that will allow hydrogen to be baked out of the hardened substrate more readily.

The alkaline zinc/nickel process is somewhat similar to conventional alkaline zinc processes, with the addition of additives containing the nickel ions and a complexor mixture designed to promote nickel alloy content. Some types of processes require that the temperature remain below 80 °F, while others operate at 90-110 °F. The anodes are typically steel, with the zinc content being maintained using the side tank. Table 5 lists the typical operating parameters for the alkaline zinc/nickel process, and Fig. 5 shows the typical thickness and alloy content profile, illustrating the lower

Table 1
Typical Acid Zinc-Cobalt Bath Concentration

Operating Parameters	Rack	Barrel
Zinc metal	6 oz/gal	4 oz/gal
Cobalt metal	1.3 oz/gal	0.9 oz/gal
Boric acid	2.5-3.0 oz/gal	2.5-3.0 oz/gal
Potassium chloride	25 oz/gal	18 oz/gal
pH	4.8-5.3	4.8-5.3
Temperature	90-110 °F	90-110 °F
Anode	zinc in titanium baskets	zinc in titanium baskets
Filtration	1-2 turnovers/hr	1-2 turnovers/hr

Table 2
Typical Alkaline Zinc-Cobalt Bath Concentrations

Operating Parameters	Rack	Barrel
Zinc metal	1.6 oz/gal	1.2 oz/gal
Cobalt metal	60 ppm	30 ppm
Zn/Co ratio	200:1	260:1
Caustic soda	16 oz/gal	16 oz/gal
Soda ash	4 oz/gal	4 oz/gal
Anodes	steel	steel
Cooling	required	required
Temperature	70-90 °F	70-80 °F

Table 3
Typical Alkaline Zinc-Iron Process Parameters

Operating Parameters	Rack	Barrel
Zinc metal	1.6 oz/gal	1.6 oz/gal
Iron metal	80 ppm	30 ppm
Zn/Fe ratio	150:1	400:1
Caustic soda	16 oz/gal	16 oz/gal
Soda ash	4 oz/gal	4 oz/gal
Temperature	70-85 °F	70-85 °F
Anodes	steel	steel
Cooling	recommended	required

Table 4
Operating Parameters for Acid Zinc-Nickel

Operating Parameters	Rack	Barrel
Zinc metal	5.3 oz/gal	5.3 oz/gal
Nickel metal	3.3 oz/gal	2.7 oz/gal
Zinc-Nickel	1.6-2.0	1.8-2.3
Ammonium chloride	37 oz/gal	37 oz/gal
pH	5.5-5.9	5.5-5.9
Temperature	90-110 °F	90-110 °F
Anodes	zinc in titanium baskets	zinc in titanium baskets
Auxiliary anodes	carbon	carbon
Filtration	continuous	continuous

Table 5
Typical Operating Parameters for Alkaline Zinc-Nickel

Operating Parameters	Rack	Barrel
Zinc metal	1.6 oz/gal	1.6 oz/gal
Nickel metal	1.2 oz/gal	0.8 oz/gal
Caustic soda	16 oz/gal	16 oz/gal
Soda ash	4 oz/gal	4 oz/gal
Temperature	70-80 °F	70-80 °F
Anodes	Steel	Steel

Table 6
Zinc Alloy Overview

	Zinc-Cobalt Acid	Zinc-Cobalt Alkaline	Zinc-Iron	Zinc-Nickel Acid	Zinc-Nickel Alkaline
Typical Alloy Content	0.4-1.0%	0.4-1.0%	0.3-1.0%	7-13%	4-7%
Electrolyte	potassium chloride ammonium chloride boric acid	caustic	caustic	ammonium chloride	caustic
Torque-Tension (No post-treat.)	Less than Zn	Less than Zn	equal to Zn	Less than Zn	Less than Zn
Plating effic'y	95-100%	50-80%	50-80%	90-95%	30-50%
Throwing power	poor	good	good	poor	good
Equipment	acid resistant	mild steel	mild steel	acid resistant	mild steel
Chromate Finishes avail.	yellow, drab	yellow, drab	yellow, black	yellow, drab	yellow, drab

efficiency of the alkaline process, resulting in better thickness distribution.

Performance Comparisons of Zinc Alloys

Any discussion of alloy zinc deposits results in an attempt to compare the properties and operating conditions. To this end, Table 6 provides a list of salient features of the range of processes. The alloy content obtained depends largely on the concentration of the alloying metal in the plating bath, but other bath conditions, such as temperature and other additives, have strong roles as well.

Typical neutral salt spray performance for the alloys and acid chloride zinc are provided in Table 7. The deposits listed were all plated to about 0.3 mil thickness, because it is important to compare equal thickness for the red corrosion numbers. Neutral salt spray results for zinc-cobalt and zinc-iron are for alloys with about 0.5-0.8 percent of the alloying metal. Lower alloy percentages do not allow a non-silver black chromate to form and produce lower salt spray numbers.

Kesternich corrosion testing results are given in Table 8. The acid and alkaline processes perform similarly to this test. Typical hardness for some of the deposits is listed in Table 9.

Hydrogen embrittlement relief is important for parts that have been hardened. In general, all the alloys mentioned may be baked, but special techniques may be required to obtain a good chromate afterward.

The zinc alloy deposits and the conventional zinc deposits do not exhibit the lubricity of cadmium. There are post-treatments that improve the torque and tension properties of a part that are suitable for a wide range of applications.

Finally, a series of post-treatments is being used and developed to improve the corrosion resistance of zinc and zinc alloy deposits beyond the results reported here. The subject of post-treatments will be addressed in the future.

Summary

The zinc alloy deposits discussed were developed to provide improved corrosion protection over and above what can be expected from conventional zinc deposits. Use of these alloy deposits has increased in Europe, Asia and the U.S., largely in automotive and aerospace applications.

The properties that designers look for include appearance, corrosion protection, good thickness and alloy distribution over the part and, in some cases, hydrogen embrittlement relief and lubricity.

Processes designed to plate these alloy deposits are both acid and alkaline, because each process type has certain advantages. The acid processes are more efficient, but distribution suffers somewhat. The alkaline processes are less

Table 7
Neutral Salt Spray Corrosion Resistance
(0.3-mil thickness)

Chromate	Tin-Zinc*		Zinc Plate		Alkaline Zn-Co		Alkaline Zn-Fe		Zinc-Nickel	
	FWC	FRR	FWC	FRR	FWC	FRR	FWC	FRR	FWC	FRR
Blue-bright**			24	48-72	24-30	72-120	24-30	72-120		
Yellow	150	1000	60-120	160-250	220-480	500-700	220-480	500-700	300-400	700-900
Olive Drab			96-150	350-450					800-1000	1200-1500
Black (silver)			48-72	160-300	48-120	100-350	48-120	160-350		
Black (non-silver)					240-500	600-800	240-500	600-800		

* Tin-Zinc results are for 0.5 mil-thick deposits.
** Blue-bright chromates are available only for zinc-cobalt and zinc-iron alloys below 0.2% cobalt or iron.

Table 8
Zinc Alloy Kesternich Results

Alloys	Performance
Zinc-Cobalt	2-3X better than zinc
Zinc-Iron	Equal to zinc
Zinc-Nickel	Equal to zinc

Table 9
Zinc Alloys Vickers Hardness

Process	Hardness HV_{50}
Chloride Zinc	100-125
Alkaline Non-cyanide Zinc	80-130
Zinc-Cobalt (alkaline)	180-210
Zinc-Iron (alkaline)	100-150
Zinc-Nickel (acid)	140-160

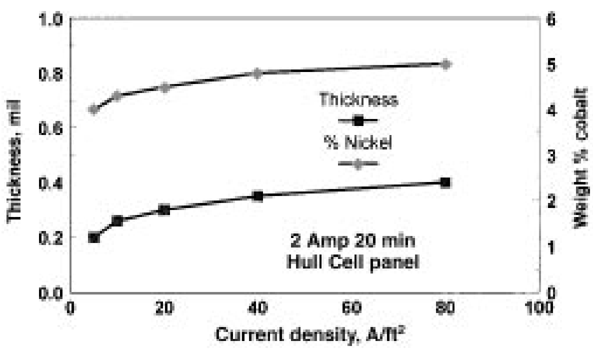

Fig. 5—Alkaline zinc-nickel profile.

efficient and, as a result, exhibit better distribution. Acid processes are easier to use when the parts are made of case iron or when parts have been hardened by heat treatment.

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Specifications (References)

1. General Motors: Zinc Alloys GM 6280M, Zinc-Nickel with organic coating, GM 6138M, Zinc-Nickel with conversion coating, GM 7153.
2. Ford Motor Co.: Zinc-Nickel WSA-M1P87-A1, Zinc-Cobalt WSH-M1P86-A,
3. Chrysler Motor Co.: Zinc Alloys PC 8955.
4. Society of Automotive Engineers: Plating Zinc-Nickel Alloy ASM 2417E.
5. Boeing: Zinc Nickel Alloy, BAC 5637.
6. ASTM: Hydrogen Embrittlement F519.
7. Chrysler Motor Co.: Hydrogen Embrittlement PS 9500.
8. Chrysler Motor Co.: Fastener Tightness PS 809.
9. Ford Motor Co.: Lubricant for Torque/Clamping Force Control, WSD-M13P7-A.
10. ASTM: Zinc-Cobalt B840, Zinc-Nickel B841, Zinc-Iron B842.
11. ASTM: Microscopic Cross Section B487.
12. ASTM: Magnetic Thickness Measurement B499.
13. ASTM: Beta Backscatter Thickness Measurement B567, B659.
14. ASTM: XRF Thickness Measurement 568.
15. ASTM: Neutral Salt Spray B117.
16. ASTM: Kesternich B605.

About the Authors

Dr. David Crotty is R&D manager for MacDermid Inc., P.O. Box Z, New Hudson, MI 48165-9741. He holds BS and MS degrees in chemistry from Xavier University, Cincinnati, OH and a PhD in chemistry from Wayne State University, Detroit, MI. He has worked in the metal finishing industry since 1980. His areas of research have included electroless nickel plating, zinc and zinc alloy plating, and associated processes.

Robert Griffin is a business manager specializing in MacDermid's anti-corrosion systems. He was previously involved in field service for zinc and chromate finishing. He attended Southern Connecticut State University and the University of New Haven, and is currently pursuing an MBA at the University of Hartford.