Zinc-Nickel Electroplate As a Replacement for Cadmium On High-Strength Steels

By D.A. Wright, N. Gage and B.A. Wilson

A need to find a suitable replacement for cadmium electroplated coatings on medium- to high-strength steels has accelerated the development of economically viable alternatives. This edited version of a presentation at the 30th annual Aerospace/Airline Plating & Metal Finishing Forum examines the development of Australia's Defence Science and Technology Organisation's (DSTO) zinc-nickel electroplate, for rack plating on mild steel (a typical stressed and microcracked alloy electroplate), as a replacement for cadmium electroplate on high-strength steel.

The presentation won the Robert C. Garland Award, named for a long-time supporter of AESF who helped to create and organize the first Forum in 1963. As the Garland Award winner, the authors of the presentation receive a certificate and an honorarium.

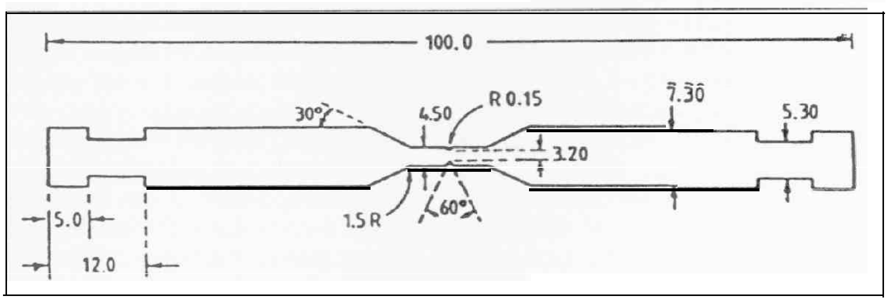

Fig. 1—Dimensions of 4340 steel specimens used in tensile testing.

The very toxic nature of cadmium, and its compounds, has raised world-wide concerns about the use of it in a number of industries.[1] The metal finishing industry has made extensive use of the unique mix of properties of cadmium for corrosion resistance, and engineering attributes in the fastener, electrical and aerospace industries. Because the electroplating industry (often erroneously) has been singled out as a main contributor to the production of cadmium wastes and the hazard it presents to the environment, there is a strong possibility of strict regulatory limitations on its use. The threat of such regulations has raised questions about the use of electroplated cadmium.[2] This has had an effect in the structural engineering, and aircraft industries, where the unique properties of cadmium are most needed on fasteners and high-strength steel components. Advantages of cadmium electroplate have included its worldwide acceptance as a non-embrittling, electroplated coating that is safe for the fasteners and structural high- and medium-strength steels that are vital for both industries. Such factors still promote the use of electroplated cadmium, even though the other factors have accelerated the search for a suitable replacement.

The properties of cadmium coatings, which include good corrosion resistance, solderability and lubricity, cannot be repeated at present for a single electroplated metallic coating. As a corrosion resistant coating on high-strength steel, however, a DSTO developed zinc-nickel electroplate [3,4] has been very successful in meeting the globally accepted criteria for a non-embrittling coating on high-strength steel. This coating is equal to, if not better than, cadmium in terms of corrosion resistance.

While the use of zinc-nickel as an electroplated coating has been discussed extensively in literature,[5] and in the plating industry,[6] it has only recently been seriously considered as a candidate for replacing cadmium on high-strength steels.[7,8]

The DSTO laboratory developed the zinc-nickel process primarily as a superior corrosion resistant coating, and as a replacement for zinc, because its corrosion resistance in the tropical areas of Northern Australia was inadequate for defense material. Both accelerated and field exposure corrosion tests have shown that zinc-nickel coatings, containing 10-14 percent nickel, are vastly superior to zinc, and comparable to cadmium.[3,4] Previous attempts to plate with zinc-nickel have encountered problems with control of the process. The difficulty of controlling an alloy solution is always a consideration in using such a process.

The extension of the zinc-nickel electroplated coating from a purely corrosion protection role, to a coating suitable for high-strength steel, was initiated by examination of the microstructure. It is understood that one of the major reasons for the success of a low hydrogen embrittling cadmium coating is the columnar and porous structure of the coating.[9] This type of structure allows hydrogen to diffuse out from the substrate through the coating during the low temperature (195 °C) heat treatment (bakeout) after plating. The micro-cracked nature of zinc-nickel alloy coating indicated it was a candidate to replace cadmium on high-strength steel. While the microstructure is normally lamellar, when he alloy coating is deposited the stress levels cause micro-cracking to occur.

For widespread acceptance, coatings need to satisfy recognized test procedures for control of hydrogen embrittlement. They must do this at east as well as the cadmium coatings currently used for the corrosion protection of high-strength steels. Several test methods are available to demonstrate low hydrogen embrittling properties in electroplated coatings. They include: ASTM 200 hr; 75 percent Ultimate Tensile Strength (UTS); constant load tests,

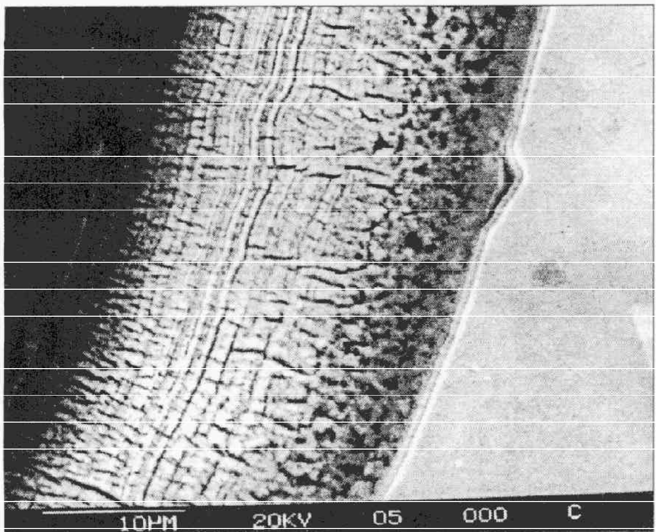

Fig. 2—SEM micrograph of the etched Zn-Ni coating, showing micro-cracked structure normal to the substrate extends through the plate. A well-defined lamellar structure normal to these cracks is apparent.

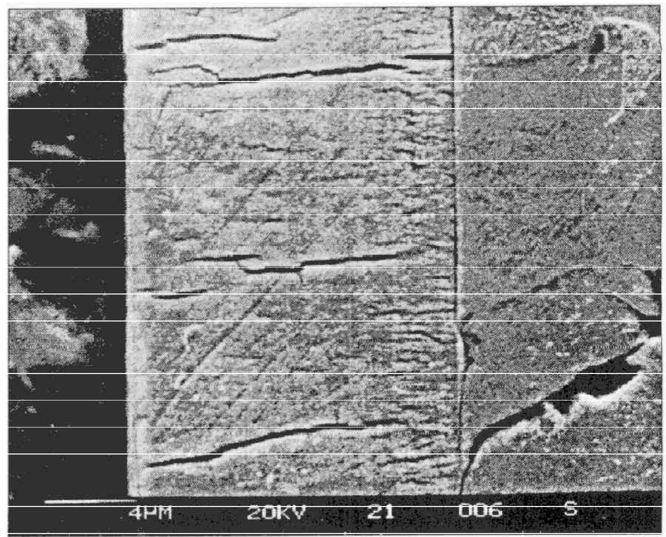

Fig. 3—SEM micrograph of Zn-Ni coating that contains more than 15% Ni. Poorly defined lamellar and micro-cracked structures, together with large continuous stress cracks, penetrate the electroplate (etched).

defined in the ASTM Standard F 519;[10] the notched C-ring test (also defined in F 51 9); and a slow strain rate extension to fracture test (a rapid laboratory method used to assess susceptibility of metals and alloys to stress-corrosion cracking, developed by R.N. Parkins and co-workers).' '-" A modified slow strain rate test has been applied to measurements of hydrogen embrittlement in ultra-high-strength steels in the DSTO laboratories. [15]

ASTM 200-hr constant load tests in Specification F 519 are based on an arbitrary 'lime to failure," and a testing load as a function of steel strength, which, together, provide a test that has universal acceptance as one that is reliable for embrittlement. Accepted internationally, the tests are applied to provide straight forward "pass or fail" results on the absence of hydrogen embrittlement, although stressing specimens to a predetermined percentage of notched tensile strength has been applied to provide a semi-quantitative approach to stress corrosion cracking of high strength materials.[16]

Slow strain rate tests, on the other hand, quantify the degree of hydrogen induced embrittlement,[15] but have not yet gained ASTM acceptance as a standard procedure. However, because they take less than 20 percent of the time of the ASTM Constant Load tests for evaluating each specimen, they were used to estimate substrate hydrogen embrittlement during the development of the low hydrogen embrittling zinc-nickel coating. For international acceptance, any zinc-nickel coating with low hydrogen embrittlement properties, deduced from slow strain rate testing, still needs to pass the slower ASTM constant load, or notched C-ring tests. ASTM Constant Load Tests were carried out on the DSTO zinc-nickel coatings. It is of interest that a rising step-load test developed in the U. S., but similar to the locally used slow strain rate (extension test) procedure, is expected to be adopted as an ASTM recognized test procedure."

Testing

As specified by ASTM Standard Method F 519 (type 1a), notched specimens (Fig. 1) of AISI 4340 ultra-high-strength steel, manufactured to MIL-S-5000E ,[18] were zinc-nickel-coated to test for residual embrittlement. The zinc-nickel alloy coatings were electroplated from an acid chloride based solution as shown:

Zinc-Nickel Electroplating Solution

Chemicals	Cone. g/L
$ZnCl_2$	50
$NiCl_2 6H_2 0$	15-100
NaCl	200
NH_4Cl	30

Plus additives for stress relief, wetting and brightness

Plating Parameters

Temperature	40 °C
pH	About 4.5
Anodes	Zn and/or Zn & Ni
Current Density	3 A/dm^2

Coating thicknesses were generally 8–1 5 µm thick, 12–15 µm at the notch. Low temperature heat treatment (bakeout) after plating was normally 23 hours at 195 °C (±5 °C), to remove labile hydrogen absorbed by a substrate during electroplating. The notched specimens met the stated requirements for sensitivity to embrittlement as required by ASTM F 519.

Cleaning and surface preparation methods were developed to ensure adhesion of the zinc-nickel to the high-strength steel. In contrast to low hydrogen embrittling cadmium plating solutions, organic bath additives are necessary to ensure controlled cracking and stability of the micro-cracked sub-structure in these coatings.

Chromate passivation of zinc-nickel was carried out, using a modified passivation solution containing a chloride activator. Zinc-nickel coatings are normally difficult to passivate because of the nickel content of the coatings. [19]

examination of The Coating Characteristics

For microstructural examination of the zinc-nickel coatings, electro beam methods were used on sections normal to the steel substrate and surface texture. The coated samples for SEM examination were lightly etched in 0.5 percent nital. Fracture surfaces of tensile specimens were scanned by stereo SEM for signs of intergranular cracking.

Slow *Strain Rate Load Tests*

The slow strain tests were uesd exclusively during development of the non-embrittling zinc-nickel coating. The type of test quantitatively estimated residual substrate embrittlement in less than 35 hr. The notched specimens used were the smaller version (Fig, 1) described in

ASTM F 519, to accommodate the limited capacity of our testing machines. The notched specimens had an ultimate tensile strength of 1850 ± 50 MPa (265 ±

fracture stress) 2450 ± 50 MPa (350 ± 7kpsi). The specimen diameter at the notch root radii were 3.2 and 0.15 respectively, giving a stress concentration factor of 3:1.

Specimens were extended in the tensile machine at extension rates of 2 x 10-5 mm/see. At this speed of extension, the test is a very sensitive one for detecting hydrogen produced by the electroplating processes."

Table 1—Fracture Stress Results
On Zn-Ni Electroplated 4340 Notched Specimens

Condition of specimen	Fracture Value
Unplated	2450 ± 35 MPa
LHE Zn-Ni coated (15µm) Max value	2490 MPa
Triplet set	2460550 MPa
Passivated Zn-Ni (baked, then chromated)	2285 MPa
Passivated Zn-Ni (chromated, then baked)	2360 MPa
Failure Rate of Specimens < 1 %	*> 2200* MPa

ASTM Standard
200-hr Constant Load Tests

A modified Parkins stress corrosion flatbed testing machine, and a slow-rate test machine in the constant load mode, were used for the ASTM constant load tests. Some 25-30 specimens have been tested so far.

Results

Tensile tests on over 100 coated specimens using the slow strain-rate-test method indicated that the electroplated and baked-out zinc-nickel coating approached the notch sensitivity of the unplated specimens (i.e., 2450 MPa), as shown in Table 1.

Zinc-nickel coated specimens, tested using the ASTM constant load test to ASTM Specification F 519, passed the 200-hr test, without failure. Test specimens were also subjected to the slow strain rate test, after the 200-hr test, and failed with a fracture stress exceeding 2350 MPa.

Coating Characteristics

SEM micrographs of normally sectioned 8-16 percent zinc-nickel electroplated coatings (Fig. 2) showed a micro-cracked structure normal to the substrate. A well-defined lamellar structure, that closely follows the surface topography, was also characteristic. With the extensive system of micro cracks superimposed on the lamellar electroplate, sectioned coatings appeared to have a pseudo columnar structure. Coatings with more than 15 percent nickel (Fig. 3) have a basic lamellar structure, with a poorer micro-crack structure, and continuous stress cracks frequently penetrating to the substrate. The most corrosion-resistant electroplate (1 2–14 percent nickel) often comprised two layers of different micro-cracking, with the outer layer having more micro cracking in most cases.

Table 2—Zn-Ni vs. Cd Electroplated Coatings
& Stress Fracture Values on AISI 4340 Steel

Condition of Specimen	Fracture Stress Value
Unplated (unembrittled fracture stress)	2450 ± 50 MPa
LHE Zn-Ni coated (15 µm in the notch) Max value	2490 MPa
Triplet set	2460 ± 50 MPa
Zn-Ni electroplate, 23-hr bakeout, then chromated	2285 MPa
Zn-Ni electroplate, chromated, then bakeout for 23 hr	2360 MPa
Bright Cd electroplate+ 23-hr bakeout	700 MPa
Bright Cd electroplate+ 100-hr bakeout	1400 MPa
Porous LHE Cd electroplate, 23-hr bakeout + chromated	2350 MPa
Porous LHE Cd electroplate, 23-hr bakeout	2430 MPa
Cd-Ti electroplate, 12-hr bakeout + chromated	2450 MPa
Cd-Ti electroplate, 12-hr bakeout	2470 MPa
Failure Rate of Specimens < 1%	> 2200 MPa
ASTM Constant Load Test To Specification F 519 (200 hr)	*Mean Applied Stress 1820 MPa*

Discussion

The slow strain-rate method, more rigidly defined that the universally accepted ASTM F 519 200-hr constant load test, is a quantitative method particularly suited for estimating residual substrate embrittlement. Fracture stresses deduced by this method were used to assess the zinc-nickel in comparison to non-embrittling cadmium electroplates, Metallurgical and SEM examinations of notch-fracture surfaces on the specimen were used to confirm the extent of hydrogen embrittlement as deduced from the slow strain rate (fracture stress) results. The depth of penetration of the intergranular cracking into the notch fracture surfaces also correlated with these results. Intergranular cracking fracture, an excellent indicator of hydrogen induced embrittlement, did not occur in the fracture surface when fracture stress parameters gave low hydrogen embrittlement at or above a 99 percent probability level. [21]

A comparison of the fracture stress results on zinc-nickel coatings, compared with cadmium coatings, is shown in Table *2.* The mean stress value for the ASTM Constant Load test is also shown.

Validation of the development of a non-embrittling zinc-nickel coating, by 200-hr constant load testing, followed the slow strain rate test routines and showed full compliance with ASTM requirements for the control of hydrogen embrittlement. Slow strain rate tests on the unbroken 200-hr constant load specimens confirmed the absence of hydrogen induced intergranular cracking (IGC) in the notch fracture surfaces. With the experimental results showing excellent control of hydrogen effects, the development of the electroplate was considered complete. The process is currently undergoing commercial testing.

The importance of structural features in developing a low hydrogen embrittling coating has been established. Physical characteristics of the non-embrittling electroplate were studied, using electron beam analytical methods on coating surfaces and sections. SEM micrographs of normally sectioned and etched coatings showed micro-crack networks in the zinc-nickel coatings (Fig. 1). These channels allow hydrogen to pass through the coating, facilitating its escape. Without the micro-cracked structure, it is likely that the coating would be embrittling. Final slow strain rate parameters show the residual embrittlement of the coated high-strength steel substrates (without chromating) to be within experimental error of those uncoated. Thus, the micro-cracked structure provides at least as good a mechanism for hydrogen bakeout as the columnar structure found in the low hydrogen embrittling cadmium-coated specimens. The micro-cracking also contributes to the excellent corrosion resistance of the zinc-nickel coatings, stabilizing a barrier film of corrosion products at the coating surface.

The micro-cracked nature of the coatings suggests that a physical barrier, such as zinc hydroxide oxidation products, held in a matrix of non-corroded nickel, may control the rate of corrosion.

A reliable zinc-nickel electroplating process has been evaluated for electroplating high-strength steels, without deleterious hydrogen embrittlement. The zinc-nickel coatings comply fully with the ASTM test requirements, and may be chromated easily, using a modified chromate passivation solution. They are strongly adherent to high-strength steel substrates, and are of uniform composition. As a result of passing the ASTM constant load tests for low hydrogen embrittling properties, they constitute a good alternative to the cadmium plating currently employed for corrosion protection of high-strength steels. •

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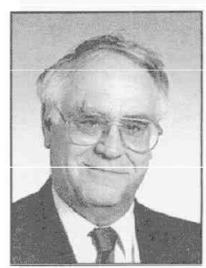

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