Nickel Plated Invar-36 Alloy for Carbon Fiber Composite Molding Tools

C.S. Wang and Yar-Ming Wang*
Materials and Processes Laboratory
General Motors R&D Center
Warren, Michigan, USA

Invar tooling has been increasingly used for low volume molding of precision carbon fiber composite parts with complex geometries. To expand its application to high volume production, this study examined the feasibility of hardening Invar-36 alloy with a thin layer of electroless nickel for surface durability improvement. Two commercial coatings were subjected to thermal cycling tests and evaluated for their changes in hardness, surface roughness, surface morphology and the coating-substrate interface. The results indicate that both coatings could withstand the heating/cooling cycles experienced by production molding cycles, but one was considerably harder than the other. With a 70 µm thick nickel surface layer, Invar samples plated with the harder coating had an HRC hardness of 50, comparable to the P20 tool steel commonly used for automotive composite molding. The surfaces were not exposed to combined molding and thermal cycling in this study. Nonetheless, the results support the choice of this electroless nickel coating for the targeted application.

Keywords: *Electroless nickel, Invar tooling, carbon fiber composite molding, alloy reinforcement*

Introduction

Corvette offered a newly developed lightweight carbon fiber composite hood on the 2004 Commemorative Edition Z06.[1,2] It was the first time carbon fiber composites were used in original equipment for a class-A panel on a North American produced vehicle. The cosmetic outer of the hood was produced by the autoclave cure of a hand lay-up of carbon fiber-epoxy prepreg in a single-sided Invar-36 alloy tool as shown in Fig. 1. In recent years, Invar tools have been increasingly used by the aircraft industry for molding precision carbon fiber composite parts with complex geometries. Their usage in the automotive industry, however, has been rare due to the fact that automotive carbon fiber composite manufacturing is still in its early stages. As the interest in carbon fiber composites increases, it is expected that the need to better understand Invar tooling will also increase in order to fabricate tools more suitable for automotive manufacturing.

Figure 1—*Invar tool for Corvette carbon fiber hood outer production.*

Invar is a family of nickel-iron alloys known to exhibit extremely low thermal expansion below their Curie temperatures.[3,4] Consisting of 36% nickel and 64% iron, Invar-36 alloy has a coefficient of linear thermal expansion (CLTE) of approximately 2×10^{-6} per °C in the temperature range of 25 to 150°C, comparable to that of the carbon fiber-epoxy prepreg composites. It is this unique characteristic that has made Invar-36 the preferred tooling material for molding precision complex composite parts in the aircraft industry. Compared with traditional steel tooling, Invar tools are generally more expensive, due to higher material and fabrication costs. Invar also has a lower thermal conductivity (10 W/m°C) that could lead to a slower heating rate in the composite molding process, as evidenced previously in the Corvette hood production.

* *Corresponding author:*
C.S. Wang
GM R&D Center
M/C 480-106-710
30500 Mound Road
Warren, MI 48090, USA
Phone: (586) 986-2849
E-mail: c.wang@gm.com

For automotive composite manufacturing, Invar tooling has another potential performance drawback. The hardness of Invar-36 alloy is significantly lower than that of the P20 tool steel, 80 HRB (Rockwell B-Scale Hardness) vs. 50 HRC (Rockwell C-Scale Hardness), suggesting that Invar tooling will likely not be sufficiently wear-durable by automotive standards even for low volume production. The surface durability of Invar tooling has been shown by the aircraft industry to be capable of producing several thousand parts. To lengthen the service life of Invar tooling, one possible approach is to harden its surface by applying a hard electroless nickel coating. Electroless nickel has been successfully plated on Invar substrates for x-ray optics applications using a very carefully monitored cleaning and plating procedure.[5] The existing commercial nickel/Invar platers, however, have not had any experience in handling and plating automotive molding tools to date. A learning period will therefore be needed for the platers to scale up their facilities and verify the process parameters before full size tools can be plated.

This study investigated the initial feasibility of plating Invar-36 alloy with a thin layer of hard electroless nickel for use in automotive production tooling. The study was focused on examining the thermal cycling stability of the nickel coatings since composite molding tools are constantly subjected to heating and cooling cycles during their service life and the mismatched CLTE between nickel coating (~13×10^{-6} per °C) and Invar substrate could cause significant stress in the coatings. The study was carried out by monitoring the hardness, roughness and morphological changes of the coating surface and the coating/substrate interface at various predetermined heating and cooling cycles.

Experimental

Four Invar-36 plaques (152 mm × 102 mm × 9.5 mm) supplied by Re-Steel (Eddystone, PA) were used in this study. Before plating, the surfaces of the plaques were prepared by Complete Surface Technologies (Clinton Township, MI) to the same conditions as the Corvette hood production tools. Two plaques were polished to a 600 grit finish and then textured by blasting with a mixture of aluminum oxide and glass beads for the hood outer surface, and the other two were polished to a 400 grit finish without texturing for the hood inner surface. The polished plaques were plated by Techmetals (Dayton, OH) with two proprietary commercial electroless nickel coatings designated as Type I and Type II.

Electroless nickel coating processes generally employ hypophosphite ions as a reducing agent. Consequently, the deposits produced are nickel-phosphorus alloys rather than pure nickel. This allows the composition to be varied (normally between 2 and 13 wt% phosphorus) thereby providing a range of useful properties, including extreme hardness, good corrosion resistance and attractive appearance. A comparison of the specifications of these two coatings is shown in Table I. The Type II coating has lower phosphorus content, higher melting temperatures, and is harder. However, its salt spray corrosion performance is not as good as the Type I coating, probably due to the lower phosphorus content.

The plated Invar plaques were then thermal cycled according to the following procedure of heating and cooling: heat for 1 hr in a 177°C hot air oven; remove from the oven and allow to cool at room temperature for ½ hr; repeat the cycle seven times daily until the desired total number of cycles is completed. The laboratory thermal cycling procedure is patterned after the molding cycles of the Corvette hood production. The laboratory test was slightly accelerated by heating the plaques to 177°C as opposed to the 150°C production peak temperature observed on the Invar molding tools.

The stability of the nickel coatings was investigated by monitoring the hardness, roughness and surface and interface morphologies of the plated plaques during the thermal cycling test. The hardness was measured using Matsuzawa MXT70 microhardness tester with a Knoop Indenter. The hardness value was then converted to the Rockwell scale using ASTM E140-05 for comparison with conventional tooling materials. The surface roughness of the coatings was measured using a Wyko 3-D profilometer. The surface morphology of the plated samples was examined using a Zeiss Evo 50 scanning electron microscope (SEM). An elemental detector (EDS) attached to the SEM was used to determine the approximate compositions of the coatings. For monitoring the interface morphology, cross-sections of each sample were mounted in Lucite and polished to a mirror finish with a Struers Prepamatic-2 using the procedure given in Table 2. Steps 2 and 3 used diamond pastes of the grit specified and an oil-based lubricant.

Following the polishing regimen in the Prepamatic-2, each sample was etched with a Kallings reagent for 10 to 15 sec. There are several Kallings recipes for micro-etchants, and the one used in this study consisted of 2.0 g $CuCl_2$, 40 mL HCl and 60 mL ethanol. Each sample was initially etched, with the etchant applied using a cotton swab, for 10 sec. The etchant was then rinsed off with deionized water and the sample was dried and examined under an Olympus BX51M optical microscope. If the etching was determined to be insufficient for that sample, an additional 5 sec of exposure to the Kallings etchant was applied. The polished sample was then reexamined under the microscope.

Results and discussion

Surface hardness

As mentioned earlier, Invar-36 alloy has an HRB hardness of 80, significantly softer than the conventional P-20 steel used for automotive molding tools. The measured hardness values of the electroless nickel plated Invar samples, both as plated and thermal cycled, are shown in Fig. 2 as a function of thermal cycles. The samples were identified by the type of the nickel coating and the initial surface finish of the Invar substrate.

The data indicate that both Type I and Type II electroless nickel coatings successfully hardened the Invar substrates, although the resultant hardness values were approximately 15 to 25% lower than those given in the coating specifications shown in Table 1. The hardness values of the as-plated samples with the Type II coating were higher than those of Type I and are comparable to the hardness of P20 tool steel, 50 HRC. The Type I coating failed to meet the target hardness value. Consequently, it should not be considered as a feasible material for the tooling application in the future.

Figure 2 also shows that the hardness values of both electroless nickel coatings were not significantly affected by the heating and cooling cycles. The hardness of the Type II-400 samples showed a minor increase at the very beginning of the test and leveled off after 100 thermal cycles. The results suggest that the hardness of the coatings will be stable in the operating temperature range of the molding tools. Additionally, the initial surface finish of the Invar substrates, 400 and 600 grit, had no influence on the hardness of the two electroless nickel coatings before and after the thermal cycling.

Surface roughness

The arithmetic mean roughness, R_a, of the nickel plated Invar samples is plotted as a function of thermal cycles in Fig. 3. The results indicate that the as-plated samples with the Type II coating had a smoother surface than the as-plated Type I samples, 0.7 μm

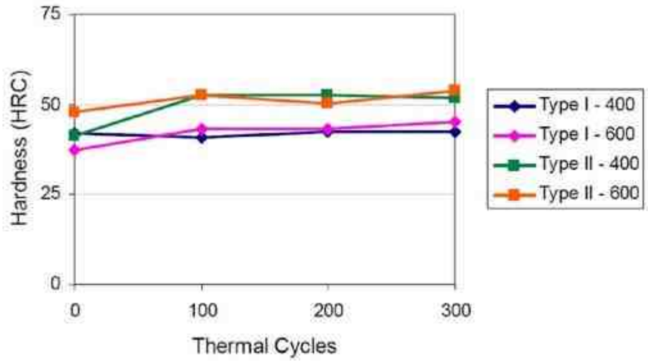


Figure 2—*Hardness of electroless nickel coated Invar as plated and thermal cycled.*

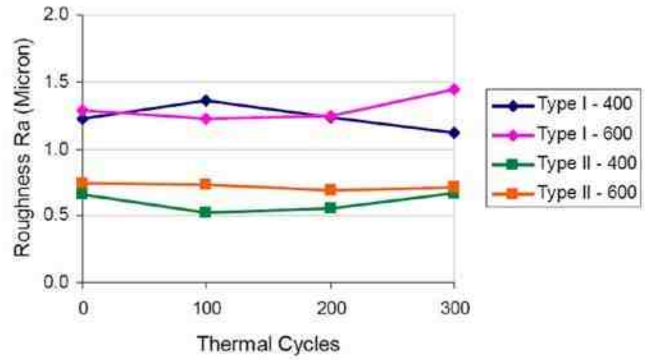


Figure 3—*Effect of thermal cycling on surface roughness of electroless nickel coatings.*

versus 1.3 μm, respectively. The surface roughness values of both coatings were not affected by the thermal cycling tests, suggesting again that the coatings will be stable in the operating temperature range of the molding tools. Similar to the hardness data, the surface roughness of the coated samples was not significantly influenced by the initial surface finish of the Invar substrates. The difference in roughness of Types I and II samples apparently is a result of the coating characteristics, at least when the substrates are reasonably finished as those used in the study. This finding should be further investigated in order to establish the required minimal surface polishing scheme for Invar tools prior to electroless nickel plating.

Coating-substrate interface

In order to examine the interface between the electroless nickel coatings and Invar substrates, optical micrographs were taken from the cross-sections of plated samples, both as plated and thermal cycled. The results are shown in Figs. 4 thru 7 for Type I-400, Type I-600, Type II-400 and Type II-600, respectively. For all the samples examined, the micrographs revealed no signs of delamination at the coating-substrate interface after 300 cycles of heating and cooling. The result provides strong evidence that the electroless nickel coatings will be stable for use as composite molding tools, consistent with previous suggestions made based on hardness and roughness data.

Furthermore, the cross-sectional optical micrographs show that the average coating thickness is about 70 μm (3 mils) for all of the electroless nickel plated samples before and after thermal cycling. This coating thickness is apparently effective in damping out any substrate influence on the coating properties as seen by the insensitivity of the hardness and surface roughness data with respect to the initial surface condition of the substrates. The constant coating thickness during thermal cycling is also consistent with the finding that the coatings on Invar substrates are stable.

SEM analysis of Type II coatings

The above hardness and stability studies have clearly identified that Invar-36 alloy plated with the Type II coating is a feasible tooling material for automotive composite molding applications. Samples with the Type II coating, both as plated and thermal cycled, were therefore further characterized using SEM analysis to determine their elemental compositions and surface morphologies.

The results of the SEM-EDS analysis of the elemental compositions of the Type II-600 samples before and after the heating and cooling cycles are shown in Table 3. The phosphorus content of the coating samples were in the range of 6 to 7 wt% and remained practically constant throughout the thermal cycling test. The elemental composition of the as plated Type II-600 sample, 7.6 wt% phosphorus and 92.4 wt% nickel, is consistent with the coating specification given in Table 1.

The results of the SEM surface microscopy are shown in Fig. 8. As expected, no noticeable surface morphological changes for the nickel plated samples before and after thermal cycling were observed. The nodular surface structure seen in the micrographs is due to the low phosphorus content of the coatings (6 to 7 wt%). The alloys containing lower phosphorus are characterized by the presence of crystalline and microcrystalline nickel, indicating that the number of phosphorus atoms is not sufficient to distort the nickel lattice to an extent where amorphous nickel is obtained. The nodular structure of nickel-phosphorus deposits decreases with increasing phosphorus content.[6] The structure of the Type II coating remained the same during the cycling test.

Summary and conclusions

The feasibility of hardening Invar-36 alloy with an electroless nickel coating was examined in this study for potential application in fabricating carbon fiber composite molding tools. The results indicate that:

1. Invar-36 alloy can be hardened with two types of 70-μm thick electroless nickel coatings. Samples plated with the Type II coating, however, are considerably harder than those with a Type I coating. The hardness of the Type II coating is 50 HRC, comparable to that of P20 tool steel commonly used for automotive composite molding.

2. Both coatings can withstand the heating/cooling cycles experienced by carbon fiber composite molding tools. The stability of the coatings is evidenced by no signs of delamination at the coating-substrate interface during the thermal cycling tests. There were also no noticeable changes in coating hardness, roughness, thickness and surface morphology.

3. The surface smoothness of the electroless nickel coatings was not strongly influenced by the initial surface finish of the Invar substrates. Further study is needed to establish the minimal polishing requirement for Invar molds prior to the nickel plating process.

4. The Type II electroless nickel plated Invar-36 is potentially a durable production tooling material for molding precision and complex automotive carbon fiber composite parts.

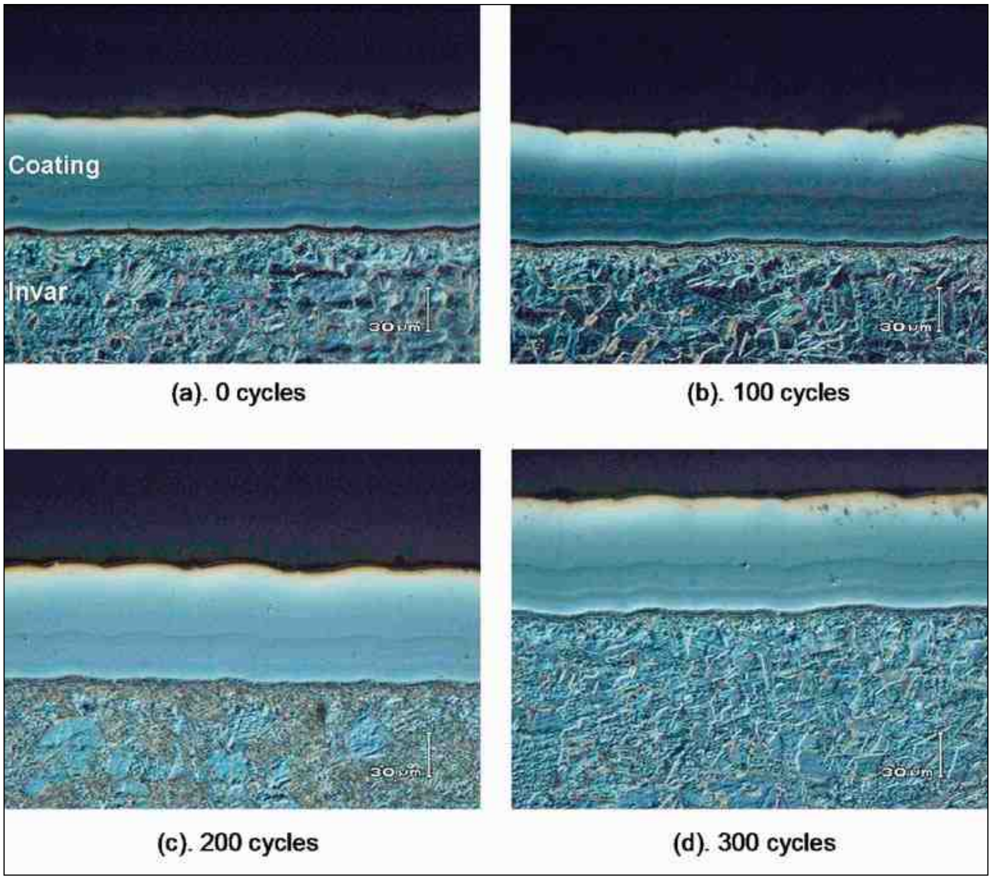


Figure 4—*Optical micrographs of cross-sectioned Type I-400 samples before and after thermal cycling.*

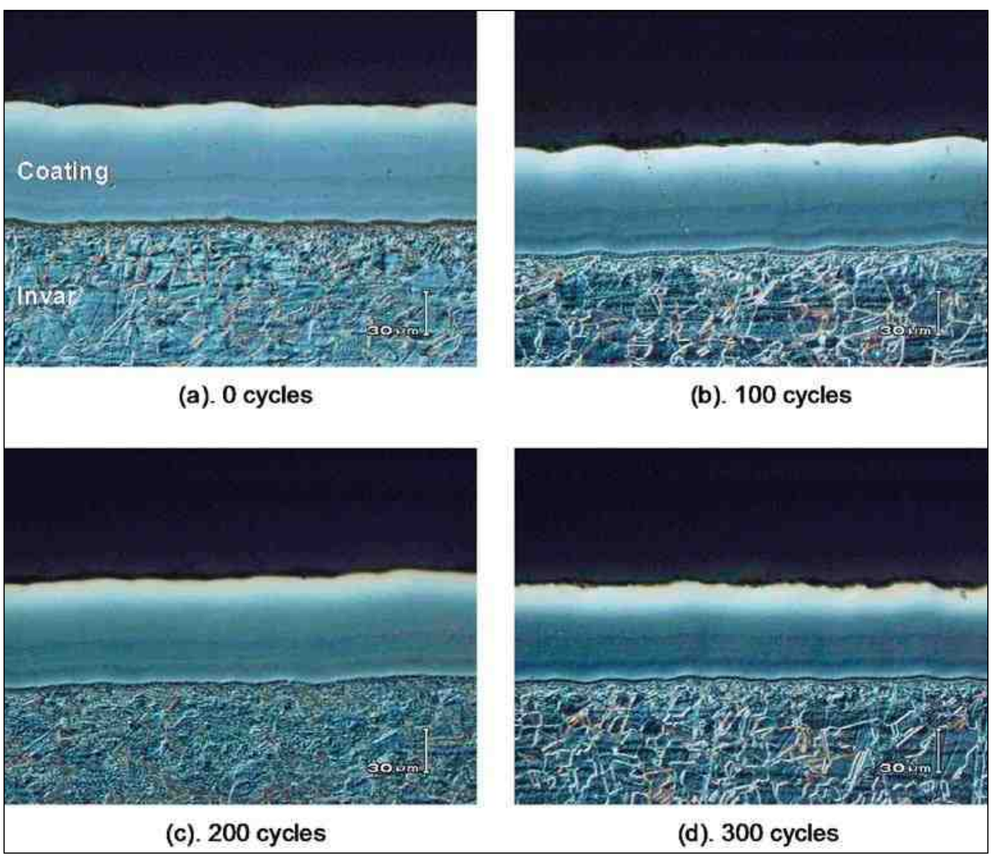


Figure 5—*Optical micrographs of cross-sectioned Type I-600 samples before and after thermal cycling.*

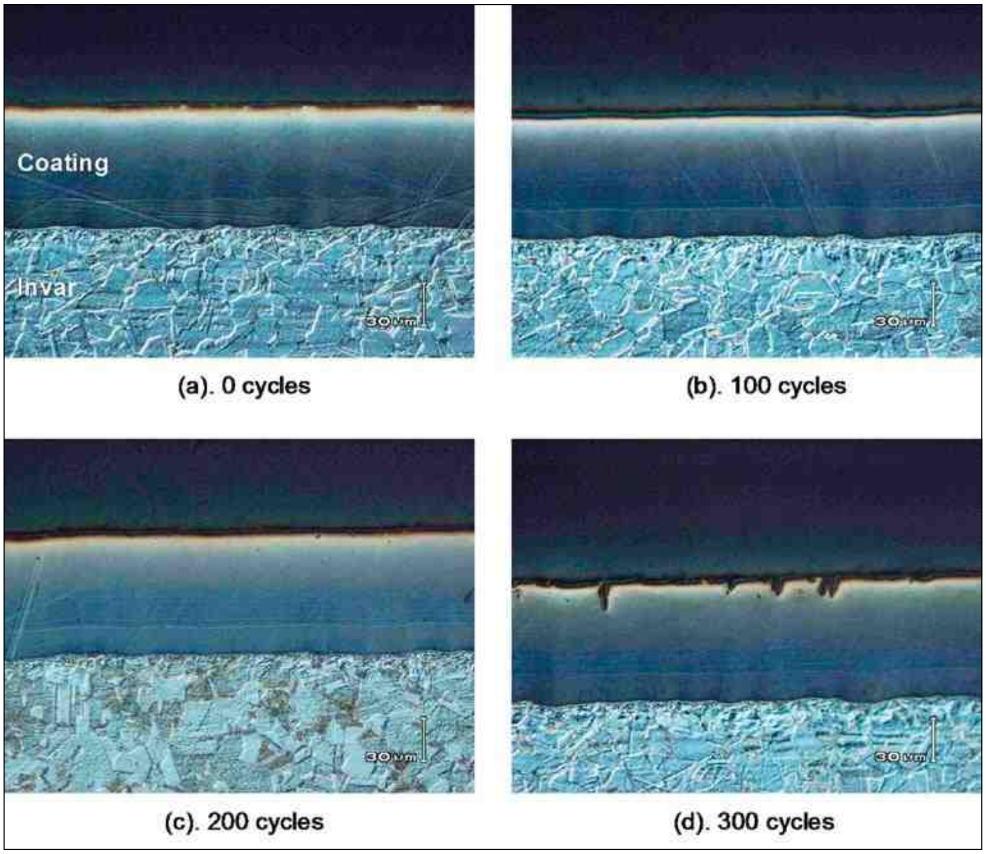


Figure 6—*Optical micrographs of cross-sectioned Type II-400 samples before and after thermal cycling.*

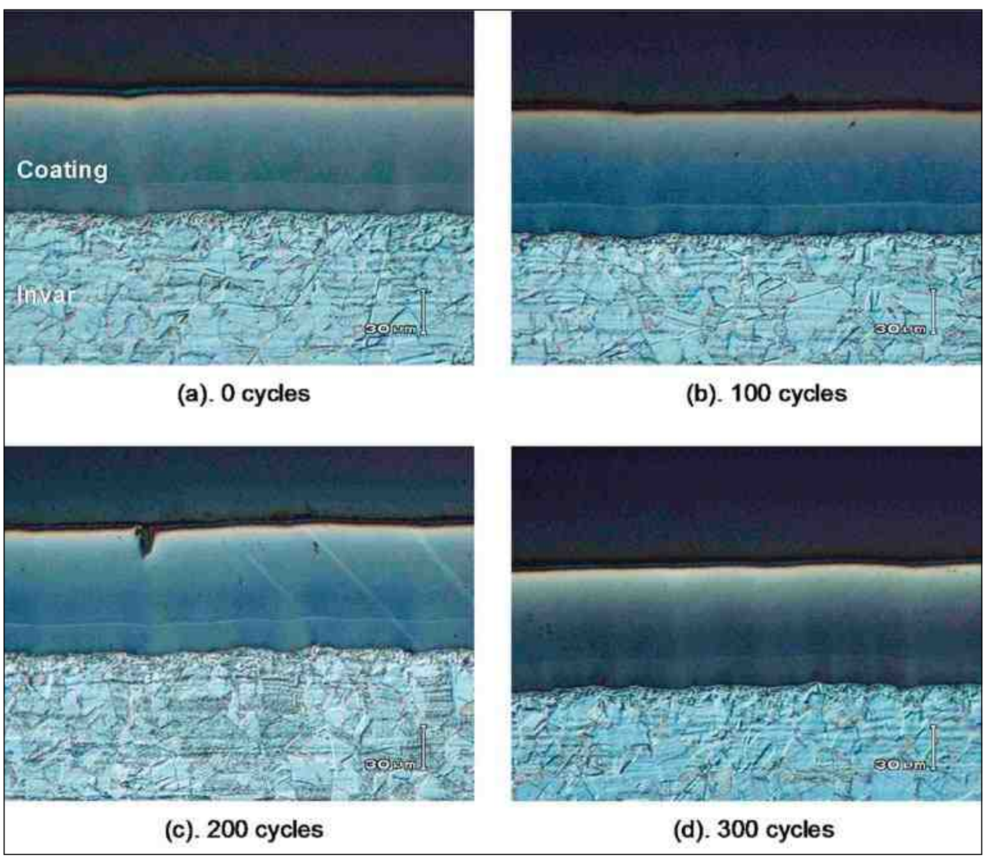


Figure 7—*Optical micrographs of cross-sectioned Type II-600 samples before and after thermal cycling.*

Table 1
Properties comparison between Type I and Type II electroless nickel coatings

Properties	Type I	Type II
Phosphorus content (wt%)	10.5 - 13.0	4.0 - 7.0
Melting point (°C)	880 (eutectic)	960 - 1205
Hardness (HRC)	45 - 50	60 - 64
Corrosion resistance (ASTM-B117)	1000 hr	300 hr

Table 2
Polishing steps for cross-sectioned samples

Step	Grit	Lubricant	Time (min)
1	#220 paper	Water	2
2	9 μm	DP-brown oil	5
3	3 μm	DP-brown oil	5
4	OPS*	None	1.5

*A colloidal silica suspension with a grain size about 0.05 microns.

Table 3
Elemental compositions of Type II-600 coatings as plated and thermal cycled

Composition	0 cycles	100 cycles	200 cycles	300 cycles
Phosphorus (wt%)	7.6	6.6	6.5	6.3
Nickel (wt%)	92.4	93.4	93.5	93.7

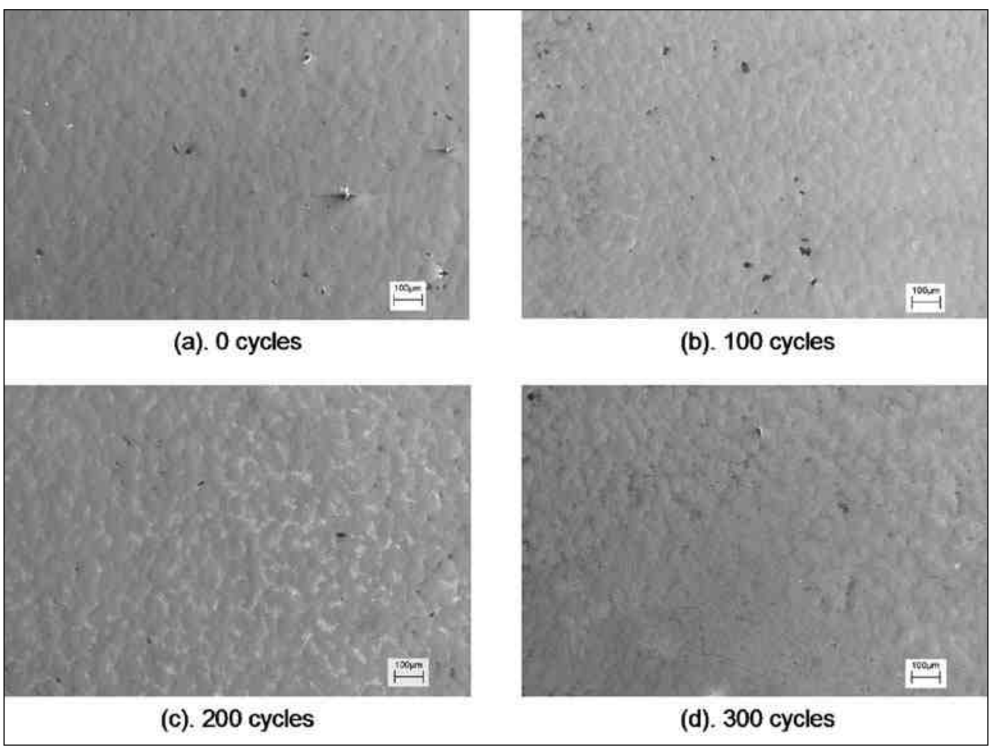


Figure 8—*SEM surface micrographs of Type II-600 samples before and after thermal cycling.*

Acknowledgment

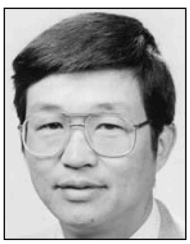
The authors wish to acknowledge Paul Kozlowski (Ricardo MEDA) for collecting the coating characterization data reported in this study.

References

1. M. Voss, J. Remy & N. Pottish, *Proc. 3rd SPE Automotive Composites Conference, Troy, MI*, Society of Plastics Engineers, Brookfield, CT, 2003.
2. D. Brosius, *High-Performance Composites*, March 2004; p. 33; http://www.compositesworld.com/articles/carbon-fiber-hood-for-corvette.aspx.
3. L. L. Harner, Technical Articles, Carpenter Technology Corp., August, 1994; http://crswnew.cartech.com/wnew/techarticles/TA00011.html.
4. L. L. Harner, Technical Articles, Carpenter Technology Corp., January, 1997; http://crswnew.cartech.com/wnew/techarticles/TA00008.html.
5. M. R. Howells, *et al.*, in *Design and Microfabrication of Novel X-ray Optics* (A.A. Snigirev & D. Mancini, Eds.), *Proc. SPIE*, **4783**, 65 (2002).
6. H. Ashassi-Sorkhabi, A. Mirmohseni & H. Harrafi, *Electrochimica Acta*, **50** (28), 5526 (2005).

About the authors

Dr. C. S. Wang



Dr. Yar-Ming Wang

Dr. C. S. Wang is a Principal Engineer at General Motors R & D Center in Warren, Michigan. He received his B.S. degree in Chemical Engineering from National Taiwan University and Ph.D. in Polymer Science and Engineering from the University of Michigan. His automotive experience includes novel polymer processing, prototype and low volume production tooling and parts fabrication, manufacturing cost, and composite material and process development.

Dr. Yar-Ming Wang is a Staff Research Engineer at the Materials and Processes Lab, General Motors R & D Center, Warren, Michigan. He received his B.S. degree in Material Science and Metallurgical Engineering from the National Cheng-Kung University, Tainan, Taiwan and his Ph.D. in Metallurgical Engineering from the Missouri University of Science and Technology, Rolla, MO. Dr. Wang's research interests include battery science, corrosion, surface coatings and anodization.

NASF Welcomes New Members

(as of May 14, 2009)

CORPORATE MEMBERS

Ames Inc, Patterson, NJ
Pingvest Tool & Dye, Brooklyn, NY
Rosco Inc, Jamaica, NY
Unitech Industries, Inc., Elk Grove Village, IL

INDIVIDUAL MEMBERS

Peter Blunk
Skills, Inc., Seattle, WA

Paul Boehler
OMG Electronic Chemicals/ OMG Fidelity, Inc.
South Plainfield, NJ

Hugh M. Buckley
Moen Inc, Hope Mills, NC

Barry S. Kimbrell
Bommer Industries, Inc., Landrum, SC

Mark Labovitz
OMG Electronic Chemicals/ OMG Fidelity, Inc.
South Plainfield, NJ

Borislava Nikolovski
Dipsol of America, Livonia, MI

Elisa Rubiralta
Swets, Barcelona, Spain

Kathy Sharifi
Atotech USA Inc., Charlotte, NC

Peter T. Tang
IPU, Kgs. Lyngby, Denmark