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AESF Research Projects and Some Related Results

The 45th William Blum Lecture
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by
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Editor's Note: Originally published as *Journal of Applied Surface Finishing*, **1** (1), 5-15 (2006), this article is an edited re-publication of the 45th William Blum Lecture, presented at NASF SUR/FIN 2005 in St. Louis, Missouri on June 15, 2005. In it, Dr. Pickering discussed the importance of the AESF-funded research program (now NASF and AESF Foundation) and its importance to the surface finishing industry. We find that his words confirm the importance of today's research program.

INTRODUCTORY REMARKS

Education is a major goal of the NASF and the AESF Foundation and it is also the goal of our universities. University students are necessarily involved in the research, data collection and analysis of the data. For faculty, it means giving up a love of the laboratory so that the students can learn by experience and achieve their final university goal of writing and orally defending their Ph.D., M.S. or B.S. senior thesis. In addition, there are any number of other collaborators on these research projects such as other faculty, visiting scholars and post-doctoral scientists. Thus, any award based on research accomplishments of a faculty member has to be accepted in the name of the members of the research group. It is in this spirit that I humbly accepted the 2004 Scientific Achievement Award of the American Electroplaters and Surface Finishers Society, and then delivered the William Blum Lecture at SUR/FIN 2005 at the America's Center, St. Louis, Missouri on Wednesday, June 15, 2005. This paper is based on my 2005 William Blum lecture.

Penn State Read Conference

Technology transfer is also a major goal of both AESF and our universities. A Gordon Research Conference on Electrodeposition had been held at one of the Gordon Conference sites in New Hampshire in the early 1960s. This meeting was successful, but not wishing to meet every year, the late Professor Harold Read offered to hold the next Electrodeposition meeting at the Pennsylvania State University in University Park, Pennsylvania where he was a faculty member. This first Penn State Conference on Electrodeposition was held in 1965. Many attendees told me that it was highly praised, appreciated and agreed upon that the conference should be held again. In 1968, Professor Read held the meeting one more time before he retired from the University. Figure 1 is a photograph taken at the 1968 meeting of Dr. Read with several other conferees who were alumni of the University.

This writer arrived at Penn State in August 1972 and shortly thereafter was asked to continue holding the Penn State Conferences at Penn State in the tradition started by Dr. Read. Although having no real experience in running conferences, I gladly accepted. The next meeting was held at Penn State in 1975 and thereafter in 1978, 1982, 1985, 1988, 1991 and 1994. These meetings were enthusiastically attended by many in the electrodeposition community with representation from many countries active in electroplating research. They were stimulating, discussion oriented and at the forefront of scientific advances in electroplating, having been carried on in the tradition of the Gordon Research Conferences.

At the 4th meeting in 1978 in honor of Dr. Read, the Conference was renamed the Penn State Read Conference on Electrodeposition. Following the last Read Conference in 1994, the meeting was held as a Gordon Research Conference on Electrodeposition at Colby-Sawyer College, New London, New Hampshire.

Figure 1 - Dr. Harold Read (second from right), Professor Emeritus of Metallurgy at the Pennsylvania State University, served as Honorary Chairman of the Penn State Read Conferences on Electrodeposition. Others are (L to R) Richard Wedel, Rolf Weil, Arthur H. Graham and George A. DiBari in this 1968 photograph at the 2nd Read Conference.

Since research topics can vary significantly over an individual's career, and did in the writer's case, it was somewhat of a dilemma to choose the topics for this William Blum Lecture. Because of the research work done with the AESF, it seemed important to discuss projects that were funded at Penn State over the last 30-plus years. In the end, I decided to choose both old and new work. This meant that some new work that could eventually be found to be applicable to the electrodeposition process or to improving the service life of electrodeposited coatings would have to wait for another day. However, two of these broader topics are first summarized in this paper. The discussion then leads into our work with AESF.

IPZ analysis for hydrogen absorption in metals

Two different approaches are available for decreasing hydrogen absorption into steel and other metals during cathodic processes like electroplating. One is the use of barrier metals like nickel and the other, catalytic in character, relies on a reduced coverage of adsorbed hydrogen for certain mechanisms of the hydrogen evolution reaction (HER). Both the well known and commercially used barrier approach and the novel catalytic approach were studied by Zamanzadeh.[1-3] The barrier approach becomes effective as the thickness on a low permeability, dense, continuous coating increases. These characterization studies led to efforts by Iyer to develop an improved method to analyze hydrogen permeation data obtained from a Devanathan-Stachurski[4] permeation cell. Iyer was successful and the so-called IPZ (Iyer-Pickering-Zamanzadeh) analysis for treating steady state hydrogen permeation data for Langmuir adsorption conditions became available.[5-7] Later, Abd Elhamid[8,9] expanded and applied the analysis. The IPZ analysis, and its successor the IPZA analysis after Al-Faqeer,[10,11] who expanded the analysis to include Frumkin adsorption conditions and to include a second adsorbate in addition to adsorbed hydrogen, provides all the important rate constants for the simultaneously occurring hydrogen evolution reaction and the hydrogen absorption reaction (HAR). A future direction is to use this hydrogen permeation technique and IPZA analysis method to evaluate the role of inhibitors in reducing the HER and HAR during the electrodeposition process. A review outlining the experimental procedures for obtaining the rate constants, concentration of hydrogen in the substrate, exchange current density and the charge transfer coefficient is available.[7]

IR voltage and hydrogen absorption during crevice corrosion

The second topic is the role of *IR* voltage in crevice corrosion and in hydrogen absorption in metals, *I* being the current flowing in the crevice's electrolyte and *R* the resistance of this electrolyte path. Results of the past two decades have verified that *IR* voltage plays a major, always present, role in crevice corrosion while changes in solution composition, *e.g.*, acidification, often also play a major role. The promoting effect of acidification on crevice corrosion has been known for over half a century whereas it was as recently as 1986 that the currently understood role of *IR* voltage in crevice corrosion was offered as a hypothesis.[12] Much earlier, large *IR* voltages were measured in pits and crevices and suggested by the authors to be important,[13-17] but there was a strong reluctance by the leading researchers in the field to consider anything other than changes in the composition of the crevice or pit solution.

Now, after a few decades, thanks to the pioneering work of Valdez[18] and followed by that of Cho,[19-21] Nystrom,[22] Xu,[23-26] Ateya,[27-29] Abdulsalam,[30,31] Al-Khamis,[32] Abdullah[33] and others, a large data base exists on crevice corrosion that can only be explained by the *IR* voltage approach.[34] The reasons and quantitative analysis showing that the traditional solution-composition-change mechanism does not satisfy the data are presented elsewhere.[35,36]

In cases where crevice corrosion does not occur immediately, an increase in size of an active peak and/or an increase in the passive current in the system's polarization curve during an induction period, can lead to initiation of crevice corrosion by meeting the *IR* criterion. An increase in size of the active peak and/or increase in the passive current can occur by either a change in the crevice solution's composition, like acidification, as was outlined in the original 1986 hypothesis,[12] or by an increase in temperature.[34] The data that were obtained on several metal/electrolyte systems in the last two decades were summarized in a recent review.[34] Additional experiments Al-Zahrani[35] and Wolfe[36-38] have recently shown the *IR* voltage's synergistic interaction with growth of an active peak in the crevice solution's polarization curve during the induction period, the latter being caused by a decrease in pH of the crevice solution.

The essence of the *IR* voltage approach to understanding crevice corrosion is that the electrode potential on the crevice walls, $E(x)$, shifts to more negative values by the amount of the *IR* voltage residing in the electrolyte between the opening, $x = 0$, of the crevice and the distance x into the crevice. Since the resistance, R, of the crevice's electrolyte increases with increasing distance into the crevice, so also does the *IR* voltage. The magnitude of *IR* and of the shift in E also depends on the magnitude of the current, I, that is flowing from the inside to the outside of the crevice. Since I is finite during all forms of localized corrosion when the anodic and cathodic reactions are separated, anodic inside and cathodic outside of the crevice, the *IR* voltage in the crevice is finite and typically large. Since the outer surface is at an electrode potential, $E(x = 0)$, which is in the passive region of the bulk solution's polarization curve, the $IR(x)$ voltage can cause the corresponding $E(x)$ at some distance, x, into the crevice to be in the active region of the crevice solution's polarization curve. As a result, rapid metal dissolution, *i.e.*, crevice corrosion, occurs at this and greater distances into the crevice.

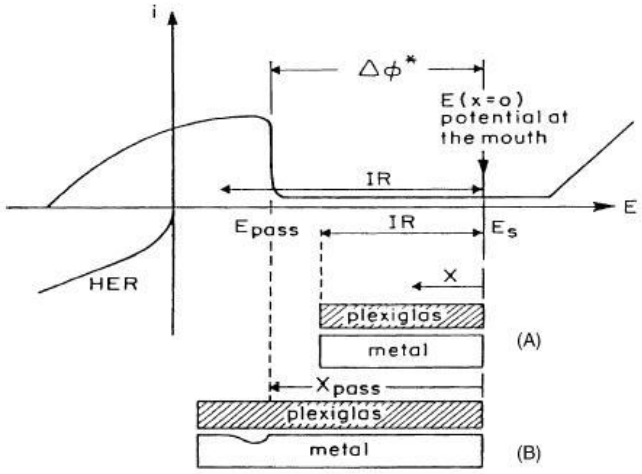

Figure 2 - Schematic anodic polarization curve and crevices of different length illustrating that for the shallower Crevice A, the *IR* voltage is less than the critical voltage, $\Delta\phi^*$, so that crevice corrosion does not immediately occur; whereas for Crevice B, $IR > \Delta\phi^*$, so that crevice corrosion immediately occurs when the open circuit or applied potential is in the passive region.[28,29]

Thus, the important role of *IR* voltage in crevice corrosion is to lower the electrode potential into the active region of the polarization curve. This role of *IR* voltage is illustrated in Fig. 2 as follows.[28,29] If $E(x)$ is shifted into the active region by the magnitude of the *IR* voltage (Crevice B in Fig. 2), crevice corrosion occurs immediately. In this case there is no need to increase the size of either the active peak or the passive current for crevice corrosion to occur. A recent review is available of results for many metal/electrolyte systems that clearly demonstrate this simple concept for immediate crevice corrosion.[34]

When the active peak of the crevice solution's polarization curve is not large enough for the existing conditions (*e.g.*, inadequate aspect ratio of the crevice[34]), as in the case of Crevice A in Fig. 2, crevice corrosion does not immediately occur. However, crevice corrosion may occur after an induction period during which time either the size of the active peak or the passive current increases. During the induction period, I is the magnitude of the passive current flowing from inside the crevice to the outside of the crevice.[34] These changes in the polarization curve typically occur in a great variety of metal/electrolyte systems when the pH of the crevice electrolyte decreases and/or when the temperature increases. For example, if the size of the active peak in the

polarization curve of Fig. 2 increases during the induction period, *i.e.*, E_{pass} in Fig. 2 moves to the right, this could enable crevice corrosion to occur in Crevice A when $\Delta\phi^*$, defined in Fig. 2, is just smaller than the *IR* voltage for crevice A.

These roles of a changing solution composition and/or increase in temperature to increase the size of the active peak and/or the magnitude of the passive current in the polarization curve is well established for bulk solutions (measured on non-creviced flat samples), but similar data have not existed until recently for crevice solutions. Firstly, Al-Zahrani[35] demonstrated the growth of an active peak in the crevice solution's polarization curve which was caused by acidification of the crevice electrolyte during an induction period, and its role in initiating crevice corrosion by the *IR* mechanism. This was recently followed by Wolfe[36] who directly measured the changes in pH(x) and $E(x)$, both as a function of time and distance, x, in the crevice, during the induction period using a combination pH/E microprobe. Wolfe[37,38] had previously constructed this novel pH/E microprobe whose diameter is small enough so as not to disturb significantly the conditions inside the crevice during the measurement.

Figure 2 also shows an *E* region of hydrogen evolution. Though not indicated for either of the crevices in Fig. 2, the potential region for hydrogen evolution often does lie on the crevice wall. Then, hydrogen ion is reduced on the crevice wall to form hydrogen gas bubbles which have been seen in many of the above mentioned experiments.[17,19] Furthermore, the adsorbed hydrogen can be absorbed into the metal, even though the system is under anodic polarization. The absorption into the metal and its diffusion from the bottom of the crevice to the opposite surface of the sample, which is expected in principle, has been experimentally confirmed by Sehgal, *et al.*[39,40]

IR voltage in recesses can also be a factor in determining the life time of electroplates. This is discussed below in the AESF research topic on tin-zinc electroplated coatings on steel. This is the same *IR* voltage, in the recesses of the electroplate, that is discussed in this section as the foundation of the mechanism of crevice corrosion.

Diffusion and recrystallization in gold, palladium and nickel overplates

Since this first of three AESF projects was carried out 25 to 30 years ago, one could think that the results will no longer be interesting or applicable to current issues in electroplating. In that case they would represent a bit of the history of electroplating but as it turns out they still have application today. Actually, they are worth rediscovering for some of the same original reasons, and could have even more relevance today with the current emphasis on nanostructures. The work on this topic was performed by three graduate students: Dan Marx, Sury Kaja and Joel Katz under the direction of William R. Bitler and the writer.

There are many good reasons for miniaturization of electronic components, but miniaturization can lead to more rapid corrosion failure, since minutely small quantities of corrosion products degrade performance or even cause total failure of a device. Atmospheric corrosion of electronic components was well recognized nearly a half century ago.[41,42] One of the possible failure mechanisms is diffusion of the base metal, usually copper, through the noble electroplate, usually gold, and its oxidation on the gold surface to form minute amounts of copper oxide. The dominant diffusion path at these modestly elevated temperatures can be considered to be the grain boundaries rather than lattice diffusion within the grains as occurs at high temperatures. To counter the diffusion of copper into the noble overplate, barrier layers can be inserted between the metals. For example, nickel and nickel alloys are used this way.[43-46] Table 1, from the thesis work of Marx,[44,47] shows the effectiveness of barrier layers by listing the amounts of copper penetration for different barrier metals.

In order to know the minimum thickness of noble metal overplates and/or barrier layers that will achieve the projected lifetime of the component, it is necessary to know the interdiffusion coefficient in the component metals. The recrystallization tendency and grain size of the overplates and barriers are also needed in order to know how quickly in the projected service life the outer surface will be contaminated with a significant amount of copper. Marx, *et al.*[44,47] made the important discovery that the grain boundary diffusion mode gave the surprising result that copper penetration increased with decreasing, rather than increasing, temperature and decreased with time at a given temperature. Since diffusion is a thermally activated process, the specimens annealed at the higher temperature would be expected to show a greater copper penetration than those annealed at a lower temperature. So, the fact that the opposite occurs with electroplates used in service at only modestly elevated temperatures was indeed interesting and prompted further investigation.

Table 1 and Fig. 3 illustrate this anomalous temperature effect. Penetration distances are seen in Table 1 to be much greater at the lower 100°C temperature than at 175°C for several noble and barrier metals. The measured diffusivity values of Marx, *et al*.[44,47] in Fig. 3 show that the apparent diffusivity is an order of magnitude higher at the lower temperature of 100°C than at 175°C, and all data points lie within the crosshatched scatter band of values obtained by Pinnel and Bennett[48] for copper/gold couples without barriers. Marx also confirmed the interesting and important result of Pinnel and Bennett that penetration through electrodeposited layers could be much greater than predicted from the extrapolation of high temperature diffusivity data such as those shown by the solid line above 300°C in Fig. 3. In later studies, Kaja[49,50] showed the same departure to higher than expected diffusivity values in the lower temperature regime for the copper-electroplated palladium couple. Furthermore, the measured diffusivities for the palladium electroplate were compared to the much larger grained wrought palladium. In the lower temperature regime where grain boundary diffusion dominates, the apparent diffusivities were much higher in the electroplated palladium than in the wrought palladium during copper penetration into the palladium. The fine-grained, nanoscale structure of the electrodeposited palladium with its very large grain boundary area accounts for the greater amounts of copper penetration and higher apparent diffusivities than measured for the large, equiaxed grain structure of the wrought palladium.

Table 1 - Low temperature copper penetration through different 1-µm-thick barriers and into 20-µm-thick gold overplates, in terms of the distance from the midplane of the barrier to the 7.5 wt% copper plane in the gold overplate. From Marx, *et al*.[44,47]

Temperature, °C	Barrier	Penetration, µm	Comments
175	None	5	……
175	Rhodium	ND	……
175	Platinum	ND	……
175	Palladium	ND	……
175	Chromium (VI)	3	……
175	Nickel-boron	ND	……
175	Nickel – 8 wt% P	ND	……
175	Nickel (Sulfamate)	ND	……
175	Nickel (10-035)	ND	……
100	None	15	Significant void formation
100	Rhodium	>20	Significant void formation
100	Platinum	>20	Significant void formation
100	Palladium	6	Significant void formation
100	Chromium (VI)	9	Significant void formation
100	Nickel-boron	>20	Copper build-up on surface
100	Nickel – 8 wt% P	3	Copper build-up on surface
100	Nickel (Sulfamate)	1	Copper build-up on surface
100	Nickel (10-035)	10	Copper build-up on surface

ND = Non-measurable copper level in the gold (implies less than 1 µm penetration).

The finding, illustrated in the Marx data in Fig. 3, that there can be an inverse temperature phenomenon in electroplates, added to the interest and importance for further studies in order to accurately predict life times in service and to improve their performance. To understand this anomalous temperature dependence of the diffusivities seen in the copper-electrodeposited gold couples in Fig. 3, one only has to look at some earlier results of Katz,[51,52] who studied the recrystallization behavior of electroplated nickel. At the time of Katz's studies, there was no general agreement on whether or not recrystallization occurs in electrodeposits. However, Katz, *et al*.,[52] found that recrystallization occurred readily and at much lower temperatures than wrought nickel. Furthermore, it was determined that several factors -- type of deposit, plating variables and substrate material – all affect the recrystallization behavior, in essence explaining the lack of agreement in the previous studies where distinctions of this kind were either not controlled or not reported. A good illustration of one of these factors, bath composition, is shown in Table 2 from Katz's paper.[52] The difference in recrystallization tendency is remarkable for nickel electroplated from three different plating baths: chloride-free sulfamate, Watts and all-chloride. Their predictions, based on measured activation energies

for full recrystallization at 300°C ranged from 58 hr for chlorine-free sulfamate to 629 yr for all-chloride. From the times in Table 2, one could thus expect full recrystallization relatively early in the service life of chloride-free sulfamate nickel and a good bit later during the service life of Watts nickel, but not at all in the case of all-chloride nickel. That even the least facile all-chloride nickel is still much more susceptible to recrystallization than non-electroplated forms of nickel is illustrated by the time for recrystallization of wrought nickel of 1044 yr in Table 2.

Thus, for long term service in the atmosphere or in any other corrosive environment, one wants the electroplate to be in the large-grained, reduced strain, recrystallized state. This may be at odds with the goal to produce a fine, nanoscale electroplate, in order to optimize other properties. As to the explanation of the anomalous temperature effect, one concludes from the combined studies of Marx, Katz and Kaja that at modest temperatures (*e.g.*, 100°C) recrystallization does not occur early in the service lifetime, the fine, nanoscale, as-plated grain structure persists during the service life, and the accompanying large grain boundary area leads to rapid accumulation of copper oxide on the surface of the overplate and early failure of the component. On the other hand, at a higher temperature (*e.g.*, 175°C), recrystallization occurs relatively early in the service life producing a new large-grained overplate and much reduced rates of accumulation of copper oxide on the overplate surface and a much longer effective service life.

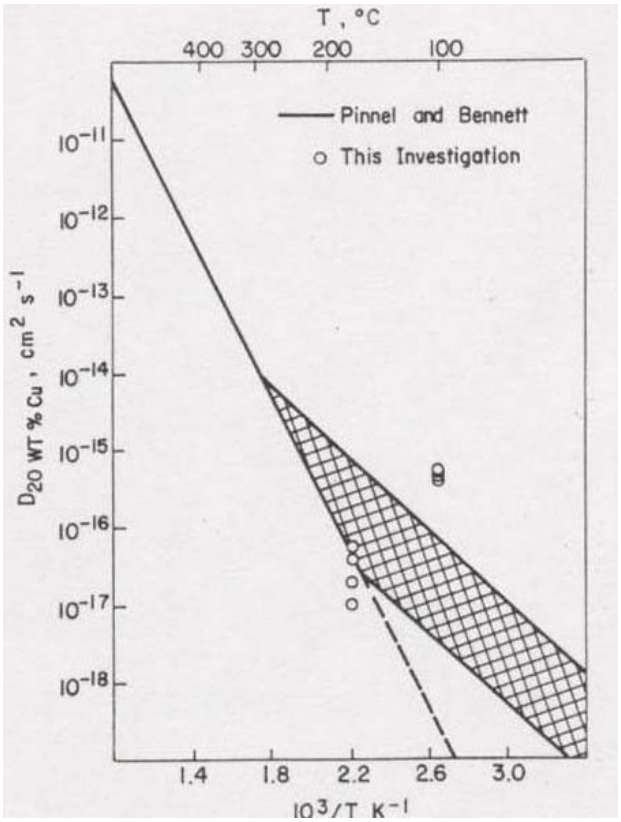

Figure 3 - A plot from Marx, *et.al.*,[47] of the measured diffusivities for copper-electroplated gold versus inverse temperature showing higher apparent diffusivities at 100°C than at 175°C (○ Marx, *et al*.) and the data of Pinnel and Bennett.[48]

Electroplated zinc-nickel for automobile bodies

In the 1990s, an ongoing effort was underway in the automobile industry to replace zinc which serves as a sacrificial overplate on automobile bodies. One candidate material was zinc alloyed with nickel, since it had been shown to be better than pure zinc in subsequent manufacturing operations and in paint performance. The major question at the time was its service life. Researchers at Bethlehem Steel's research laboratory reported that zinc – nickel outperformed pure zinc in salt spray tests, with 12 to 15% nickel alloy exhibiting the best general corrosion resistance.[53,54] However, it is well known that alloying pure metals can cause additional forms of corrosion, including localized corrosion, dealloying and stress corrosion cracking. The possibility of these forms of corrosion occurring in the alloy coatings made it impossible to predict lifetimes of the coating either in the laboratory or in actual service conditions. These considerations led the industry to ask: How good is the corrosion resistance of zinc-nickel?

Table 2 - Time for complete recrystallization at 300°C of nickel deposited from three different plating baths. From Katz, *et al*.[52]

Nickel plating solution	Recrystallization time
Chloride-free, sulfamate	58 hr
Watts	5.1×10^{4} hr (6 yr)
All-chloride	5.5×10^{6} hr (629 yr)
Nickel-60% deformation	7.4×10^{46} hr (8×10^{43} yr)

In response, our AESF research focused on this question. Students Stein, Owen and Zaky did the experiments. This Zn-Ni topic and the next Sn-Zn topic were directed by Konrad G. Weil and the writer. In both of these topics the electrochemical quartz crystal microbalance (EQCM) was used, in order to independently measure the rate of metal deposition or corrosion. The EQCM directly and continuously measures the amount of mass per unit time that crosses the metal/solution interface. It does this with an

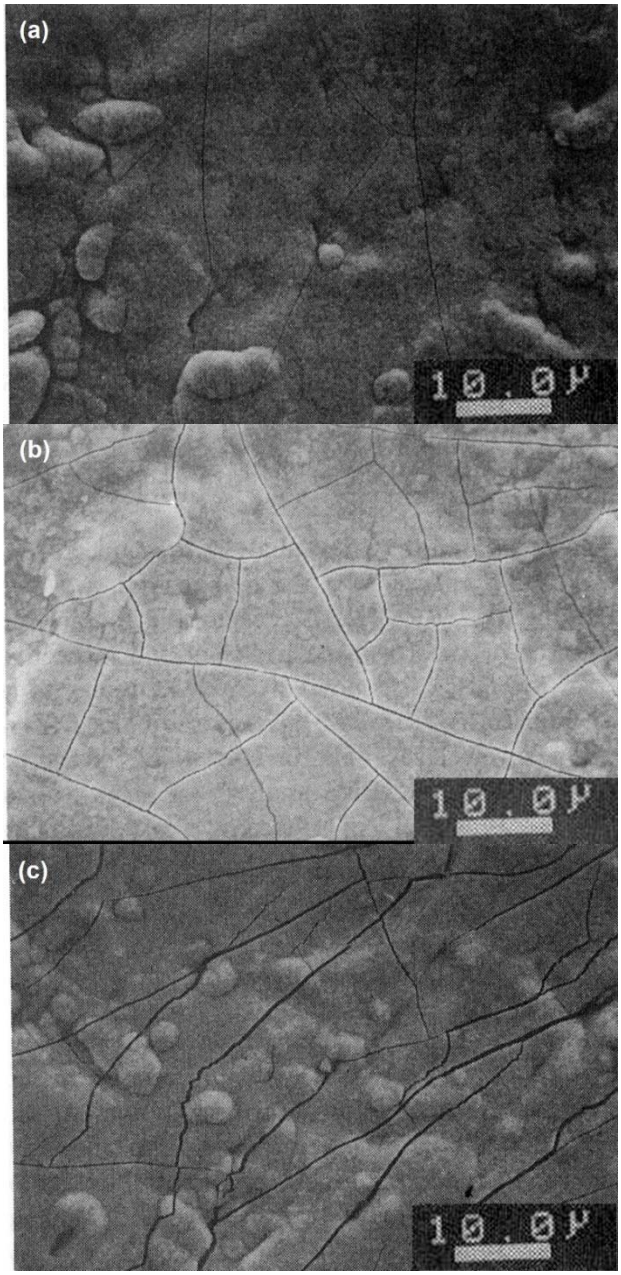

Figure 4 - SEM images at the same magnification of electroplated Zn-12% Ni: (a) freshly deposited surface; (b) after 1 sec in the pH 3.6 corrosive solution at –0.85 V_{SCE} which is below the critical potential, E_c = –0.65 V_{SCE}; (c) after 1 sec at –0.45 V_{SCE} which is more positive than E_c showing severe crack propagation. From Stein, *et al*.[58]

extraordinary sensitivity. Mass changes of a few nanograms per square centimeter can be detected and this makes the
EQCM an ideal tool for the study of metal deposition and uniform corrosion.[55,56] The electroplating rate obtained with the EQCM can be compared with the rate obtained from the measured current to determine the efficiency of the plating operation, or the EQCM can be used to obtain the corrosion rate.

Zinc-nickel coated steels, supplied by Bethlehem Steel Corporation, consisted of drawing-quality aluminum killed steel sheets, electroplated to a thickness of 4.15 μm and a composition of Zn-11.5 wt% Ni. Shastry[57] reported that these coatings consisted of only the γ-phase, rather than the equilibrium two-phase γ and δ structure. The corrosion behavior was studied at 21°C in 0.1M sodium sulfate solution acidified with sulfuric acid to pH 3.6 in order to simulate the acidity of the most aggressive acid rain environment. In these experiments on the plated Zn-11.5 wt% Ni coated steels, current transients at potentials more positive than the corrosion potential showed the existence of a critical potential, E_c, with passive-type behavior below E_c and a sharply increasing current at increasingly more positive potentials above E_c.[58] These features are a characteristic of the dealloying form of corrosion. Below E_c the metal dissolution rate, both from the measured current and the EQCM measurements, is very low. Only some grain boundary etching is observed. Hence, there is little or no threat of failure within the service design life for corrosion potentials below E_c. However, at corrosion or applied potentials more positive than E_c, scanning electron microscopy (SCE) shows that crack propagation readily occurs through the thickness of the plate, exposing the steel substrate.[58] Figure 4 shows these SEM images.

To overcome these corrosion issues new bath formulations were developed and tested in order to determine the phase compositions and the corrosion behavior of the deposits. Zaky[59] electroplated zinc-nickel alloy on cold rolled steel sheets from a proprietary alkaline bath .* X-ray diffraction results indicated that the stable γ-Zn-Ni phase coexisted with the terminal, metastable η-Zn-Ni phase in these as-plated alloys whose overall composition was in the 5 to 9% Ni range. During corrosion the latter terminal phase with its higher zinc concentration dissolved first but the more stable phase also dissolved. By 10 hr of corrosion, the stable γ-Zn-Ni phase was nearly gone and only the steel substrate gave rise to

* Dipsol-Gumm Ventures, Kearny, NJ (now Dipsol of America, Livonia, MI.)

x-ray reflections. The pH of the corrosive solution at 10 hr had risen from 3.6 to 6.0, indicating that the cathodic reaction was hydrogen evolution in this deaerated solution. Hence, the corrosion reaction can be written as:[59]

$$Zn(Ni) + 2H^{+} \rightarrow Zn^{+2}(Ni^{+2}) + H_2\uparrow \qquad (1)$$

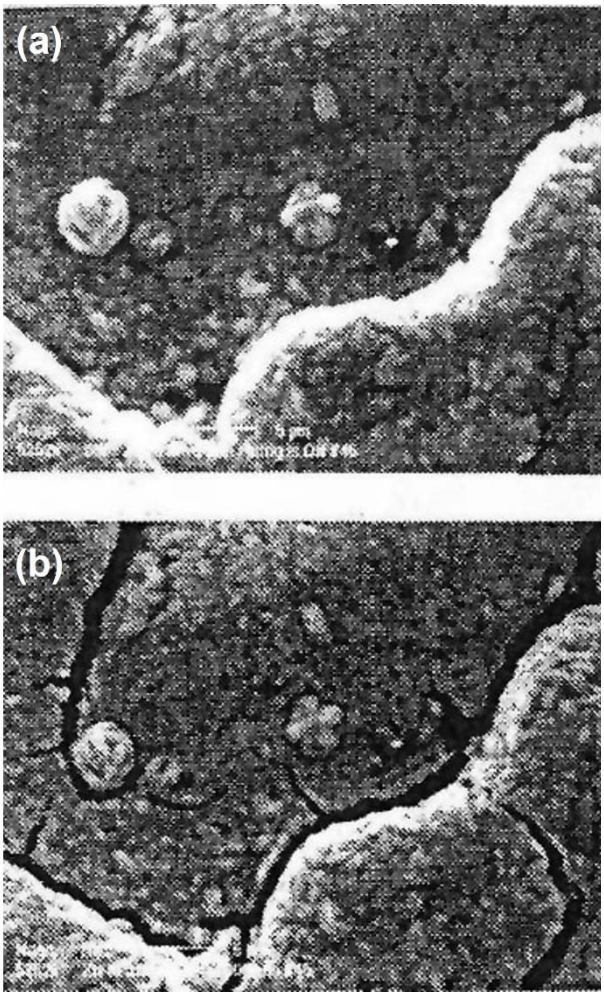

Figure 5 - SEM of the surface of electrodeposited Zn-Ni: Top image: after removal from the plating bath under 2.0 A/dm^2 deposition current; bottom image: same area after 30 min in the corrosive pH 3.6 solution showing severe cracking along the phase boundaries. From Zaky, *et al*.[59]

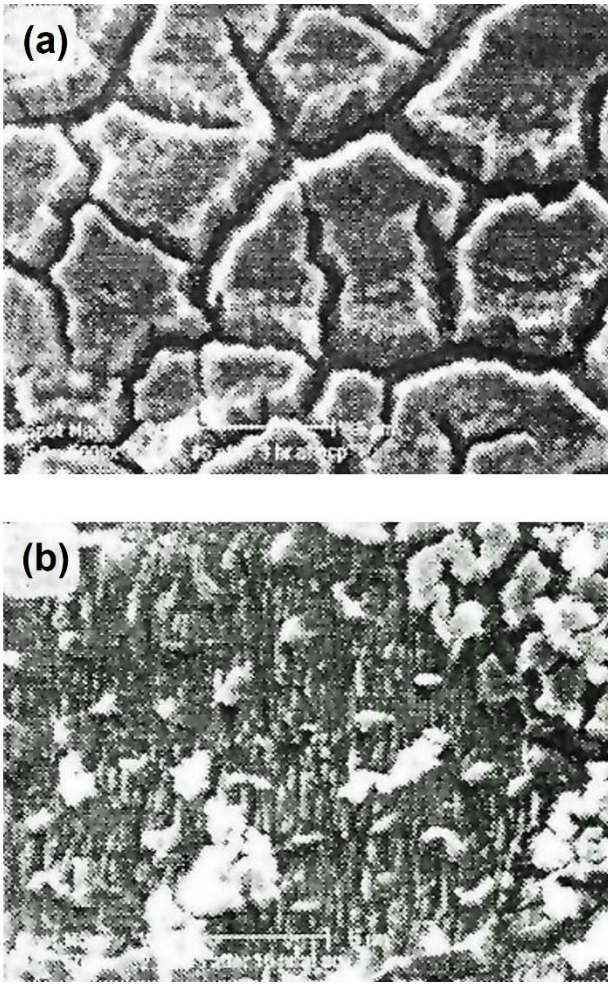

Figure 6 - As in Fig. 5 after longer times in the corrosive solution: (a) 3 hr, (b) 10 hr. From Zaky, *et al*.[59]

SEM analysis showed that the morphology of attack was not uniform. Cracks appeared along the network of the faster-dissolving, more Zn-rich η-phase. Figure 5 (bottom) shows these cracks after 30 min in the corrosive solution for a Zn-Ni deposit formed at 2 A/dm^2. The cracks are along the phase boundaries seen in Fig. 5 (top). Zn-Ni deposits were also formed at the higher plating rates of 4 and 7 A/dm^2, but these showed the same cracking result (Fig. 6). The cracks grew, and the deposit thinned as the time in the corrosive increased. By 10 hr there was only fragmentary Zn-Ni alloy remaining on the steel substrate surface as seen in Fig. 6(b).

It was revealing to find that these small amounts of zinc-nickel remaining after 10 hr of corrosion on the now, largely exposed steel surface were sufficient to completely protect the steel substrate. This was indicated by a corrosion potential that remained

negative to the steel potential during the experiment. Zaky also confirmed this protective action with only fragments of the alloy remaining on the steel surface by the following experiment. Two coupons, one with the original steel surface and one covered with the Zn-Ni deposit, were exposed to the corrosive solution for more than 10 hr.[59] Small amounts of potassium ferricyanide were then added to both solutions. The solution in contact with the unprotected steel coupon immediately showed an intense blue color, indicating the formation of Prussian blue with the ferrous ions produced by corrosion of the steel. The other solution showed no observable color effect.

In other experiments using the EQCM, Zaky showed that the mass change with time during plating was constant and very reproducible.[59] This rate was much less than that indicated by the plating current of 2.0 A/dm^2. From these rates the plating efficiency was found to be 44.7%. The mass loss due to corrosion of the Zn-Ni overplate when immersed in the pH 3.6 sodium sulfate solution was also monitored using the EQCM. Over periods of 1 hr, the corrosion rate was found to be approximately constant. This constancy is surprising considering there is severe localized corrosion in the form of crack propagation, as shown in Figs. 5 and 6.

Environmentally friendly tin-zinc electroplates

Although tin-zinc electrodeposited coatings have been around for decades, there are many reasons today to consider them seriously as sacrificial, high performance coatings on ferrous-base metals in the metal finishing industry. Significantly, there are now commercially available baths that are environmentally friendly.** These baths are nonflammable and easily disposed of when diluted to a neutral pH. Earlier tin-zinc plating baths were toxic and difficult to control.[60-62] Sn-Zn coatings have several attractive properties besides good protection of the steel substrate which exceeds that of pure zinc, such as good frictional properties, wear resistance, solderability and ductility and low electrical contact resistance.[63,64] Because of these attributes tin-zinc coatings are regarded as candidate replacements for some popular coating materials. In particular, there is a strong driving force to use them in place of cadmium coatings because the latter are toxic and carcinogenic[65,66] and because they have a better corrosion resistance than cadmium coatings. Tin-zinc deposits provide cathodic protection of the steel substrate by the preferential dissolution of the zinc from the alloy.

Tin-zinc coatings of compositions across the phase diagram have a two–phase structure consisting of essentially pure tin and pure zinc because of the restricted solubility of either component in the other below its liquidus temperature and the absence of any intermetallic compounds. A 70 to 80% tin and 20 to 30% zinc range of compositions for Sn-Zn coatings has been reported to have the best comprehensive properties.[67,68]

The goal of our AESF projects on tin-zinc coatings have and continue to be twofold:

1. To develop a protective coating for steel surfaces that can be prepared from an environmentally-friendly bath, and that does not require a cadmium coating or any additional inhibiting surface treatment, such as chromating and

2. To understand the corrosion mechanism associated with 70/30 wt% Sn-Zn alloy electrodeposits in order to improve and predict their lifetime under service conditions.

Graduate students Wang, Maurer and Simsek-Gokcesu performed the experiments.

Wang[63,64] electroplated a 70% Sn-30% Zn coating onto a steel substrate from a neutral, non-cyanide bath. Using the plating current and EQCM data, he found that the electroplating current efficiency was 71%. X-ray diffraction confirmed that the coating was composed of the terminal Sn and Zn phases, and energy dispersive x-ray spectroscopy indicated that the Sn and Zn phases were finely mixed together.[64] SEM images of the surface of the as-deposited Sn-Zn alloy shows a micron-scale deposit,[64,69] as shown in Fig. 7. The Sn-Zn/steel in cross section is also shown in Fig. 7. When inserted in the corrosive pH 3.6, 0.1M sodium sulfate solution and scanned from the open circuit potential to more positive potentials that lie below (negative) the Sn potential, there was little change in the microstructure, but the boundaries between the deposits showed more contrast. This result was also found by Maurer, as seen in Fig. 8. This contrast enhancement was interpreted to be localized attack along the

** Dipsol SZ-242, Dipsol of America, Inc., Livonia, MI.

boundaries.[64,69,70] When scanned to potentials positive with respect to the tin potential, tin also dissolved and the microstructure took on a much more locally corroded appearance.[64]

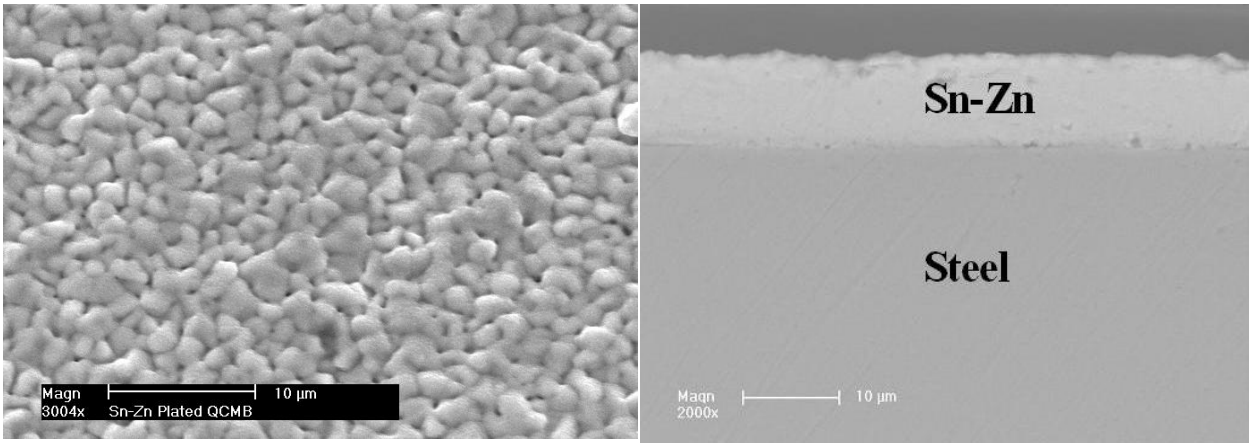

Figure 7 - SEM images of an as-plated Sn-Zn alloy electrodeposit: (a) surface, (b) cross section. From Maurer, *et al*.[69]

The open circuit potential (OCP) was initially the same as that of pure zinc indicating that only zinc was dissolving from the Sn-Zn deposit. Though shifting in the positive potential direction with time, the OCP remained well below the potentials for tin and steel dissolution throughout the 20 or 24-hour tests.[64,70] Inductively-coupled plasma spectrophotometry (ICP) of the corrosive solution indeed showed zinc ions but no tin or iron ions (1.9, <0.1 and <0.1 ppm, respectively[64]). From the measured increase in pH of the bulk solution, the cathodic reaction at OCP is hydrogen evolution, as expected for this deaerated, pH 3.6 solution.[64] As the depth of the local cells increased with time during the selective corrosion of zinc, the shift in OCP could be indicative of an increasing *IR* voltage in the narrow crevices and pits that formed during the selective dissolution of the zinc.[64,69,70] From EQCM measurements of the mass loss during corrosion, the corrosion rate in the pH 3.6 solution was found to decrease to a quasi-steady value of 7.0 µA/cm^2.[64]

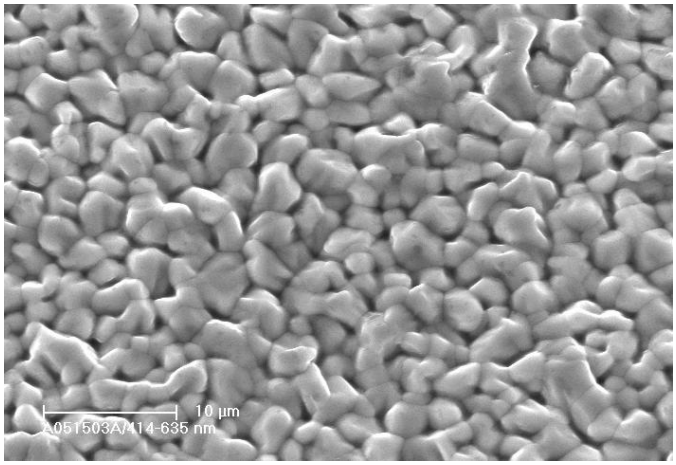

Figure 8 - SEM image of the surface of the Sn-Zn deposit after a potentiostatic scan from the OCP to –800 mV_{SCE} in the 0.1M Na_2SO_4 (pH 3.6) corrosive solution. From Maurer, *et al*.[69]

Anodic polarization curves were obtained for the alloy and its component pure metals.[64] As the potential increased from the OCP for the Sn-30% Zn alloy plate, the current stayed low until the potential for dissolution of tin was reached. Thereafter, it rose steeply with increasing potential. Thus, the zinc dissolution rate is suppressed over a broad potential region by the barrier action of the tin.[64,69] This means that during open circuit corrosion, not only is the steel substrate cathodically protected by zinc dissolution but also tin contributes by maintaining a lower than otherwise zinc oxidation rate. This can be interpreted as tin shielding much of the zinc from the electrolyte. The remaining zinc that is in contact with the electrolyte dissolves and provides cathodic protection of the steel.

It is this dissolving zinc from the bottom of the pores whose dissolution rate decreases with time as a result of an increase of the *IR* voltage with time in the pore's electrolyte. The *IR* voltage shifts the potential of the receding zinc surface, E_{zinc}, in the negative direction, as described above in the section on crevice corrosion. In turn, the zinc current decreases as E_{zinc} shifts more and

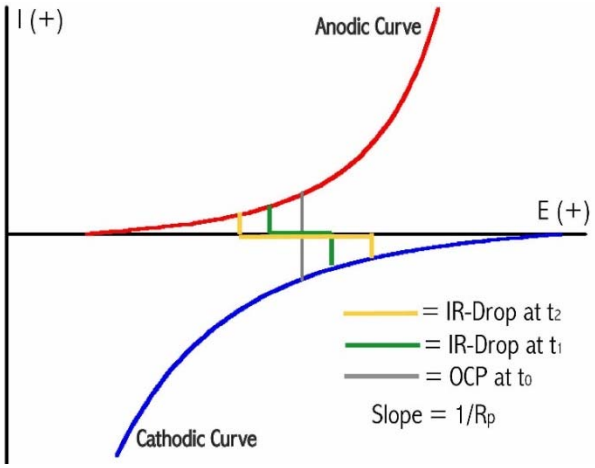

Figure 9 - Anodic and cathodic polarization curves of a corroding system illustrating the decrease in current as the anodic and cathodic reactions are separated by a larger and larger IR voltage. From Wang, *et al*.[70]

more negative with increasing depth of the pore and increasing *IR*, as illustrated in Fig. 9.[70] Figure 9 shows schematic anodic and cathodic polarization curves and the *IR* voltage that increases with time because of the increasing separation of the anodic and cathodic reactions, anodic at the bottom of the pores and cathodic at the outer surface. As shown in Fig. 9, this lowering of the zinc dissolution rate necessarily means also an equal lowering of the cathodic reaction rate. The potential of the cathodic reaction at the opening of the crevice is what is measured and referred to as the corrosion potential that becomes more positive with time. The sum of the anodic and cathodic potential shifts is the *IR* voltage between the opening and bottom of the cavity. Thus, both shielding by the tin and the *IR* effect are mechanisms available in the electrodeposited tin-zinc but not in a pure zinc coating, that contribute to a longer lifetime for the Sn-Zn coated steel.

Wang,[70] Maurer[69,71] and Simsek-Gokcesu[72] performed electrochemical impedance spectroscopy (EIS) experiments to investigate the above mentioned *IR* mechanism for decreasing the zinc dissolution rate below that existing initially at the outer surface of the Sn-Zn alloy and the increase in its OCP with corrosion time. Figure 10 is a schematic diagram showing the pore structure that develops and deepens with corrosion time, and an analog circuit that represents the dissolution process at the bottom of the pore structure.[70] The EIS measurements provided values of the circuit elements with time that were in accordance with the IR voltage mechanism.

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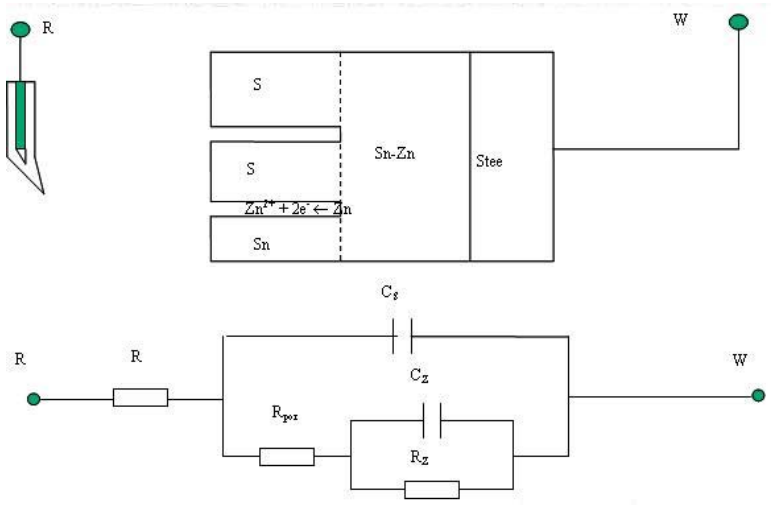

Figure 10 - Schematic cross-section of the partially corroded Sn-Zn coating and the equivalent circuit for the corroding sample. From Wang, *et al*.[70]

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About the author:

This slightly edited piece was written at the time Dr. Pickering was announced as the recipient of the 2005 Scientific Achievement Award.

Dr. Howard W. Pickering is Distinguished Professor of Metallurgy at The Pennsylvania State University, University Park, Pennsylvania. Dr. Pickering had long been a mainstay in the field, particularly in the area of corrosion research. His life's work has been devoted to studying corrosion, understanding it and slowing its relentless action as much as technologically possible. He has been a leader in corrosion research, particularly as it applies to metal coatings, and electroplated coatings in particular. His work has

led to an understanding of the mechanisms of corrosion processes for over 30 years with the collaboration of more than 60 graduate students and 45 colleagues.

Specifically, he has elucidated corrosion phenomena in electrodeposited alloys, including zinc-based materials of commercial interest. His work in stress corrosion cracking and hydrogen absorption and cracking (i.e., hydrogen embrittlement) has contributed to the understanding of this phenomenon in metal finishing applications, including plated fasteners and aerospace components. Other work has contributed to other corrosion phenomena, including pitting and crevice corrosion, corrosion prevention, grain boundary phenomena and analytical techniques for corrosion study.

In his work, he has advanced the knowledge and science of the corrosion field and has mentored an abundance of Graduates who have entered the field and made contributions in their own right. These and the many accomplishments too numerous to mention here speak well of Dr. Pickering's selection for the AESF Scientific Achievement Award.

In 1958, Dr. Pickering received his B.S. in Metallurgical Engineering from the University of Cincinnati, which included CO-OP training in industry as well as academic pursuits. He then went on to Ohio State University, where he received his M.S. (1959) and Ph.D. degrees (1961), under the tutelage of Professor M.G. Fontana, one of the pioneers in corrosion research. Not content to stop there, he continued with Post-Doctoral research as a U. S. Steel Fellow at the Max-Planck-Institut fur Physikalische Chemie, in Gottingen, Germany, under Professor C. Wagner from 1964 to 1965.

His connection to U.S. Steel continued thru 1972, where he attained the position of Senior Scientist, Physical Chemistry Division, at the Edgar C. Bain Laboratory for Fundamental Research, of U.S. Steel Corporation, in Monroeville, PA.

This industrial research background served as a superb qualification as Dr. Pickering returned to the academic world at Penn State in 1972, where he has remained to this day. He worked his way through the various levels, achieving the rank of Distinguished Professor of Metallurgy in 1990. During that time he served as Chairman of the Metallurgy Program at Penn State (1975-1980) and was a Founding Director of the Corrosion Center at the Center for Advanced Materials.

Professor Pickering has been an active participant in the AESF Research program for many years, providing valuable research in the corrosion of coatings, particularly in the application areas of zinc and zinc-alloy plated steels, from electrogalvanized sheet to fasteners. In the process he has produced a number of capable scientists and teachers in their own right, many of whom have made their own contributions to our industry. Indeed, he has been responsible for the education of graduate and undergraduate students (approximately 12 annually) working on research projects in electrochemical corrosion, electrodeposition and surface science for their graduate degrees since the start of his academic career in 1972.

He has also been active in several sister professional societies, including the Electrochemical Society, ASM International and the National Association for Corrosion Engineers. He was Editor, (in charge of N. America) of the journal *Corrosion Science* (Pergamon Press), from 1975 to 1995 and has been a member of its Editorial Board, since 1975.

In addition to the AESF Scientific Achievement Award, he has been the recipient of many honors over the years, including the H. H. Uhlig Award of the Electrochemical Society in 1987. He is a Fellow of ASM International (2002), a Fellow of the Electrochemical Society (1995) and a Fellow of the National Association of Corrosion Engineers (1994).