Thermal-Spray Coatings for Coastal Infrastructure

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ABSTRACT

Several protection strategies for coastal infrastructure using thermal-spray technology are presented from research at the Albany Research Center. Thermal-sprayed zinc coatings for anodes in impressed current cathodic protection systems are used to extend the service lives of reinforced concrete bridges along the Oregon coast. Thermal-sprayed Ti is examined as an alternative to the consumable zinc anode. Sealed thermal-sprayed Al is examined as an alternative coating to zinc dust filled polyurethane paint for steel structures.

INTRODUCTION

The use of thermal-spray metallic coatings is increasing for infrastructure applications. Currently, there are three reinforced concrete bridges (Yaquina Bay, Cape Creek, and Depoe Bay for at total of 428,000 ft^2 (39,763 m^2) covered area) along the Oregon coast that were rehabilitated using thermal-sprayed zinc as anodes in impressed current cathodic protection (ICCP) systems. More bridge restoration projects are in the bidding and planning stages. A 3015 ft^2 (280 m^2) section of the Depoe Bay bridge has thermal-sprayed Ti as a field-test of a nonconsumable anode in an ICCP system. The Albany Research Center and the Oregon Department of Transportation (ODOT) are involved in the characterization of these ICCP systems, in the development of improved installation procedures, and in the development of alternative systems. The results of electrochemical aging thermal-sprayed zinc and Ti anodes are presented.

EXPERIMENTAL PROCEDURES

Zinc Anode ICCP Experiments

Sample Preparation--Concrete samples ("slabs" measuring $9 \times 13 \times 2$ inches ($23 \times 33 \times 5$ cm)) were cast to physically, mechanically, and electrochemically approximate a section of bridge substructure in a thermal-sprayed zinc anode ICCP system. More complete descriptions of the experimental procedures are presented elsewhere.[1-4] The concrete mix design included 5 lb/yd^3 (3 kg/m^3) of NaCl. A steel mesh was embedded in the slab, with 1.25 inches (3.2 cm) of concrete cover, to simulate rebar and to act as the cathode. After curing, the top surfaces of the slabs were sandblasted and prepared to receive a thermal-sprayed zinc coating. Immediately prior to thermal-spraying, the top surfaces of half of the slabs were heated with a propane torch to between 250 and 320°F (120-160°C). The remaining slabs were not heated prior to spraying. These are the "preheated" and "unheated" conditions.

A twin-wire arc-spray process was used to apply zinc to the concrete surface. The spray parameters for zinc were a current of 300-350 A_{dc}, a voltage of 25 V_{dc}, a spray distance of 6-9 inches (15-23 cm), and a wire diameter of 1/8 inch (3.2 mm). A custom designed and constructed programmable X-Y traversing system was used to control the movement of the spray head to obtain a nominal zinc coating thickness of 20 mils (0.5 mm).

Electrochemical Aging--Electrochemical aging of the slabs was conducted in a warm, high humidity room. The temperature was about 75°F (24°C) and the relative humidity (RH) was 80 to 85%. The slabs were wired in series, the zinc as the anode and the steel mesh as the cathode. The slabs were polarized at a current density of 3 mA/ft^2 (32 mA/m^2) using constant current power supplies. The total voltage, the impressed current, and the laboratory temperature were recorded hourly to provide long-term performance data for the system.

Even in the high humidity room, the slabs would tend to dry out and the voltage needed to maintain the current density of 3 mA/ft^2 (32 mA/m^2) would rise. Therefore, the slabs were sprayed as needed with deionized water; midway in the experiment they were being sprayed every day or every other day.

Adhesion Strength Measurements--Preheated and unheated slabs were removed from the experiment at regular time intervals following the passage of a given total charge through the zinc coating. The slabs were equilibrated with dry air for one day, then prepared for adhesion strength measurements by attaching aluminum dollies (1.9 inches (50 mm) in diameter) to the zinc coating at six predetermined locations using epoxy. A high viscosity, high strength, short cure time (300 sec) epoxy was used to eliminate failures at the epoxy-dolly interface and to prevent epoxy penetration through the coating to the concrete. Zinc adhesion strength measurements were made using a universal tensile testing machine. Initial zinc adhesion strengths were determined by measurements on two preheated and two unheated slabs, for a total of 12 measurements for each condition. All subsequent adhesion strengths were the result of six measurements each time a slab was pulled from the experiment.

Comparison to Coastal Bridges--Conditions within the experimental slabs differ from those expected to exist within coastal bridges in two important ways. First, the chloride was uniformly distributed throughout the slab (obtained by dissolving NaCl in the mix water prior to mixing), rather than diffused into the concrete from the outer surface with the associated concentration gradient. The salt distribution obtained by mixing may also put chloride in locations not readily accessible by diffusion, *i.e.*, in isolated pores and blind channels. Second, the current density in the accelerated test is a factor of 15 higher than the approximately 0.2 mA/ft^2 (2.2 mA/m^2) used by ODOT on coastal bridges. This could have the effect of altering transport processes and reactions so as to give results that vary, at least in fine detail, from those being approximated by the experiment and that may occur over much longer times on cathodically protected bridges. However, the California Department of Transportation (CalTrans) reports[5] obtaining higher current densities (up to 1.7 mA/ft^2 (18.3 mA/m^2)), which would be much closer to the experimental current densities.

Richmond-San Rafael Bridge (CA)--The south column of pier 4 of the Richmond-San Rafael Bridge has five thermal-sprayed zinc anode zones, applied in 1983 as part of a cathodic protection study conducted by CalTrans.[5] Each anode is 4 ft (1.2 m) in vertical height, surrounds the column, and is separated from the one above and below it by a 6 inch (15 cm) gap. The lowest anode was operated as a galvanic cathodic protection (GCP) system. The four above it, bands 1 through 4, were operated as an ICCP system. The low edge of band 1 is within 10 ft (3 m) of the water surface and fully exposed to the action of waves and precipitation. Band 4 is higher on the column, roughly 22 ft (6.7 m) above the water, partially sheltered from precipitation by the roadbed immediately above it, while fully exposed to the

drying effects of the wind. The driving (or operating) voltage and system current for each anode was monitored continuously for 12 years from 1983 through 1994.

Titanium Anode ICCP Experiments

Sample Preparation--Laboratory procedures using Ti anodes instead of zinc are described else-where,[6-8] and follow much the same procedures as for zinc. The spray parameters were a current of 300 A_{dc}, a voltage of 36-40 V_{dc}, a spray distance of 6-9 inches (15-23 cm), and annealed wire with a diameter of 1/8 inch (3.2 mm). Only 2-4 mils (0.051-0.13 mm) of Ti was applied instead of 20 mils (0.51 mm) in the case of zinc. A lower impressed current was used than that for zinc--2 mA/ft^2 (21 mA/m^2) instead of 3 mA/ft^2 (32 mA/m^2). A major difference with Ti was the use of a cobalt nitrate catalyst that was applied onto thermal-sprayed Ti surface. A catalyst is used because the passive films that form on Ti would block or reduce current flow. For characterization purposes, some Ti coatings were applied to pyrex glass instead of concrete, and one on concrete was electrochemically aged without catalyst.

Depoe Bay Bridge (OR)--The Depoe Bay Bridge consists of the original structure built in 1926 and another bridge built adjacent to the west face in 1939 to widen the bridge. Installation of an ICCP system began in 1993. A Ti anode was thermal-sprayed to the underdeck and beam areas of the southern-most approach span of the bridge built in 1939. The remainder of the bridge was cathodically protected using a thermal-sprayed zinc anode system. Considerable experience was gained from this and the details of that installation have been published.[6-7]

The thermal-sprayed Ti anode was catalyzed with cobalt nitrate. The catalyst was sprayed onto the Ti anode surface at an application rate of 0.355 L/m^2 (0.0087 gal/ft^2) with 5.4 mA/m^2 (0.5 mA/ft^2) cathodic protection current density flowing between the Ti and the rebar. This zone measured 280 m^2 (3015 ft^2) and was operated at a current density of 2.8 to 3.8 A/m^2 (0.26 to 0.35 mA/ft^2) and a voltage of 1.4 -1.7 V. The anode was operated approximately 1.4 years after the system was energized when two 5.1 cm (2 in) diameter core samples were taken for purposes of characterizing the Ti-concrete interface. At the time of coring the anode electrochemical age was about 146 kC/m^2 (3.8 A-h/ft^2).

Surface Resistance Measurements--The resistance of the Ti anode was measured with a multi-pin resistance probe before and after electrochemical aging. No surface preparation was required for these measurements which, for the laboratory concrete slabs, were made prior to and at the conclusion of the electrochemical aging experiment. Measurements from the Depoe Bay Bridge were taken under field conditions. The initial measurements were made immediately after the anode was applied to the concrete and prior to catalyzing the anode. Measurements were then made on the catalyzed anodes after electro-chemical aging.

Interfacial Chemical Analysis

X-Ray Diffraction (XRD)--XRD analysis was used to identify crystalline phases in the reaction products formed by electrochemical dissolution of the zinc anode and by secondary mineralization. The samples examined were reaction products taken from the zinc concrete interface and from the surface of the zinc coating, and included samples taken from laboratory slabs and from the Cape Creek Bridge. XRD analysis was also used to characterize the phases formed during the thermal-spraying of Ti coatings.

Analytical Scanning Electron Microscope (ASEM) and Electron Microprobe (EMP)--Cross-sections of electrochemically aged slabs were examined using ASEM to determine physical, chemical, and mineralogical characteristics of the coating-concrete interface and changes that may be associated with electrochemical aging and that affect adhesion strength and operation of ICCP systems. To keep the con-

crete from crumbling during grinding and polishing, the samples were embedded in ring forms using a 5:1 ratio epoxy, infiltrated under vacuum, and then cured overnight.

The cross-sectioned samples were carbon coated prior to imaging. Chemical analysis was performed using a wave-length dispersive (WDS) x-ray analyzer with 4 crystals, and an energy-dispersive x-ray analyzer (EDS) with atmospheric thin window for low atomic number elements.

Interfacial pH Measurements--Electrochemically-aged thermal-sprayed zinc and Ti coatings were carefully pealed from the concrete substrate. Some of the zinc minerals formed during the aging process were retained on the peeled zinc. A drop of high purity water was placed on the metal surface that had been in contact with the concrete and mixed, using a glass rod, with minerals adhering to the surface. The pH of the droplet was measured using a micro-combination pH electrode and required as little as 0.1 mL of solution. A similar measurement using powder scraped from the exposed concrete surface generally resulted in pH values somewhat higher than that measured on the exposed metallic surface because of the larger amount of cementatious material included in the measurement.

RESULTS AND DISCUSSION

Thermal-sprayed Zinc ICCP Anodes

Zinc Pull-Off Failure Mechanism--A backscattered electron (BSE) ASEM photomicrograph of a cross-section of the zinc concrete interface from a preheated slab aged an equivalent of 13.2 years (1100 kC/m^2 or 28.4 A-h/ft^2) is shown in Fig. 1. The white and light gray zones are areas with high atomic number elements (primarily zinc). The brightest zone is the zinc coating. Voids and delaminations between the zinc splats typical of thermal-sprayed zinc are evident within the coating. Figure 1 shows the zinc coating followed the topography of the concrete surface. There was no obvious difference between the interfaces for the preheated and unheated slabs. The reaction zones identified in Fig. 1 are discussed later.

The primary failure mode when the coating is pulled from the concrete substrate was cohesive fracture within a thin layer of the zinc minerals and zinc-rich concrete immediately adjacent to the zinc. As failure occurs, cracks propagate through the hardened cement paste and around sand particles, causing some pull-out of the particles. The layer of concrete where failure occurs is roughly 0.05-0.20 mm (2-8 mils) thick. This failure zone coincides, as will be shown later, with zones affected by the zinc reaction products. In contrast, tensile failure of the underlying concrete, using the same test technique, produced massive pullout of the concrete matrix.

Adhesion Strength--Adhesion strength as a function of charge passed during electrochemical aging is shown in Fig. 2 for the preheated (a) and unheated (b) zinc-coated slabs. The six individual measure-ments from each test slab are given for the purposes of illustrating the scatter in the data. The lines through the data arise from an empirical model developed to describe the adhesion behavior.[4] The scatter in adhesion strength values is typical of measurements on these types of samples. In spite of the scatter, it is evident that there are several trends associated with the data. To aid interpretation, note that 200 kC/m^2 (5.2 A-h/ft^2) is roughly equivalent to 3 years of service for the zinc anode ICCP systems used by ODOT.

The average initial adhesion strength was 2.06 MPa (299 psi) for the preheated slabs and 1.15 MPa (167 psi) for the unheated slabs. These strength values show the benefits gained from preheating the concrete, at least in terms of initial adhesion strengths. Values for the preheated slabs are 80% higher than for the unheated slabs. This benefit is consistent with the results of Brousseau et al.[9]

With charge transfer across the zinc-concrete interface, Fig. 2 shows the adhesion strength decreases during the early stages of aging for both the preheated and unheated slabs. This decrease is more pronounced for the preheated slabs. The adhesion strength reaches a minimum for both types of slabs at about 50 kC/m^2 (1.3 A-h/ft^2) and then begins to increase for larger values of charge. The minimum corresponds to roughly nine months for the ICCP systems used by ODOT.

For charge values of about 200 kC/m^2 (5.2 A-h/ft^2), adhesion strengths for the preheated and unheated slabs are nearly identical. The adhesion strength then continues to increase for larger values of charge. This increase concludes at strengths greater than the initial adhesion strengths--strengths of about 2.5 MPa (363 psi) at 400 to 600 kC/m^2 (10.3 to 15.5 A-h/ft^2).

With further charge transfer, the adhesion strengths of both preheated and unheated slabs decrease. This is in contrast to Brousseau et al.[10] where adhesion strengths decreased rapidly after much smaller values of charge were passed. Adhesion strengths near zero, observed in the later stages of aging for both preheated and unheated slabs, occur when there is significant delamination of the coating from the concrete. When the zinc coating is removed, the exposed concrete has a mottled appearance produced by a mosaic of white corrosion products and gray concrete (representing remaining points of attachment for the coating). Many of the remaining points of attachment were characterized by "fingers" of the zinc coating projecting deeply into the concrete at locations of deep narrow surface hollows. The nonhomogeneous distribution of the coating dissolution products undoubtedly contributes to much of the scatter found in the adhesion strength measurements.

Voltage Response--The electrochemical performance of the zinc anodes was examined by the voltage required to maintain a constant anodic current density. Even though laboratory tests were conducted in an environment where the RH was controlled between 80 to 85%, the concrete continually lost water during electrochemical aging due to evaporation or consumption. To avoid exceeding the operating range of the current sources used in the aging experiment, it was necessary to periodically wet the zinc anodes with deionized water. The potential-charge record for one group of slabs is shown in Fig. 3. The saw-tooth pattern is a result of the wetting and drying periods. Potentials rapidly dropped after wetting and gradually climbed during drying. As electrochemical aging preceded, the minimum voltage reached upon wetting gradually increased. The rate of voltage increase during drying also increased with electrochemical aging.

Operating results for the Richmond San Rafael Bridge are shown in Fig. 4 for bands 1 and 4, expressed in terms of a circuit resistance (voltage divided by current) to normalize variations in voltage and current over the 12 year period. The circuit resistance of band 1 (dashed curve) increased slowly over this period, reaching 1 kΩ within 7 years, and 2 kΩ in an additional 4 years. The periodic rise and fall of the circuit resistance reflects seasonal variations of moisture within the concrete delivered by fog, precipitation, and humidity. The resistance of band 4 (solid curve) increased much more rapidly, reaching 2 kΩ within 4 years. Furthermore, the circuit resistance of band 4 exceeded 7 kΩ at the end of the 12 year period, more than three times the resistance of band 1. The seasonal fluctuations in circuit resistance for band 4 are greatly exaggerated compared to those for band 1, presumably reflecting drier conditions during part of the annual cycle for the concrete in contact with band 4. This interpretation is reinforced by the fact that the annual minimum resistance, when conditions are wettest, are often the same for both bands. Laboratory research has shown that the rise in the minimum circuit resistance is associated with mineral formation from zinc dissolution products at the zinc-concrete interface.[3] The effect of this mineral formation is a requirement for increasing system voltage with increasing electrochemical age of the ICCP system.

Zinc-Concrete Interfacial Chemistry--The zinc-cement interface in Fig. 1 was characterized by WDS and EDS analyses. Two reaction zones, "zone 1" and "zone 2", are observed in Fig. 1 between the zinc and cement paste. Zone 1 is primarily Zn and O in roughly equal amounts of each. Zone 1 was also found to be enriched in Cl and S. Silica particles in zone 2 (the roundish dark areas) serve as markers for the original location of the cement paste in contact with the zinc. The presence of these silica particles shows that zone 1 formed from the original zinc coating and zone 2 formed from the original cement paste. Zone 2 is cement paste enriched in Zn and depleted in Ca. The presence of Zn within this zone indicates reactions where Zn has modified the mineralogy of the original cement paste during repeated wetting and drying cycles. This modification of the original cement paste with Zn is termed "secondary mineralization".

The thickness of these zones show significant variation within aged samples. Nevertheless, observations of several samples[2-4] indicate that the zones develop over time and that zone 1 forms prior to zone 2. Cape Creek core samples show evidence of zones similar to those found in the laboratory samples (zone 1 and one case of zone 2). However, in the laboratory, accelerated aging takes place without accelerated diffusion (from concentration gradients). So the mass transport mechanisms associated with Zn enrichment and Ca depletion that define zone 2 may bear a somewhat different relationship to the electrochemical processes at the Cape Creek Bridge.

The white corrosion products found underneath the zinc coatings after the later stages of aging were examined with XRD. The corrosion products were primarily zincite (ZnO). Also present as minor constituents were wulfingite ($Zn(OH)_2$), simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$), and hydrated zinc hydroxide sulfates ($Zn_4SO_4(OH)_6 \cdot xH_2O$). The presence of the zincite phase supports the WDS and EDS results where the corrosion product in zone 1 has a one-to-one Zn-to-O ratio.

White corrosion products were also formed on the surface of the zinc coatings on both the laboratory slabs and on the Cape Creek Bridge (after 3.7 years of ICCP). Simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) was found in the Cape Creek Bridge samples. Simonkolleite was also the primary constituent from the surfaces of laboratory samples, along with hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and $Zn_4SO_4(OH)_6 \cdot xH_2O$. The presence of simonkolleite as the major surface corrosion products from both the Cape Creek Bridge and the laboratory samples suggests a good correspondence between the conditions in the natural and accelerated aging processes.

Interfacial pH--The pH measured under the zinc coating dropped rapidly from about 10 to 7.5 after aging 500 kC/m^2 (12.9 A-h/ft^2) in laboratory studies where the concrete was periodically wetted. With further aging, the pH approached 7.[11] Similar measurements on samples removed from the Cape Creek Bridge (OR) after 250 kC/m^2 (6.4 A-h/ft^2) gave pH values in the range 8.6 to 10.[11] A sample from the East Camino Undercrossing (CA) aged 1670 kC/m^2 (42.9 A-h/ft^2) gave a value of 9.5.[11] Many samples taken from the south column of pier 4 of the Richmond-San Rafael Bridge (CA) aged 2170 kC/m^2 (55.8 A-h/ft^2) gave values in the range 7 to 8. Clearly, the pH at the interface decreases with aging for structures in service, with the values depending upon wetting, sheltering, and the amount of reaction product at the interface. For anodes that are exposed to significant wetting and drying, such as those on Pier 4 of the Richmond-San Rafael Bridge, the pH decreases to values similar to those observed in the laboratory for periodically wetted anodes.

Strengthening and Weakening Mechanisms--The initial bonding of the zinc to the concrete is purely mechanical. The "tooth" given to the concrete by sand blasting and by surface porosity allows the zinc to mechanically adhere. Preheating the concrete prior to spraying increases this initial adhesion strength.

The early decline in adhesion strength is from the degradation of some of the initial mechanical bonding. The current passing through the concrete follows paths of least resistance. Other things being equal, these paths would be where the zinc is closest to the rebar--at the recesses of surface roughness. These places would tend to be the first places to react to form zone 1. The tendency of the concrete to channel current (another example would be around aggregate) would lead to "hot spots" where current densities are higher and more zinc is reacted. The reaction is Zn oxidizing to ZnO. Since ZnO has a volume a factor of 1.6 larger than Zn, this expansion loosens the mechanical grip and reduces the adhesion strength.

Since both preheated and unheated slabs decline to the same strength levels (preheated strengths decline more), the advantages of preheating are lost. It may be that the extra strength provided by preheating is from the same locations that are degraded by the first reactions to form ZnO.

The subsequent increase in adhesion strength results from secondary mineralization. Secondary mineralization (the dissolution and reprecipitation of zinc reaction products) allows cracks and pores within the cement paste to fill. This filling of cracks and pores eliminates stress-risers within the cement paste, as well as increasing the effective cross-sectional area under stress. No significant differences between preheated and unheated samples were observed.

Later declines in adhesion strength are due to the volume expansion in forming ZnO, combined with the nonhomogeneity in the thickness of the ZnO layer (from "hot spots") that result in local stresses at the coating-concrete interface. The stresses increase with increasing electrochemical aging. Cracking within zone 1 and between zone 1 and zone 2 (Fig. 1) results from these stresses and leads to a reduction in adhesion strength. Eventually, the cracks lead to widespread delamination of the coating. No significant differences between the preheated and unheated samples were observed.

The presence of cracks at the coating-concrete interface would presumably cause delamination much sooner in applications where freeze-thaw cycles exist. Water, when present in the cracks, would freeze and expand, adding further stresses to the coating-concrete interface.

Lifetime Predictions--Based on adhesion strength (Fig. 2), the lifetime of the zinc coatings, for both preheated and unheated concrete, was approximately 1800 kC/m^2 (46.4 A-h/ft^2). Based on ODOT ICCP currents of 0.2 mA/ft^2 (2.2 mA/m^2), this represents a lifetime of 27 years. Figure 2 was for experiments that experienced frequent wetting and drying cycles. When the concrete slabs were not wetted,[12] the adhesion strengths continually declined. The life estimate for slabs that were not wetted was 10 years rather than 27 years for the periodically wetted slabs.

Thermal-Sprayed Titanium ICCP Systems

The primary advantage to using Ti anodes for ICCP rather than zinc is that Ti anodes are non-consumable. Titanium is also very corrosion resistant due to passivation. However, passivation means that Ti alone would not work as an effective anode material since the passive layer would prevent significant current flow. Hence, a cobalt nitrate catalyst is used and Ti simply acts as a conductor for the cathodic protection current and as a support structure for the catalyst. Neither the catalyst nor the Ti is consumed in the anodic reaction, which is reported[13] to be:

$$4\,OH^- \rightarrow O_2 + 2H_2O + 4\,e^-$$ **1**

The catalyst may need to be reapplied due to migration, leaching, or reaction with other compounds, but

this could be done without requiring replacement of the Ti.

Coating Characterization Prior to Aging--The major phases identified by XRD were α-Ti having a close-packed hexagonal structure, and a phase similar to TiN and/or TiO having a face-centered cubic (fcc) structure. The fcc phase appeared to have a slightly contracted lattice structure (relative to the lattice dimensions for the TiN standard)--not unusual considering the nonequilibrium nature of the thermal-spray coating. TiO and TiN have the same fcc crystal structure and similar lattice parameters, which, in this case, made them indistinguishable by XRD. No TiO_2 was detected by XRD nor was there any body-centered cubic β-Ti.

A cross-section of Ti applied on pyrex glass using air atomization is shown in Fig. 5. The BSE image (b) shows banding in the Ti coating related to composition differences which are not evident in the SE image (a). The banding is produced by gradients in composition of the coating. The brighter bands contain higher concentrations of metallic Ti, and the darker bands higher concentrations of TiO and/or TiN. Thus, there are alternating layers first rich in α-Ti and then poor in α-Ti (but rich in TiO and/or TiN). EMP depth profiling indicates the presence of gradient bands corresponding to the banding in Fig. 5(b). The brighter bands are 70 to 80 at% Ti; the darker bands are 60 to 70 at% Ti.

Electrochemical Performance--Five Ti-coated concrete slabs were aged electrochemically for 1.8 years at a current density that was a factor of 6 to 8 higher than that used by ODOT at the Depoe Bay Bridge. The actual electrochemical age was 1520 kC/m^2 (39.2 A-h/ft^2), which is equivalent to 10 to 14 years at 2.8 to 3.8 mA/m^2 (0.26 to 0.35 mA/ft^2) as used by ODOT. The current was controlled in this experiment and thus the voltage varied due to changes in the environment and at the Ti-concrete interface. The minimum voltage after wetting remained low throughout the experiment for the catalyzed slabs, but increased for the uncatalyzed slab (similar to zinc anodes).

Figure 6 shows the response of the voltage of the five slabs to different levels of humidity at a current density of 21.5 mA/m^2 (2 mA/ft^2). The behavior of the four catalyzed slabs is similar and shows only a slight increase in voltage at lower levels of humidity. The uncatalyzed slab, however, shows a strong dependence on humidity, with lower levels of humidity causing greater voltage demands for the system. This is not unexpected because Ti oxide films have been considered for use as humidity sensors because they show increased levels of ionic conduction when water is adsorbed to the surface.[14] The increased levels of humidity may also reduce the voltage requirement for the system by reducing the resistance of the cement paste near the Ti-concrete interface.

Voltage decay following the application of water to the anode-concrete interface was reported to indicate the formation of a barrier layer of reaction products.[12] The voltage decay behavior of thermal-sprayed zinc anodes was exponential with the slope of that decay decreasing with greater levels of electrochemical aging. The decreasing slope was interpreted as an indication that a barrier layer was formed and that the layer retarded the inward transport of moisture to the interface. This was not the case for thermal-sprayed Ti anodes. Wetting of the Ti anode caused the voltage to drop to stable low levels within 60 s of wetting, even after 1520 kC/m^2 (39.2 A-h/ft^2) of electrochemical aging. This indicates that no barrier layer was formed at the Ti-concrete interface.

Physical and Mechanical Properties--Electrochemical aging of the thermal-sprayed Ti anode resulted in changes in physical and mechanical properties of the anode. There was no apparent change in thickness due to electrochemical aging. This means that, as suspected, the Ti anode does not dissolve significantly nor is the coating lost in other ways during the electrochemical aging process. Anode resistivity was observed to increase due to aging. The resistivity increased from an average of 1470 to 4177 $\mu\Omega$-cm

for the catalyzed slabs and from 1178 to 3192 $\mu\Omega$-cm for the uncatalyzed slab--both after 1520 kC/m^2 (39.2 A-h/ft^2) of aging. For the Depoe Bay Bridge, the increase was from 1934 to 2070 $\mu\Omega$-cm after 146 kC/m^2 (3.8 A-h/ft^2) of aging. These resistivity measurements were taken using a surface probe that sampled only the thermal-sprayed anode and not the cement paste beneath the anode. The increase in resistivity was, therefore, due to physical or chemical changes within the Ti coating that retard the conduction of electrons. Increased cracking of the coating to lengthen the conduction path or further oxidation of the Ti anode are possible causes of this increase.

Anode bond strengths were observed to decrease markedly with aging. This decrease was more severe for the uncatalyzed sample where the bond strength dropped from an average of 1.17 MPa (171 psi) to 0.01 MPa (0.92 psi). For all of the catalyzed slabs, the bond strength decreased from an average of 1.17 MPa (171 psi) to an average of 0.29 MPa (43 psi). Most of this decrease in bond strength appeared to be due to a weakening of the cement paste beneath the thermal-sprayed Ti.

Interfacial Chemistry after Aging--Polished cross-sections of the anode-concrete interfaces of an aged (1520 kC/m^2 or 39.2 A-h/ft^2) catalyzed slab show two altered layers beneath the Ti coating.[7] The two layers are a "reaction zone" just beneath the Ti coating and a "dense zone" between the reaction zone and unaltered cement. The reaction zone is more porous than the unaltered cement and the dense zone is less porous than the unaltered cement. The formation of a dense zone has been reported previously for Ti mesh anodes embedded in concrete.[15]

The chemical composition of the reaction zone, the dense zone and the interface were studied using EDS x-ray maps. Maps for Ti, Ca, and Co along with a BSE ASEM photo for a cross-section of an aged (1520 kC/m^2 or 39.2 A-h/ft^2) catalyzed slab are shown in Fig. 7. Matching the BSE photo to the x-ray maps makes it possible to see the distribution of the elements of interest at the interface and within the reaction zone. Figure 7(b) shows that the thermal-spray Ti anode is not consumed because there are no Ti reaction products evident within the concrete. Figure 7(c) shows that the reaction zone contains essentially no calcium in what was originally a calcium-rich cement paste. The region below the reaction zone is the dense zone and it contains calcium (it is not possible, using this analytical technique, to see if the calcium from the reaction zone is now part of the dense zone). The final x-ray map, Fig. 7(d), shows that cobalt that was added to catalyze the anodic reaction is still present, but has moved into the reaction zone. Note that it does not appear to have moved into the densified cement paste.

pH measurements of the cement paste at the Ti-concrete interface gave values as low as 6.2 for the uncatalyzed slabs and 7.2 for the catalyzed slabs. These values are acidic enough to favor the dissolution of calcium minerals. Beyond the reaction zone, the Ca and Si levels (20 and 25 at%, respectively) are similar to those reported previously for zinc-concrete interfaces subjected to accelerated electrochemical aging.[12] Previous research[15] on Ti mesh anodes showed that calcium carbonate is removed from the region near the Ti anode and reprecipitated in voids further from the anode as calcite and vaterite, both being mineral forms of calcium carbonate ($CaCO_3$).

A cross-section of the Ti-concrete interface from the Depoe bay bridge after 146 kC/m^2 (3.8 A-h/ft^2) of aging appears similar to cross-sections of the laboratory slabs with the exception of the numerous cracks in the Depoe Bay sample.[7] The Depoe Bay cross-section, like Fig. 7(b), revealed that the Ti anode does not dissolve into the cement paste. This contrasts with the results of cross-sections from the Cape Creek Bridge and East Camino Undercrossing (CA) where zinc from the thermal-sprayed zinc anode migrated into the cement paste.[15] After 146 kC/m^2 (3.8 A-h/ft^2), the calcium has not been leached from the cement paste adjacent to the Ti coating. It is possible that the leaching of the calcium is not yet detectable after only 146 kC/m^2 (3.8 A-h/ft^2) of aging. Alternatively, there may be a critical current

density for Ti anodes below which the cement paste does not deteriorate by leaching of calcium minerals.[7]

ONGOING AND FUTURE RESEARCH

Rocky Creek Viaduct

The Rocky Point Viaduct is located on the south central Oregon Coast. It was constructed in 1955 and observed to have corrosion problems as soon as 1967. It was replaced in 1995, after approximately 40 years of use. One beam from the substructure is being studied to determine the causes of the early failure of this bridge. Measurements being done include potential mapping, corrosion rate determination, delamination survey, chloride distribution, compressive strength of the concrete, and aggregate character-ization. Slices from the beam were cut and thermal-sprayed with zinc for electrochemical aging and chloride migration experiments.

Alternative ICCP Anode Materials

Thermal-spray zinc anodes have been used to cathodically protect reinforced concrete structures. Research has shown some of the limitations of the zinc material when used in an ICCP system.[1-4] A new zinc hydrogel anode,[16-17] which combines rolled zinc sheet with a hydrogel adhesive, is easy to apply to structures of simple geometry and may eliminate some of the problems of the thermal-spray zinc anode. The use of thermal-spray zinc for GCP systems has had mixed results.[18-19] A new Al-Zn-In thermal-spray anode has been reported[18] to provide adequate protection current for longer periods of time than thermal-spray zinc when used in GCP systems. Both of these novel anode materials and thermal-spray Zn-15Al are part of a new accelerated electrochemical aging study aimed at determining changes in the power requirements for the cathodic protection system, adhesion of the anode to the concrete, chemistry at the anode-concrete interface, and other anode-concrete interactions.

Humectant Use with Zinc Anodes

The presence of moisture is critical at the zinc-concrete interface of thermal-spray zinc cathodic protection systems.[12] This moisture facilitates current flow and aides in secondary mineralization reactions which cause an initial strengthening of the zinc-concrete bond. Estimated service life decreases from 27 to 10 years when the interface is kept dry.[12] A new research effort is underway to determine the usefulness of humectants in maintaining moisture at the zinc-concrete interface. Humectants are chemicals that absorb water easily and can be applied to the thermal-spray zinc anode after installation. Studies will determine the effectiveness of the humectants in extending the useful service life of newly-installed thermal-spray zinc anode cathodic protection systems and in rejuvenating older previously-installed thermal-spray zinc anode cathodic protection systems.

Atmospheric Corrosion of Thermal-Sprayed Aluminum Coatings

Coated panels of 1010 mild steel were boldly exposed (with horizontal and vertical orientations) on seven coastal Oregon bridges[20] along U.S. 101 for 3 years (Fig 8). The panels were sandblasted before coating. One set of panels (T) were thermal-sprayed with Al to a thickness of 8-10 mil (0.20-0.25 mm), which was then immediately sealed with a 1 mil (0.025 mm) thick epoxy coating, followed with a 2 mil (0.051 mm) thick pigmented urethane coating. A second set of panels (P) were coated using a three-coat paint system. This coating system consisted of a 3 mil (0.076 mm) zinc-dust filled urethane primer, a 3 mil (0.076 mm) moisture-cured urethane intermediate coat, and a 3 mil (0.076 mm) pigmented moisture-cured urethane topcoat. All paint coating thicknesses were wet thicknesses. Prior to exposure, the

coating on each panel was cut with a tungsten carbide scribe in an X-pattern through to the mild steel substrate to exposed the steel along the scribe lines.

Panels thermal-sprayed with Al (T) showed little evidence of corrosion along the scribe lines or elsewhere at any of the bridge locations and at all orientations, Fig. 8. Panels using the three-coat paint system (P) showed varying degrees of corrosion, blistering, and undercutting depending upon bridge location and orientation, Fig. 8. In all cases, the paint system panels experienced corrosion of the steel along the scribe. In some cases, the panel damage was severe, as at the Spencer Creek Bridge on the central Oregon coast. In others, such as at the Rogue River Bridge on the southern Oregon coast, the damage was much less severe. The damage was more extensive for horizontal exposures, where moisture could pool on the surface for long periods, than for vertical exposures. For highly corrosive environments, such as at the Spencer Creek Bridge, the corrosion was severe regardless of orientation.

CONCLUSIONS

Electrochemical aging of thermal-sprayed zinc anodes results in the formation of reaction zones at the zinc-concrete interface. Zone 1 forms due to the oxidation of the thermal-sprayed zinc anode. Zone 2 forms when the zinc dissolution products replace Ca in the cement paste (secondary mineralization). Anode dissolution and secondary mineralization result in a lowering in pH and an increase in the voltage required to maintain a protective current. With wetting and drying cycles, adhesion strengths initially decreased due to zinc reactions degrading the mechanical bond and then increased due to the filling of voids and cracks by secondary mineralization. Eventually, the adhesion strength drops towards due to cracks arising from volume expansion in zone 1. Laboratory predictions of service lives until detachment are 27 years with wetting and drying cycles and 10 years without wetting. Preheating the surface prior to spraying made no difference in long term adhesion strengths of wetted anodes. Accelerated laboratory electrochemical aging of zinc is similar to field experience in terms of voltage response and interfacial chemistry (similar zone formation, mineral formation, and pH).

Thermal-sprayed Ti in air results in a layered $TiO/TiN/\alpha$-Ti structure with sufficient conductivity to carry cathodic protection currents. After electrochemical aging, two zones are formed from the cement paste--a reaction zone just beneath the Ti and a dense zone below that. The reaction zone is depleted in Ca and has a low pH. No Ti products were found in the reaction zone. The Co in the catalyst was found in the reaction zone. The catalyst was found to keep operating voltages low, even under low humidity conditions. The catalyst also resulted in better long term adhesion strengths than without catalyst.

Thermal-sprayed Al coatings on mild steel performed well after 3 years of coastal atmospheric exposure, especially in comparison with a zinc-filled three-coat paint system.

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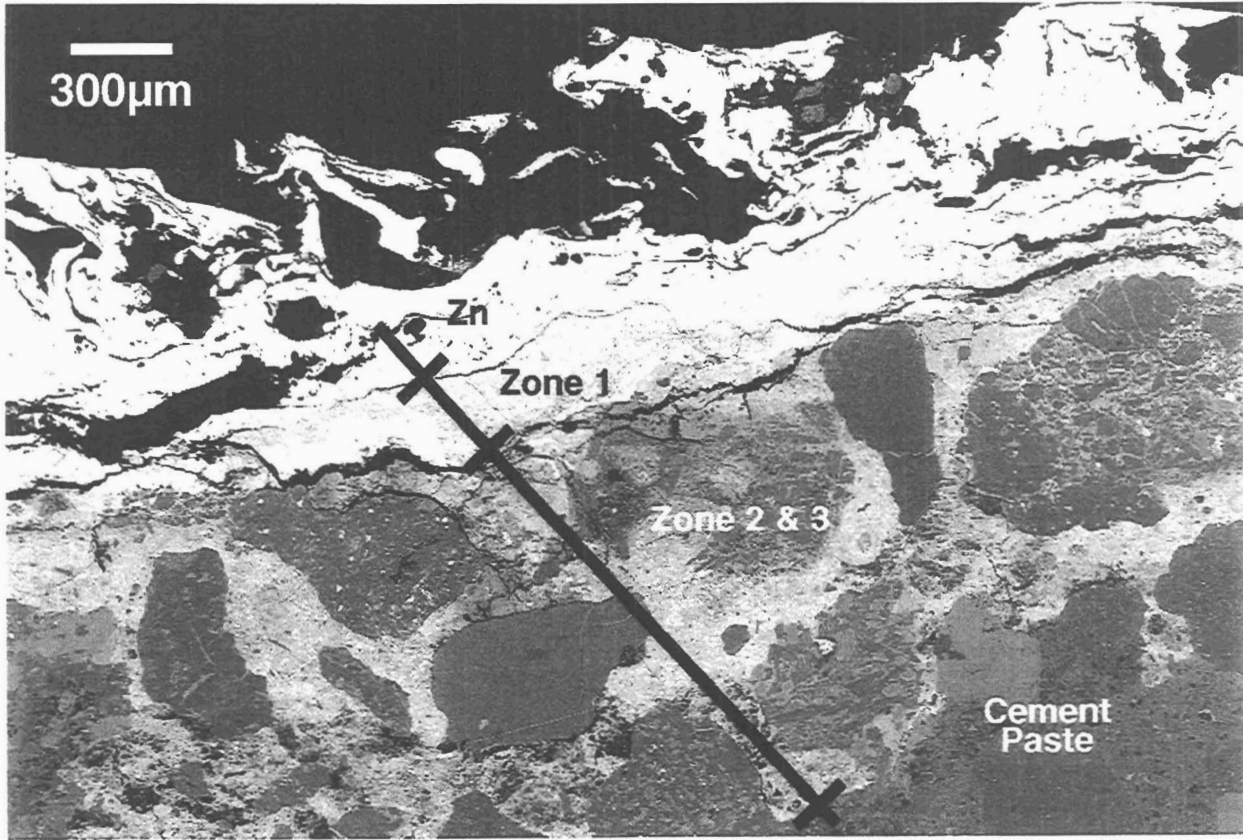
Fig. 1. Back-scattered ASEM micrograph of an electrochemically-aged zinc-concrete interface showing voids in the coating and failures along the interface. Reaction zones 1 and 2 are shown. Preheated with an effective aging time of 13.2 years.
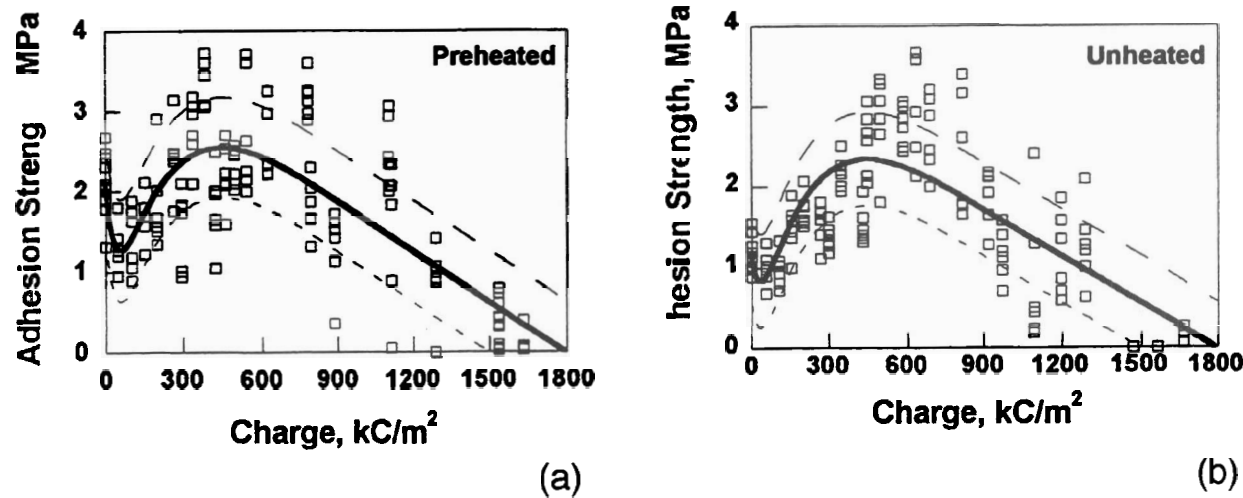

(a)

(b)

Fig. 2. Adhesion strength of electrochemically-aged arc-sprayed zinc on preheated (a) and unheated (b) concrete slabs as a function of aging charge. A multiplying factor of 0.0257 converts kC/m^2 to $A\text{-}h/ft^2$.
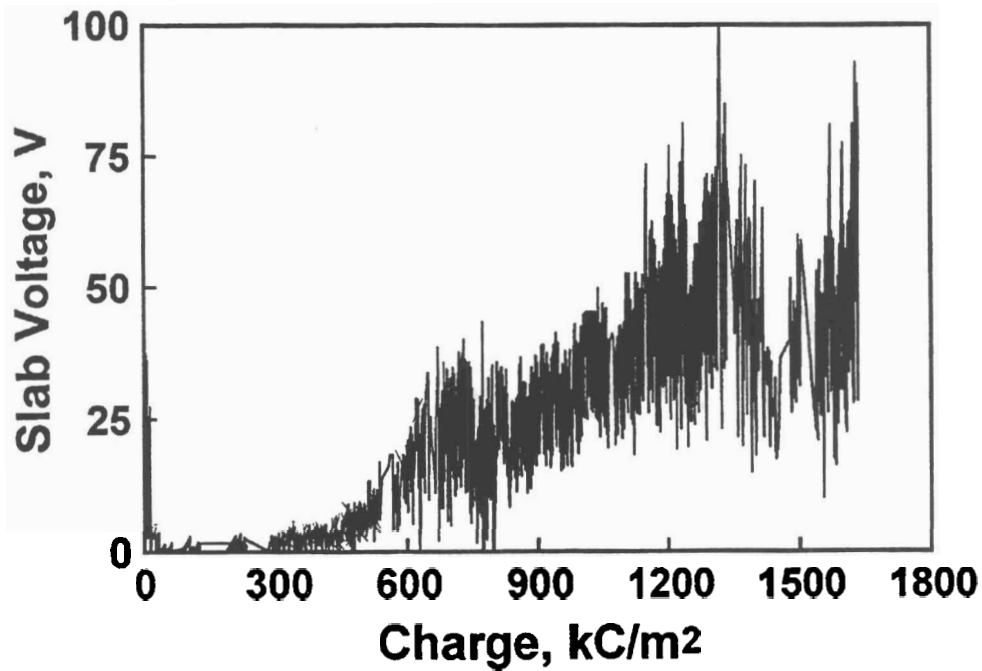
Fig. 3. Variation in voltage of a laboratory thermal-sprayed zinc ICCP system as a function of charge passed. A multiplying factor of 0.0257 converts kC/m^2 to $A\text{-}h/ft^2$.
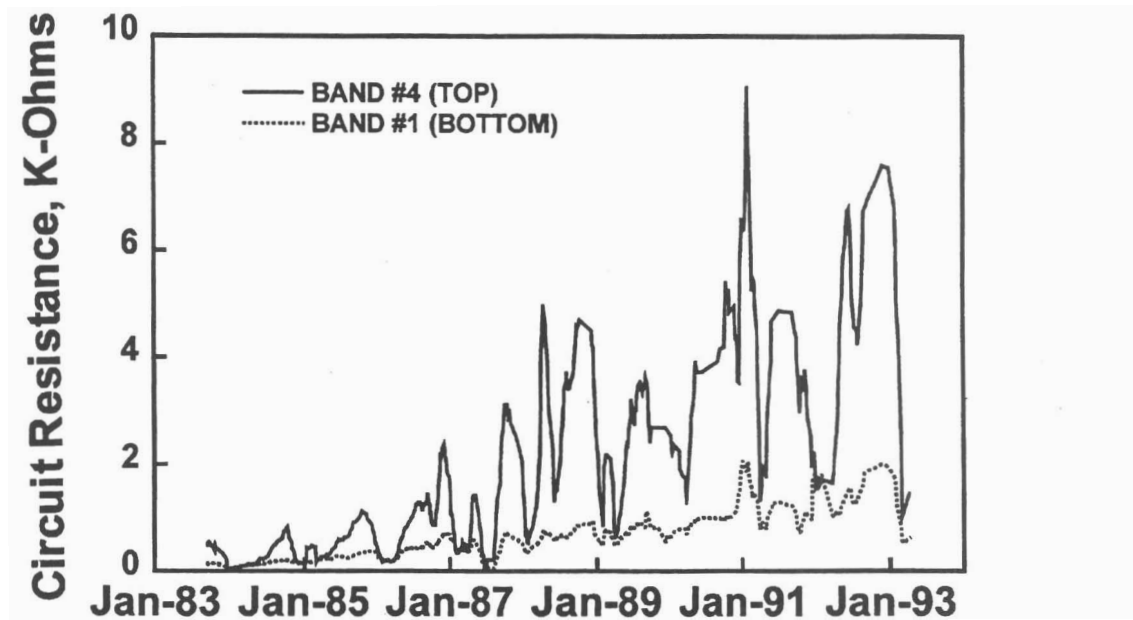
Fig. 4. Circuit resistance over 12 years of operation of the zinc ICCP system on pier 4 of the Richmond-San Rafael Bridge (CA). Band 4 is more sheltered to precipitation and wave action than band 1.
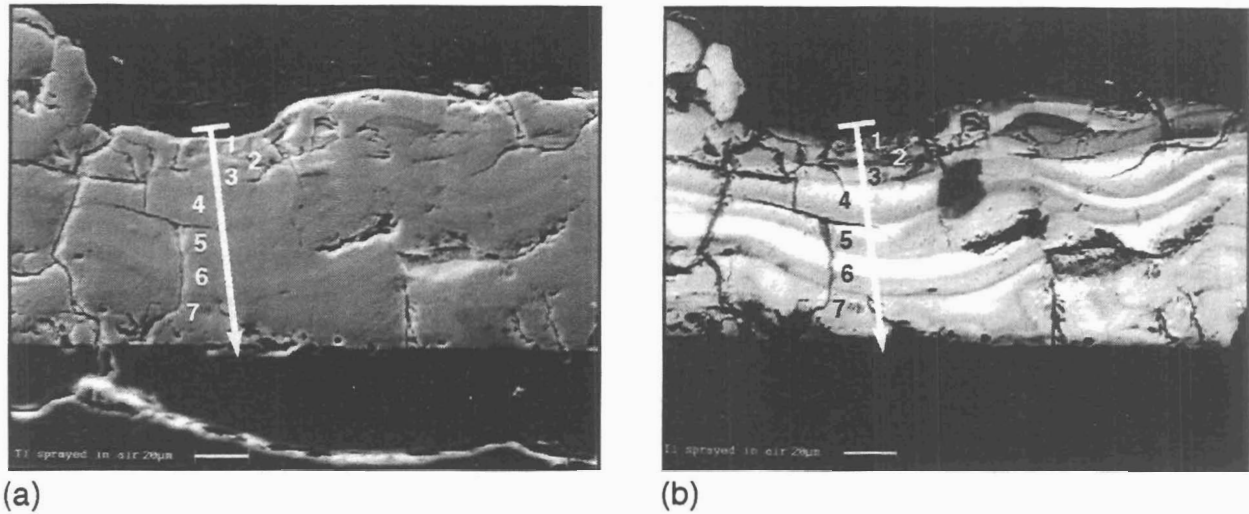
Fig. 5. Cross-section of thermal-sprayed Ti on pyrex glass: (a) SE image; (b) BE image. Arrow shows path of EMP traverse and the location of seven Ti gradient bands in the coating.
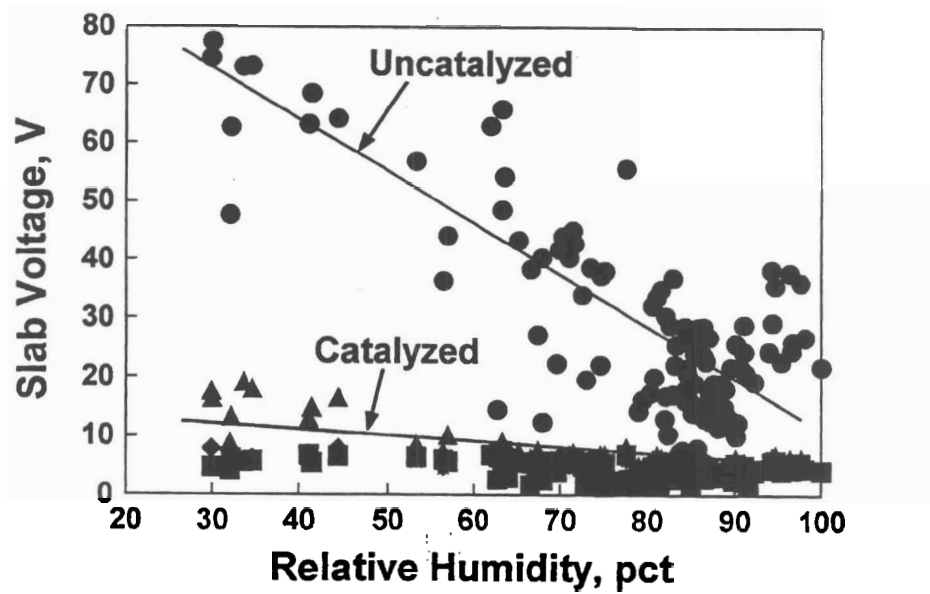

Fig. 6. Effect of humidity on voltage requirements during electrochemical aging of thermal-sprayed Ti in a laboratory ICCP system.
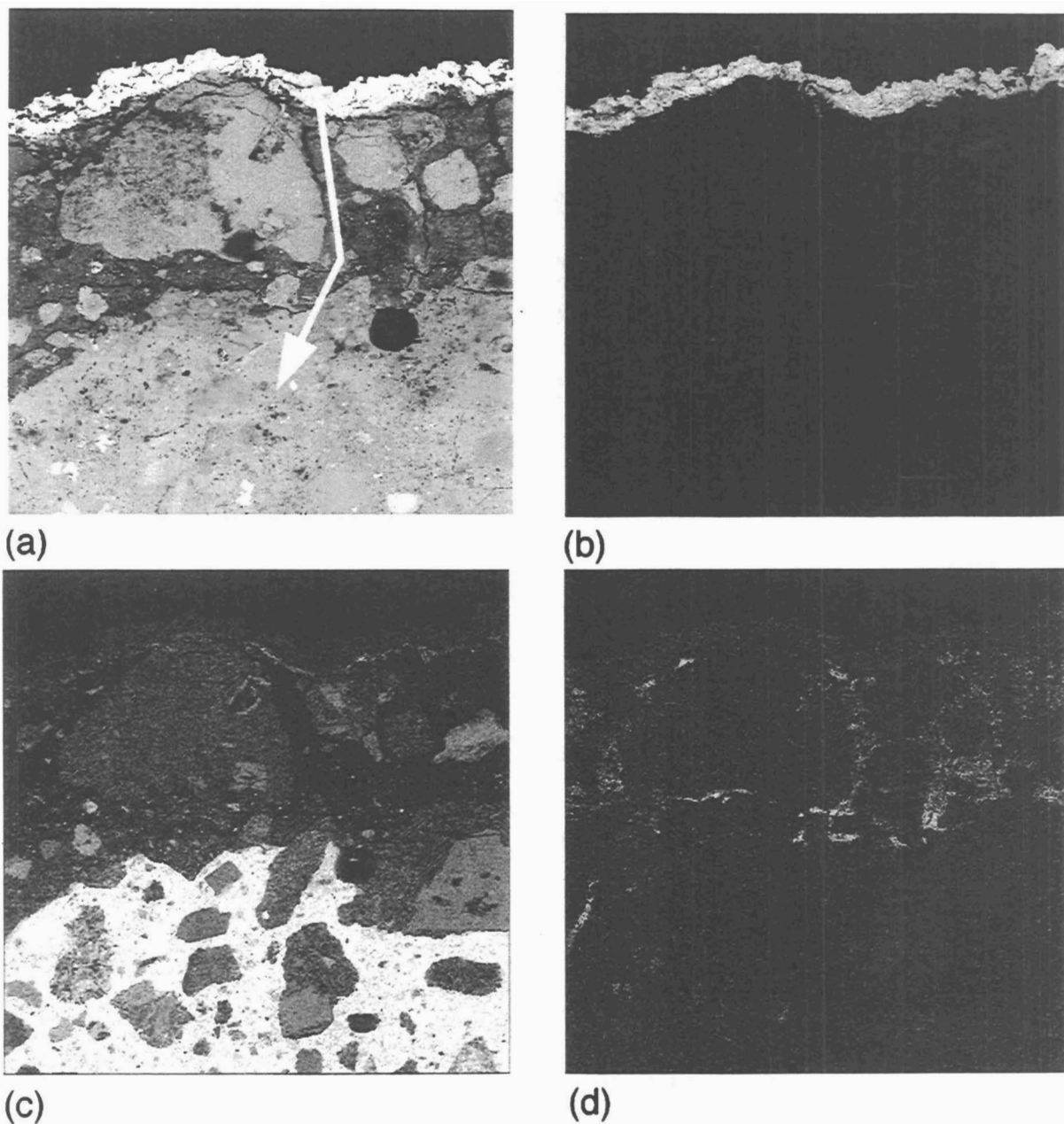
Fig. 7. Catalyzed thermal-sprayed Ti anode cross-section after electrochemical aging: (a) backscattered electron ASEM image; (b) Ti K_α x-ray map; (c) Ca K_α x-ray map; (d) Co K_α x-ray map.
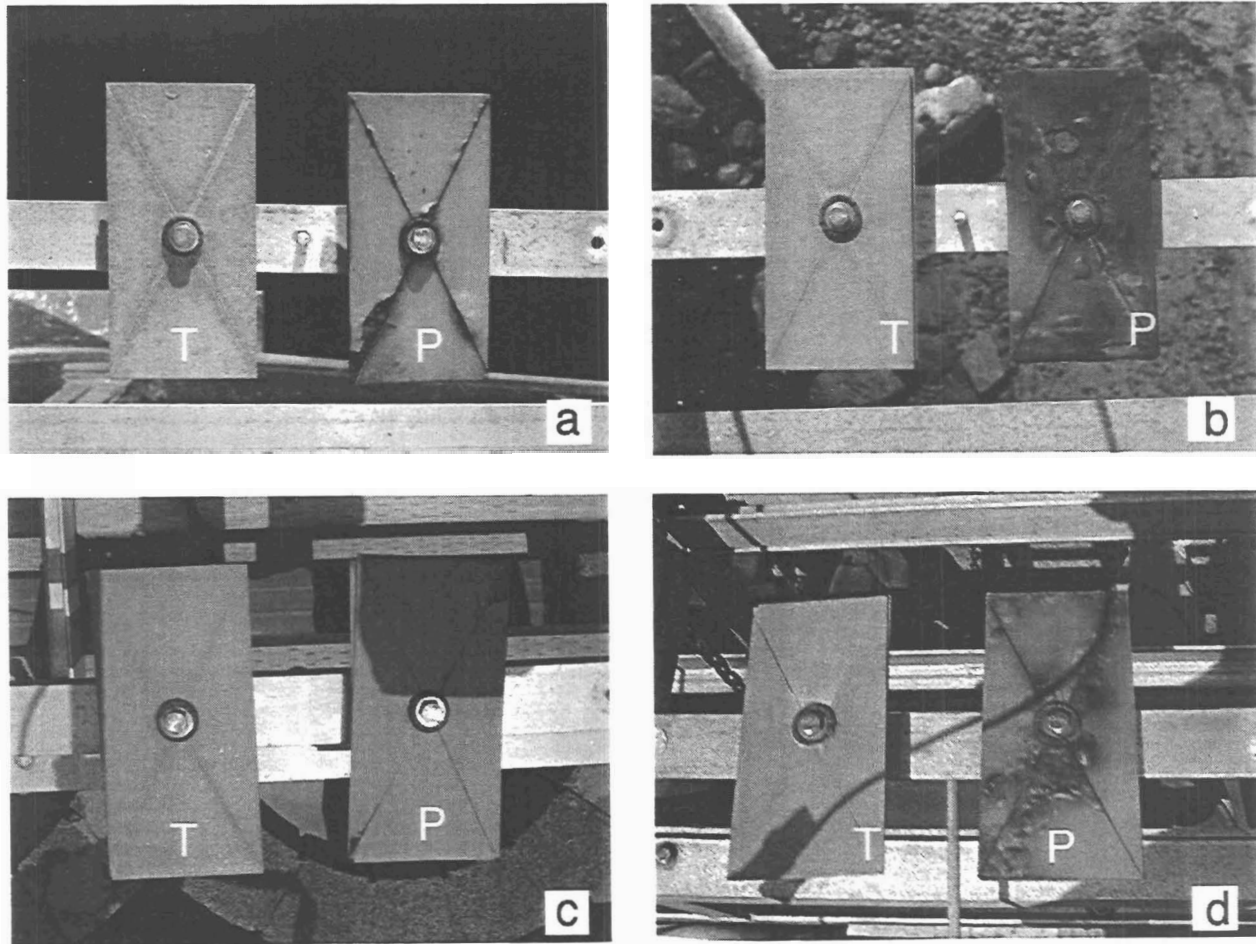
Fig. 8. Comparison of sealed thermal-sprayed Al coatings on mild steel (T) and three-coat moisture-cured urethane paint coatings on mild steel (P) in bold exposures. Photographs (a) and (c) are horizontal and vertical exposures from the Rogue River Bridge (OR). Photographs (b) and (d) are horizontal and vertical exposures from the Spencer Creek Bridge (OR).