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Sprayed Titanium Coatings for the Cathodic Protection of Reinforced Concrete

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Thermally sprayed titanium coatings were investigated in the laboratory as anodes for the cathodic protection of reinforced concrete. Three proprietary catalyst systems were used to activate the titanium anode coatings. Some experiments were conducted that applied the catalyst as a precoat on the metallizing wires; in other experiments, the catalyst solution was applied onto concrete blocks before or after arc spraying with titanium. The coated reinforced concrete blocks were powered at a constant current density and in a 95% relative humidity for more than 95 days. The driving voltages measured across the samples demonstrated that precoating the catalyst on the titanium wires had little effect on the driving voltage over the recorded lifetime. In other experiments, where the catalyst was directly applied to the surface of the reinforced concrete blocks, only the cobalt oxide catalyst significantly reduced the driving voltage requirements. The cobalt oxide reduced the driving voltages regardless of whether it was applied on the concrete blocks before or after arc spraying with titanium.

Keywords arc spraying, cathodic protection, concrete, infrastructure

Introduction

Reinforced concrete corrosion is a costly problem, particularly in coastal areas or in areas where extensive amounts of deicing salts are applied. One approach to reduce the rate of corrosion is cathodic protection. Cathodic protection is the mitigating reinforcement corrosion on several hundred bridges in the United States and Canada. Overlayed titanium anodes are increasingly becoming recommended because of their predicted long service life (greater than 30 years) and ease of installation on flat horizontal surfaces (Ref 1, 2). Possible anodes for substructures (Ref 3) include conductive coatings, titanium mesh anodes overlayed with shotcrete, metallized zinc, and more recently, metallized titanium.

Metallized titanium is an attractive anode candidate because it offers a much longer service life than conductive coatings (5 to 10 years) or metallized zinc (15 to 20 years). Also, it does not have potential delamination problems associated with the shotcrete overlays required to encapsulate the titanium mesh when applied on vertical and suspended walls of substructures. Finally, metallized titanium can be relatively easy to apply to existing substructures, while conventional embedded anodes require more cumbersome installation procedures.

Published research work on the metallized titanium anode remains limited. Bennett et al. reported in an earlier study (Ref 4) how thermal spray parameters such as gun speed, air pressure, and spray distance affected the properties of the titanium coating, that is, linear resistance. It is often believed that pure uncatalyzed titanium will not function as an impressed current anode because of the formation of a passivating oxide film under anodic polarization (Ref 5). Although metallized titanium can be used as an anode for concrete (Ref 6), it will be shown that the anodic oxygen evolution reaction is greatly facilitated by the application of a cobalt oxide catalyst.

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Experimental

Performances of the various catalyzed titanium coatings were monitored by powering reinforced concrete samples at a constant current density in a 95 ± 5% relative humidity. Twenty-four reinforced concrete samples were made with Type 10 (CSA A5) normal portland cement, admixed with 1% NaCl by mass of cement, and made with a water to cement ratio of 0.5. Samples were manufactured with a single level of two steel reinforcing bars, illustrated in Fig. 1. After curing the samples for 28 days at 100% relative humidity, the top surface of each concrete block

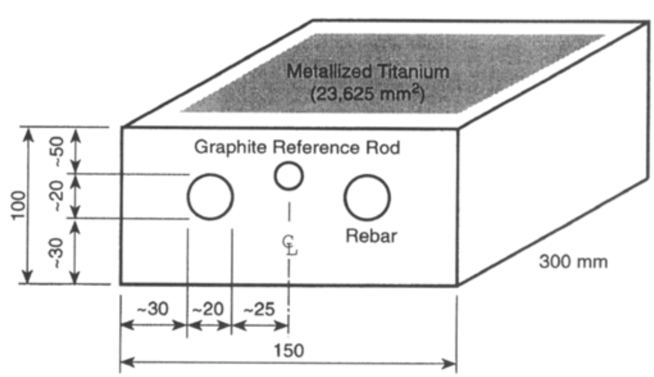

Fig.1 Schematic (dimensions in mm) of the concrete samples reinforced with two steel rebars and metallized with a titanium coating anode. The graphite pseudo-reference electrode centrally placed in the samples was not used in this experimental project.

was grit blasted with No. 40 silica sand and air dried for a few days. The grit blasting was sufficient to roughen the surface without exposing the aggregate in the concrete. Any dust or loose particles remaining on the surface after grit blasting were removed by blowing with compressed air. The surface of the concrete was preheated to 50 °C immediately prior to arc spraying to ensure adequate bond being obtained between the metallized titanium coating and the concrete substrate. All arc sprayings were performed at 620 kPa air pressure, 26.2 ± 0.5 volts arc voltage, 175 ± 15 amps arc current, and at a spray distance of 15 cm. The titanium was arc sprayed onto the concrete blocks using 1.5 mm pure titanium wires either as received or coated with a catalyst. The anode surface area metallized on each concrete block was 46 000 mm^2.

The 95 ± 5% relative humidity environment was achieved by placing the concrete block in sealed polyethylene containers which also contained small amounts of water. The containers were lined with weather stripping so that when the lids were closed a seal was formed allowing approximately 100% relative humidity to form. The blocks were then connected electrically so that the arc sprayed titanium surfaces were anodically polarized, and the rebars were polarized cathodically. The anodic current density applied at the titanium coating was 135 mA/m^2 except for blocks 23 and 24 which were subjected to 22 mA/m^2. The driving voltage for each block was measured by the connection of a voltmeter to the anode and cathode lead wires.

Several strategies were investigated for introducing the catalyst to the thermally sprayed titanium coating. One approach

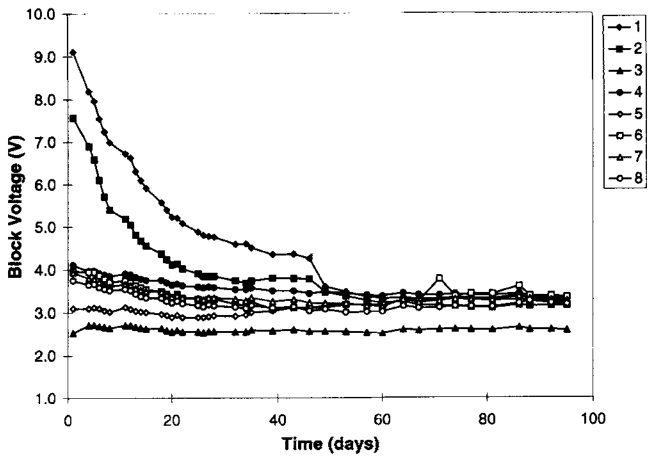

Fig. 2 Driving voltage versus time for blocks 1 to 8

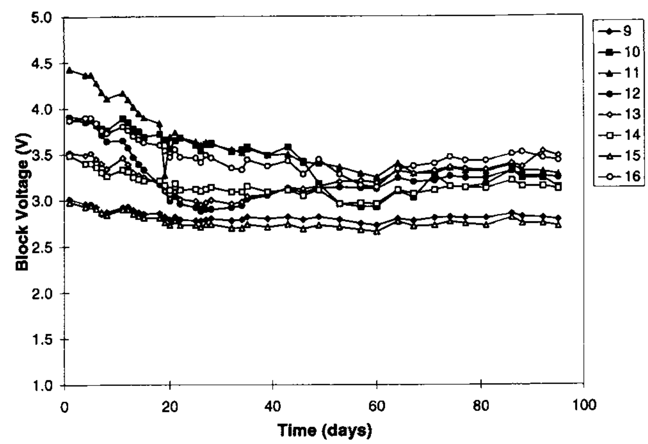

Fig. 3 Driving voltage versus time for blocks 9 to 16

Table 1 Sample preparation summary

Block No.	Catalyst type	Relative mass of catalyst precursor concentration	Catalyst application method	Additional activation method after application
1	Pt-Ir	1	AOB after ASTA	TDWF
2	Ru-Ti	1	AOB after ASTA	TDWF
3	Co-oxide	1	AOB after ASTA	TDWF
4	Pt-Ir	2	AEW before ASTA	none
5	Ru-Ti	3	AEW before ASTA	none
6	Co-oxide	1	AEW before ASTA	none
7	Pt-Ir	1	AOB before ASTA	TDWF before ASTA
8	Ru-Ti	1	AOB before ASTA	TDWF before ASTA
9	Co-oxide	1	AOB before ASTA	TDWF before ASTA
10	Pt-Ir	10	AEW before ASTA	none
11	Ru-Ti	6	AEW before ASTA	none
12	Co-oxide	2	AEW before ASTA	none
13	Pt-Ir	1	AOB before ASTA	none
14	Ru-Ti	1	AOB before ASTA	none
15	Co-oxide	1	AOB before ASTA	none
16	Pt-Ir	1	AW before ASTA	none
17	Ru-Ti	1	AW before ASTA	none
18	Ru	6	AW before ASTA	none
19	Pt-Ir	10	AOB before ASTA	TDWF before ASTA
20	Ru-Ti	3	AOB before ASTA	TDWF before ASTA
21	Co-oxide	2	AOB before ASTA	TDWF before ASTA
22	None—AST only on block	...	...	...
23	Co-oxide	1	AOB after ASTA	TDWF
24	None—AST only on block	...	...	...

Note: All samples powered at 135 mA/m^2 except blocks 23 and 24 which were powered at 22 mA/m^2. AOB, applied to concrete block. ASTA, arc sprayed titanium application. TDWF, thermally decomposed with flame. AEW, applied to etched titanium wire. AW, applied to titanium wire. AST, arc sprayed titanium was to first apply the catalyst to the prepared concrete surface, followed by arc spraying the titanium coating on top of the catalyst. A second approach was to co-spray the catalyst together with the titanium wire. This involves precoating the titanium wires with a catalyst precursor. The third approach was to apply the catalyst solution on the concrete surface after it had been metallized with titanium. Three different catalysts were investigated, that is, Pt-Ir, Ru-Ti, and Co. The procedures employed to catalyze the 24 concrete blocks are summarized in Table 1.

Results and Discussion

The driving voltages across each of the samples were recorded for more than 95 days, as presented in Fig. 2 to 4. From the examination of the driving voltage data in Fig. 2 for blocks 1, 2, and 3—on which the titanium was first metallized, followed by the application of the catalyst and its thermal decomposition with a hot flame—it can be concluded that cobalt oxide (block 3) is the best catalyst. In fact, cobalt is the best catalyst when comparing the data from all the samples in Fig. 2 to 4. However, the results do not necessarily predict which catalyst system will exhibit the longest service lifetime.

Precoating the metallizing titanium wires with a catalyst precursor, as was done for blocks 4, 5, 6, and 12, did not provide any noticeable reduction in driving voltage. The driving voltages were not lowered when the catalyst was co-sprayed with the titanium wires most likely because the majority of the catalyst is locked inside the titanium matrix and will be unavailable for the anodic reaction, which takes place only at the titanium-concrete interface. Although applying a catalyst coating on the metallizing wires is relatively simple, the resulting metallizing wires are significantly more difficult to arc spray. Blocks 1 to 3 were appreciably heated with a hot flame to thermally decompose the catalyst precursors. This could explain why the driving voltages for blocks 1 and 2 were initially high. The hot flame used to decompose the catalyst possibly dried the concrete which later regained its moisture content after exposure to approximately 100% relative humidity.

In comparing the driving voltage for the samples differing in the relative concentrations of the catalyst precursors used, a conclusion can be drawn that the increased concentrations for all of

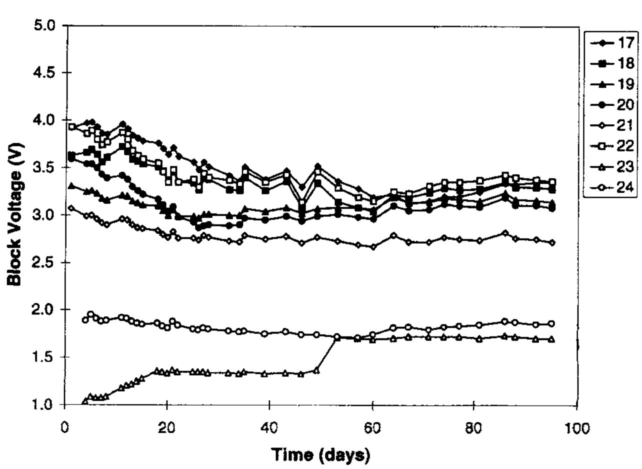

Fig. 4 Driving voltage versus time for blocks 17 to 24

the catalysts had no significant effect on lowering the driving voltages. This can be seen from Fig. 2 to 4 in comparing the voltages for the pairs of the Pt-Ir catalyst (blocks 7 and 19), the Ru-Ti catalyst (blocks 8 and 20), and the Co-oxide catalyst (blocks 9 and 21). Presumably, at catalyst concentrations lower than those for this study, there would be an increase in the driving voltages.

Samples activated with the cobalt catalyst and titanium blanks were compared in Fig. 2 to 4 for two anodic current densities, that is, 135 and 22 mA/m^2. Blocks 22 and 24 correspond to catalyst free samples polarized respectively at 135 and 22 mA/m^2 (Table 1). Blocks 3 and 23 were polarized respectively at 135 and 22 mA/m^2, and both consist of samples on which the cobalt catalyst was applied on top of the metallized titanium followed by thermal decomposition with a hot flame. Blocks 9 and 15 were both catalyzed with cobalt and polarized at the higher current density. For both of these blocks, the catalyst was applied to the concrete prior to the thermal spray of the titanium coating, with the exception of no thermal treatment of the catalyst for block 15. Results show that the cobalt catalyst reduces the driving voltage requirements for both applied current densities. As expected, the driving voltage directly varies with the applied current density. From the data presented in Fig. 2 to 4, no thermal treatment is required to activate the cobalt catalyst directly applied on the concrete block if the blocks are arc sprayed with the titanium after the catalyst application. The heat from the arc sprayed titanium facilitated thermal decomposition of the catalyst.

Conclusions

- Metallized titanium samples catalyzed with cobalt oxide significantly lower driving voltages and were required to polarize the steel reinforcement under constant current.
- In comparison to the uncatalyzed samples, only a small improvement was obtained by catalyzing with platinum/iridium oxide or with ruthenium/titanium oxide.
- Co-spraying the catalyst by arc spraying catalyst precoated titanium wires did not induce any reduction in the driving voltages.
- There was no difference in current/voltage characteristics whether the catalyst was applied on the concrete prior to or after the arc spraying with titanium.
- Results indicate that further thermal treatment of the cobalt oxide catalyst is unnecessary for lowering the driving voltage requirements if the arc-sprayed titanium is applied after the cobalt oxide catalyst.

Acknowledgments

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