

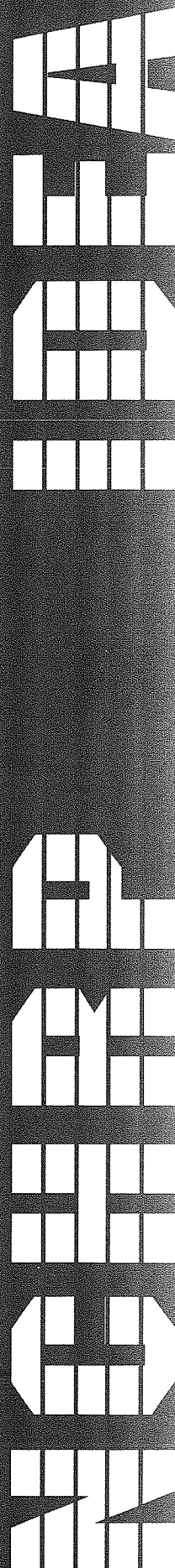
TRANSPORTATION RESEARCH BOARD
NATIONAL RESEARCH COUNCIL

IDEA *Innovations Deserving
Exploratory Analysis Project*

NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM



Report of Investigation



IDEA PROJECT FINAL REPORT
Contract NCHRP-93-ID010

IDEA Program
Transportation Research Board
National Research Council

August 16, 1995

LOW-COST, CORROSION-RESISTANT
COATINGS FOR STEEL REBARS
AND COMPONENTS

Angel Sanjurjo, Palitha Jayaweera,
David Lowe, and Kai Lau
SRI International

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EXECUTIVE SUMMARY

During this project we demonstrated that corrosion resistant coatings of various metals and alloys such as Si, Ti, Ni, and Ti-Ni can be formed on steel rebars by fluidized bed reactor chemical vapor deposition (FBR-CVD), paint-and-heat, or FBR-plasma spray techniques. The paint-and-heat metallization and FBR-plasma spray are innovative powder coating techniques that can be applied easily and economically on new components as well as on existing steel structures, such as bridges. Because the powder coatings are not sacrificial, they will provide much superior corrosion protection for a long time.

FBR-CVD coatings are generally thin and compact, and they provide excellent corrosion resistance. However, throughput (rate of production) and the chemical complexity of the process are major technical barriers for commercialization of the technique. Metallic deposition on rebars can also be achieved by spraying or painting of metal powders coated in a fluidized bed reactor or a modified rotary kiln. This approach simplifies the deposition process at the rebar coating plant and removes most of the technical barriers to commercialization. The complex powder coating chemistry can be performed by specialized powder manufacturers. We demonstrated this innovative concept with paint-and-heat metallization and plasma spray techniques. Paint-and-heat and plasma spray using metal powders coated in a fluidized bed reactor produced fairly thick metallic coatings resistant to chloride corrosion.

In the paint-and-heat technique, a coated metal powder mixture was painted on the rebar from a slurry followed by flash heating to set the coating. Adherent coatings on steel rebars can be prepared by using proper combinations of metals and fluxes. In the plasma spray technique, FBR-CVD coated metal powders were sprayed on the rebar to form a thick adherent metallic coating. When the coated powder was sprayed through the high temperature flame, powder was melted to form alloys *in situ* and deposited on the rebar. An extremely corrosion resistant alloy layer can be formed on the rebar using an appropriate base metal and coating metal(s) combination. We demonstrated the feasibility of these powder coating concepts by depositing various metal combinations on 1-m-long (3 ft) rebars. The paint-and-heat and plasma spray techniques can be applied on new and existing steel components and structures and can be easily scaled-up to meet the industrial demand.

IDEA PRODUCT

During this project we demonstrated that corrosion resistant coatings of various metals and alloys such as Si, Ti, Ni, and Ti-Ni can be formed on steel rebars by fluidized bed reactor chemical vapor deposition (FBR-CVD), paint-and-heat, or FBR-plasma spray techniques. The paint-and-heat metallization and FBR-plasma spray are innovative powder coating techniques that can be applied easily and economically on new components as well as on existing steel structures, such as bridges. Because the powder coatings are not sacrificial, they will provide much superior corrosion protection for a long time.

CONCEPT AND INNOVATION

Corrosion of steel rebars used for reinforced concrete structures, such as bridges, can be accelerated by a variety of agents. For example, Cl^- ions (arising from deicing salts or marine environments) diffuse through the concrete and destroy the passive oxide layer on the rebar surface, leading to hostile corrosion reactions. The stresses created by the increase in volume due to the formation of corrosion products can lead to cracking of the concrete followed by delamination and spalling. The corrosion will continue and the damage will spread unless protective steps are taken. However, the protective techniques have only a limited effectiveness if the deterioration has progressed beyond certain limits. Rehabilitation involves removing chloride contaminated or deteriorated concrete, cleaning the corroded steel, and repairing the concrete. Rehabilitation is extremely expensive, labor intensive, time consuming, and disruptive to the flow of traffic.

Because of the inherent problems associated with rebar corrosion resulting from Cl^- ion ingress into concrete, it is extremely important to explore methods of rebar protection before the corrosion sets in. Among these methods, coating of rebars with fusion-bonded epoxies and galvanized coatings has resulted in considerable success. Fusion-bonded epoxy coats, although twice as expensive as the conventional gray steel bars, have shown excellent corrosion resistance, except in subtropical marine environments such as the Florida Keys. Galvanized bars show good corrosion resistance but have the disadvantage that the zinc coating gradually corrodes as a result of its action as a sacrificial anode. Thus, in the long term, galvanized bars have only a limited advantage over the simple gray steel bars.

Metallic coatings have been proved to reduce the rate of corrosion of steel in various environments. In this NCHRP-IDEA-funded research program, SRI studied novel approaches for coating steel bars with various corrosion protective metals and alloys such as Si, Ti, Ti-Ni, and Sn for large-scale concrete reinforcement applications. We investigated three approaches for coating rebars with metals and alloys. The first approach was direct chemical vapor deposition of metals onto the rebar in a fluidized bed reactor (FBR-CVD). We demonstrated the feasibility of this approach with small rebar coupons in a previous NCHRP funded project. The rebar was immersed in Si and Ti powder, and small amounts of hydrogen and hydrogen chloride gases were added to an inert gas such as argon, which fluidized the powder bed. The metals were deposited on the rebar through subhalide chemistry of Si and/or Ti as explained in detail in our previous NCHRP-IDEA report.

In the current project, we scaled-up our reactors to coat rebars up to 1 m (3 feet) long. However, obtaining the highest deposition rates and best coatings of Si and Ti directly on the rebars by FBR-CVD, requires careful control of fluidized bed reactor chemistry. Also, the rate of deposition depends strongly on the trace metals such as Mn present in the rebar. The trace metal composition of rebars varies widely depending on the original source of steel. In addition, we found that technology transfer to industry would be more difficult than anticipated.

After consultation with our industrial partner, Mr. Reed of Western Coating, Inc., and approval from the TRB project manager, we modified our approach by minimizing the chemistry to be done in the coating plant to satisfy industrial requirements. This effort resulted in the development of two simple techniques for depositing corrosion resistant metallic alloy coatings on steel rebars and components: paint-and-heat metallization, and fluidized bed reactor-plasma spray technique. In both of these coating approaches, we divided the rebar coating process into two stages. We decoupled the complex chemistry of the fluidized bed reactor from the application of the coating on the rebar. First, a low-cost metal powder such as Fe was coated in a fluidized bed reactor with Si, Ti, Ni, and/or Cu to obtain the required alloy composition and to avoid oxidation when heated in air. In the paint-and-heat metallization, the coated powder was mixed with a low melting metal (e.g., Sn) and applied on the rebar by spraying or painting a slurry followed by flash heating the surface. High melting metals such as Ti, Ni, and Fe have substantial solubility in Sn and thus form a corrosion resistant alloys on the rebar surface by dissolution and diffusion upon surface heating. The coated metal powders were

also applied on the rebar by the plasma spray technique. When the coated powders were thermally sprayed, alloys were formed during the spraying process and deposited on the rebar to form a corrosion resistant, metallic alloy coating.

These coating techniques combine the low cost of pack metallization with the high heat and mass transfer of a fluidized bed reactor. The paint-and-heat and FBR-plasma spray techniques may satisfy low cost and low temperature requirements to deposit protective and durable inorganic coatings on steel rebars. The process can be scaled up easily and economically. The metal powders can be prepared in large scale by experienced powder manufacturers and shipped to the coating plant where the powders are applied on the rebars by paint-and-heat or plasma spray techniques. These coating techniques can also be used easily to apply corrosion protective metallic coatings on existing steel structures. Preliminary findings of the application of metallic coatings on rebars by paint-and-heat and FBR-plasma spray techniques are discussed in this report.

INVESTIGATION

Radio frequency (RF) induction heated reactors capable of coating rebars up to 1 m long (3 feet) were designed and built to demonstrate the feasibility of scale-up. Corrosion resistant coatings were formed on steel rebars by fluidized bed reactor chemical vapor deposition (FBR-CVD), paint-and-heat metallization, and FBR-plasma spray techniques. The composition and the microstructure of the coatings were determined using x-ray and electron microscopic techniques. The corrosion resistance of coated rebars was determined by salt spray and AC impedance techniques.

RF REACTOR DESIGNS

We designed and constructed two reactors for coating 1-m-long (3 feet) rebar samples. In the first design shown in Figure 1, rebar is fed horizontally into the reactor where it is heated directly by an induction coil powered by radio frequency at 450 kHz. The power supply is rated at 25 kVA, but we are using less than 5% of the available power to heat the rebar up to 600°C in a few minutes. A quartz boat is loaded with Cu-coated Si and/or Ti particles. Argon with about 1% to 5% by volume of an HCl-H₂ mixture is used to transfer the Si and Ti to the steel rebar, which is fed continuously while being rotated over the 25-cm-long (10 inch) boat. The rebar is contained in a long quartz reactor that consists of two stations: the feed station and the reaction station. Although our laboratory reactor was limited to rebars up to 3 ft long, rebars of any length can be coated in this reactor with simple modifications to the rebar feeding mechanism so that rebars exit from the other end of the reactor tube.

In the second design shown in Figure 2, the reactor and rebar mounts were arranged vertically. This reactor was used mainly for paint-and-heat metallization. A 15-cm (6-inch) graphite tube, placed in the center of the reactor, is heated by an induction coil powered by radio frequency at 450 kHz. The rebar is indirectly heated by the radiation from the graphite tube. The system is flushed with a small amount of Ar and H₂ gas to provide an inert to slightly reducing atmosphere. This arrangement promotes rapid surface heating of the rebar and thus minimizes changes to the bulk microstructure. Rebars, up to 1-m long (3 ft. in length) can be coated in this vertical reactor.

COATING TECHNIQUES

We investigated three approaches for forming a metal coating on the rebar surface. First, we used the FBR-CVD approach to coat rebar samples. The second approach was painting the rebar with coated or as-received metal powder slurries followed by heating in the RF reactor. The third approach was plasma spraying of coated metal powders to form alloy coatings on the rebar surface. These techniques are described in detail below. All the samples were sand-blasted and degreased before coating.

Fluidized Bed Chemical Vapor Deposition

The metal powders (Si and Ti) were fluidized by passing Ar with about 1% to 5% of HCl-H₂ through the powder bed. Si and Ti were transferred onto the rebar through subhalide chemistry as previously described. (1, 2) Small coupons (2 to 2.5 cm) were coated in a small vertical reactor, and long rebar samples (0.15 to 1 m) were coated in the horizontal reactor. The samples were either immersed within or held above the bed during coating.

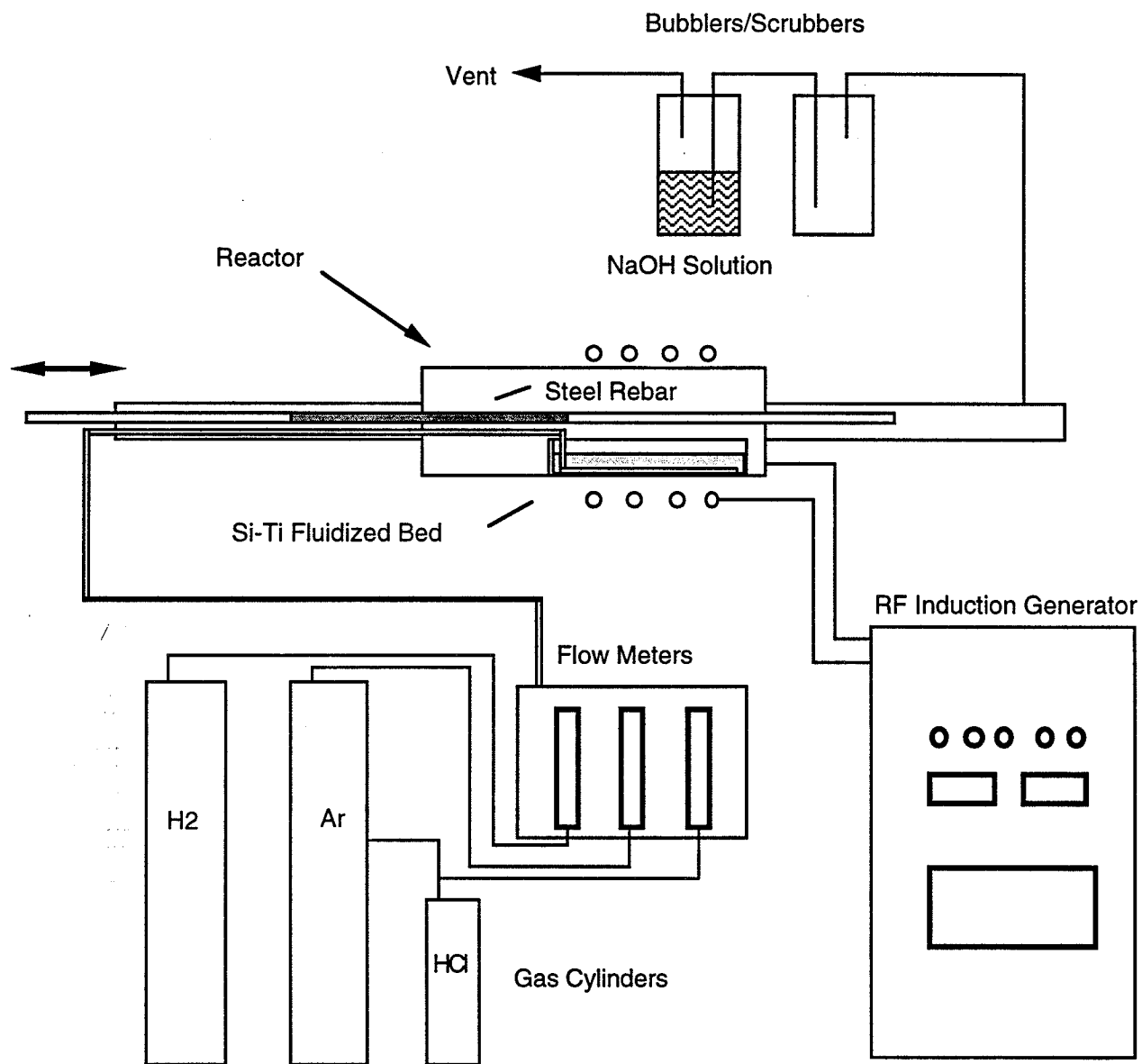


Figure 1. Horizontal reactor and associated equipment.

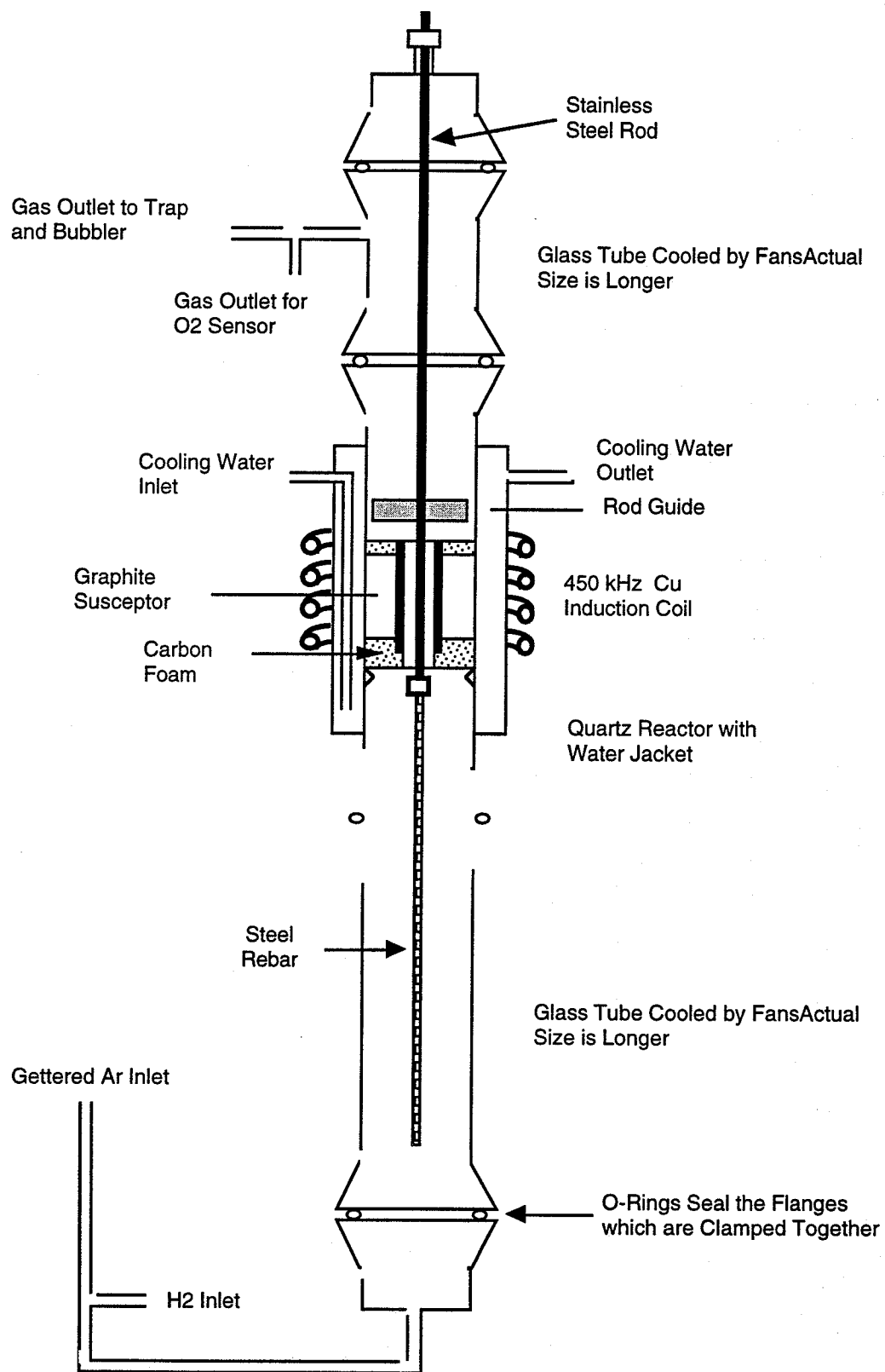


Figure 2. Vertical reactor for coating steel rebars.

The fluidized bed was also used to coat metal powders to form microcomposites. Powders such as Ni, Fe, FeSi, or Si were coated with a more reactive and corrosion resistant metal such as Si or Ti and then with Cu, Ni, or Sn on the surface to prevent oxidation. These microcomposite powders were used with the paint-and-heat approach described below.

Paint-and-Heat Metallization

The reactive metal powders such as Si and Ti were first coated with a more noble metal such as Cu or Ni in a fluidized bed reactor to prevent surface oxidation when exposed to air. These metal powders were mixed with a low melting metal such as Sn and a suitable flux in appropriate amounts, then dispersed in alcohol or water to form a thick slurry. The rebar samples were painted with a premixed metal powder slurry and heated with a heat lamp to dry the paint to form a thick, somewhat adherent powder coating. The painted rebar samples were placed inside the vertical reactor and heated slowly to degas and to allow the flux to clean the metal particles and the molten metal (Sn). The surface of the sample was then quickly heated to a high temperature to diffuse and/or melt the coating components into/onto the steel rebar. Cooling took place inside the reactor under a low flow of Ar. The sample was taken out and the excess powder/oxide/etc. was removed with a plastic-bristle brush under a stream of water. Rebar samples 15 cm long (6 inch) were heated in the vertical reactor to try various coating compositions. The paint-and-heat approach was attempted with as-received metal and alloy powders. Various metal and alloy powder compositions and fluxes were used to form coatings on rebar samples.

Plasma Spray Coatings

We used as-received metal and alloy powders and FBR-CVD coated metal powders for plasma spray coatings. Metal powders were thermally sprayed on rebars to form thick adherent coatings. The bond strength and density of the coating were maximized through optimization of the process. Rebars up to 1 m (3 ft) long were coated with various combinations of metal and alloy powders.

SURFACE AND CROSS-SECTION ANALYSIS

The coated rebar samples were first polished with a series of SiC grit paper then etched with a 1% to 5% solution of HNO₃ in ethanol before being examined with an optical microscope. The coating surface and cross-section of the coating were further examined by scanning electron microscopy (SEM). The metal composition of the coating was obtained by energy dispersive X-ray analysis (EDAX).

CORROSION RESISTANCE TESTS

Salt Spray Test

Selected uncoated and coated rebar coupons were sprayed with 5% sodium chloride solution and allowed to dry in air. The coupons were visually inspected for corrosion and photographed. This process was repeated daily for a week.

AC Impedance Test

AC impedance measurements of selected rebar coupons were performed using a PAR 173 potentiostat and a Solartron 1260 gain phase analyzer. The electrochemical cell consists of a platinum counter electrode, a saturated calomel reference electrode, and a 16-mm-long rebar coupon as the test electrode. The ends of the rebar coupon and the electrical contact wire exposed to the electrolyte were coated with epoxy to avoid contribution from these areas to the measured impedance. The test specimens were left in the electrolyte (unbuffered 5% sodium chloride solution) for 15-20 minutes to reach a stable corrosion potential before starting impedance measurements. The AC frequency scan was performed at the corrosion potential from 0.01 Hz to 10 kHz with a 10-mV perturbation amplitude.

Scratch and Damage Tests

The ductility of the coating was checked by scratching it with a knife and by striking with a hard object (hammer). Corrosion of the exposed surface under salt spray conditions was observed visually. Further tests such as 90° bend test were performed with coated rebar samples to test the integrity of the coating under stress. Detailed testing for field handling were precluded due to time and funding constraints.

RESULTS AND DISCUSSION

REACTOR DESIGNS

Horizontal Reactor

Although the horizontal reactor design is more appealing in the industrial scale, it is difficult to work with in the laboratory because of the complexity of the rebar feeder system. Long rebars tend to sag when heated without supporting rollers. Also it was very difficult to maintain a fluidized powder bed in the horizontal reactor with our present powder container, resulting in an uneven coating. The powder container and the fluidizing gas flow nozzle must be redesigned to maintain a sufficiently fluidized powder bed. We did not pursue this redesign due to time and funding constraints.

Vertical Reactor

The vertical design was more favorable for laboratory use and was put together with a minimal cost. Rebars up to 1 m (3 feet) long could be coated in our vertical reactor. The heated zone of the reactor was about 15 cm (6 inches) long. A hollow graphite cylinder in the quartz tube was heated by an RF source. The radiant heat from the graphite cylinder surrounding the rebar heated the surface of the rebar. This arrangement minimized the bulk heating of the rebar compared with direct induction heating. Alternatively, a high frequency RF source could be used to reduce the induction penetration depth and heat the rebar surface directly. This arrangement may be more attractive in large scale applications since the throughput can be increased dramatically.

In the vertical reactor, rebars were manually fed in 15-cm (6-inch) steps to perform the coating process. Although this process was time consuming and tedious, it satisfied our needs to demonstrate the concept. In an industrial environment, the complete process can be easily automated to coat rebars of any length. The vertical reactor was used mainly for paint-and-heat experiments. For direct fluidized bed CVD, the graphite cylinder was replaced with the fluidized powder bed.

COATING TECHNIQUES

Fluidized Bed CVD

The CVD coatings that we obtained from our fluidized bed reactors were compact and adherent. Figure 3 shows a representative scanning electron microscopy (SEM) photograph of an FBR-CVD silicon-titanium coating on a rebar specimen. The sample was coated at 650°C, followed by surface nitridation. The rebar was cut, polished, and etched to reveal the bulk steel and coating interface. Silicon diffused into bulk whereas titanium stayed near the surface. Because the bulk rebar etched faster than the coating, it is lower in the SEM picture of the cross section. The average coating thickness (including the diffusion layer) was about 40 μm (1.6 mil). The elemental analysis about 5 μm (0.2 mil) below the surface revealed the metal composition to be 7% Cu, 14% Ti, 16% Nb, 17% Si, and 46% Fe. In this case Nb was also present in the powder bed. The bulk composition of the rebar was 3% Si, 4% Mn, and 93% Fe.

Table 1. Selected 15-cm Rebar Samples

Experiment No.	Category	Paint Solids	Gas Flow	Surface Heating Conditions	Observations	Appearance	Microstructure	Coating Thickness, μm
1	Ti, Si, Sn, and flux	1.0 g Ti 3.0 g Si 1.0 g Sn 4.0 g NH_4Cl ID No. 7	0.8 L/min Ar 0.5 L/min H_2 1.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	All powder came off but looks better than previous samples; surface diffusion layer	Metallic	Some coarsening near surface	10 to 20
2	Ti, Si, Sn, and flux	1.0 g Ti 3.0 g Si 1.0 g Sn 1.0 g NH_4Cl ID No. 8	0.8 L/min Ar 0.5 L/min H_2 1.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Same as previous but some powder adhered to the rebar; doesn't rust in air; surface diffusion layer	Matte gray	Some coarsening near surface	10 to 20
3	Ni, Ti, Si, Sn, and flux	2.0 g Ni 1.0 g Ti 1.0 g Si 6.0 g Sn 0.05 g NH_4Cl ID No. 12	0.8 L/min Ar 0.5 L/min H_2 3.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Crust that can be scratched off but also thick base layer	Light gray metallic crust with darker base layer	Unchanged; Sn melt with alloyed grains	60
4	Ni, Ti, Sn, and flux	1.0 g Ti/Ni (70/30) 1.0 g Sn 0.3 g CuCl_2 ID No. 28	0.1 L/min Ar 1.7 L/min H_2 5.3 cm/s	Degas for 5 min at 400°C then heat for 3 min at 600°C	Crust well stuck but easily scratched through; some rust after salt dip	Rough thin metallic crust	Unchanged; coating is uniform, dense, continuous	5 to 10
5	Ni, Ti, Sn, and flux	1.0 g Ti/Ni (70/30) 1.0 g Sn 0.1 g NH_4Cl ID No. 11	0.8 L/min Ar 0.5 L/min H_2 3.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Thick crust and rough base layer coating; no rust in water, minor rust in salt dip after sandblasting, scratching, deforming	Metallic with dark blue patches	Some coarsening near surface; coating is uniform, dense, continuous	20 to 30
6	Ni, Ti, and flux	1.0 g Ti/Ni (70/30) 0.5 g $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$ ID No. 20A	0.8 L/min Ar 0.5 L/min H_2 3.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Smooth melted side and rough melted side; no powder came off; can't be scratched or broken off from rebar; no rust from salt dips; definitely best in series	Bright metallic even after salt dip	Some coarsening near surface; some areas have melted crust while others have porous crust and thin coating	5 to 500 (depending on area)

Table 1. Selected 15-cm Rebar Samples (Concluded)

Experiment No.	Category	Paint Solids	Gas Flow	Surface Heating Conditions	Observations	Appearance	Microstructure	Coating Thickness, μm
7	FBR, Sn, and flux	1.0 g FBR Ni-Ti-Si-Cu 2.5 g Sn 0.8 g $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$ 1.7 g Microbraz ID No. 23	0.1 L/min Ar 1.7 L/min H_2 5.3 cm/s	Degas for 5 min at 400°C then heat for 3 min at 600°C	Thick crust hard to scratch off; only minor rust after several salt dips	Dark gray crust over metallic base	Unchanged; coating is uniform, dense, continuous	20 to 30
8	FBR, Sn, and flux	1.0 g FBR Ni-Ti-Si-Cu 1.0 g Sn 0.05 g NH_4Cl All-state flux ID No. 31	0.1 L/min Ar 1.7 L/min H_2 5.3 cm/s	Degas for 5 min at 400°C then heat for 3 min at 600°C	Coating can't be scratched or broken off and doesn't rust in air or water	Thick bright metallic rough coating	Unchanged; Sn melt with a few fbr particles inside	10 to 20
9	Hastelloy, Sn, and flux	0.5 g Ni 2.0 g Co 1.0 g Cr 0.2 g Mo 0.1 g W 4.0 g Sn 0.05 g NH_4Cl ID No. 14	0.8 L/min Ar 0.5 L/min H_2 3.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Powdery crust easily removed with wire brush	Shiny gray	Unchanged; Sn melt on top alloyed grains near interface	20 to 40
10	Hastelloy, Sn, and flux	2.5 g Ni 0.1 g Co 1.0 g Cr 0.5 g Mo 0.2 g W 0.2 g Ti 0.05 g NH_4Cl Surface Layer: 5.0 g Sn 0.05 g NH_4Cl ID No. 16	0.8 L/min Ar 0.5 L/min H_2 3.8 cm/s	Degas for 5 min at 400°C then heat for 3 min at 800°C	Very thick and dense crust that is stuck to rebar except on ribs; only minor rust after many salt dips; can't be scratched or broken off	Dark gray melted crust metallic when scratched	Unchanged; crust/coating is dense and continuous but has some pores at interface	20 to 80

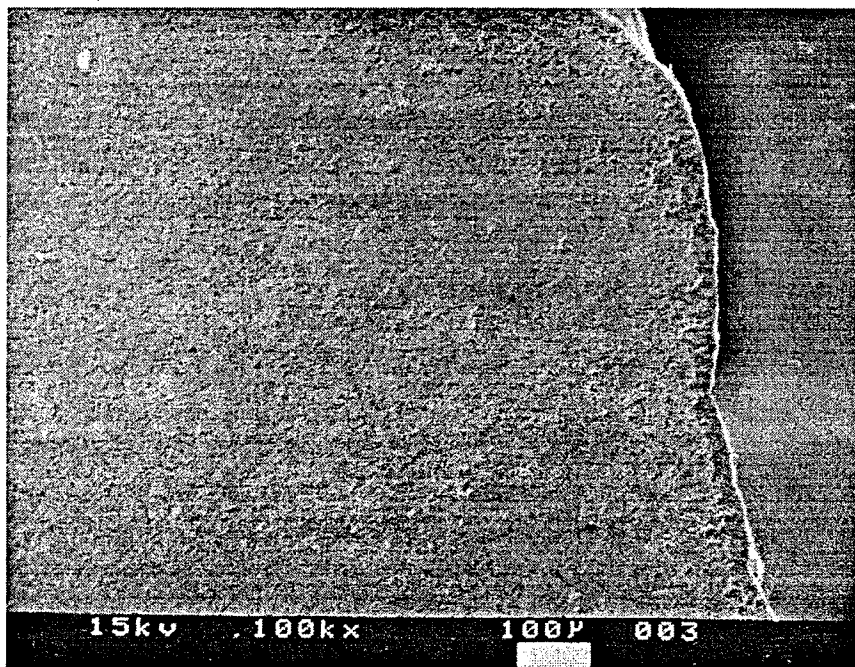
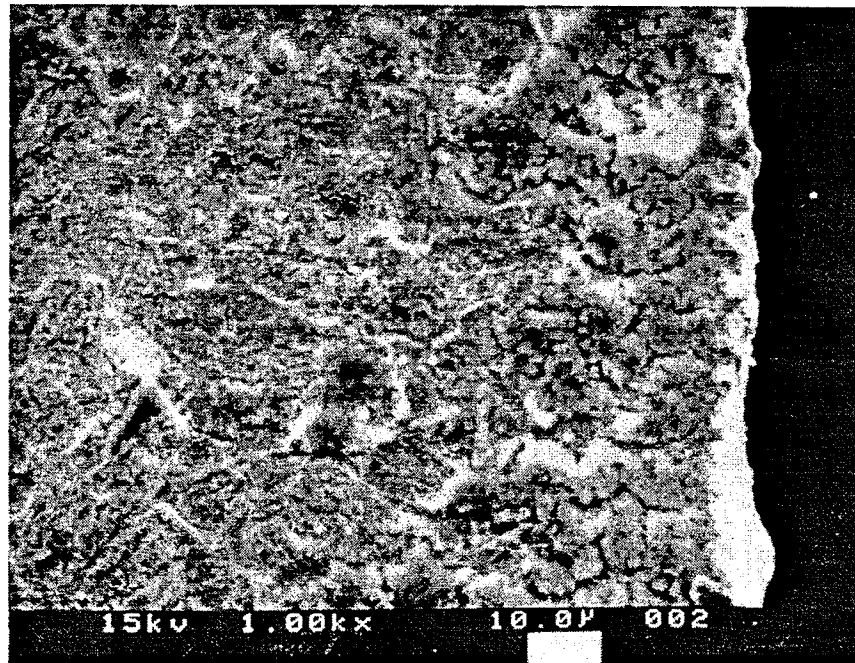


Figure 3. SEM photographs of an FBR-CVD coating on steel rebar.

In spite of many fine features of FBR-CVD coatings, the metal deposition rates were slower at low temperatures. Also, the deposition rate of Si (or Ti) depends strongly on the trace metals in the rebar. For example, manganese reduces the deposition rate of silicon. Trace metal contents in rebars vary widely depending on the source of iron. Rebars we received from Western Coating, Inc., had much higher manganese content than rebars obtained from CALTRANS and some that we purchased from a local hardware store. Therefore, in the coating plant, the chemistry of the coating process would need to be carefully controlled to obtain uniform, adherent coatings. This control may be difficult in an industrial rebar coating facility without specially trained personnel. In addition, throughput of the fluidized bed CVD process at 600°C may not be sufficient to meet current industrial demand. In light of this, the conventional fluidized bed coating approach seemed to be difficult to adopt in the industrial environment, at least in its present form.

Paint-and-Heat Metallization

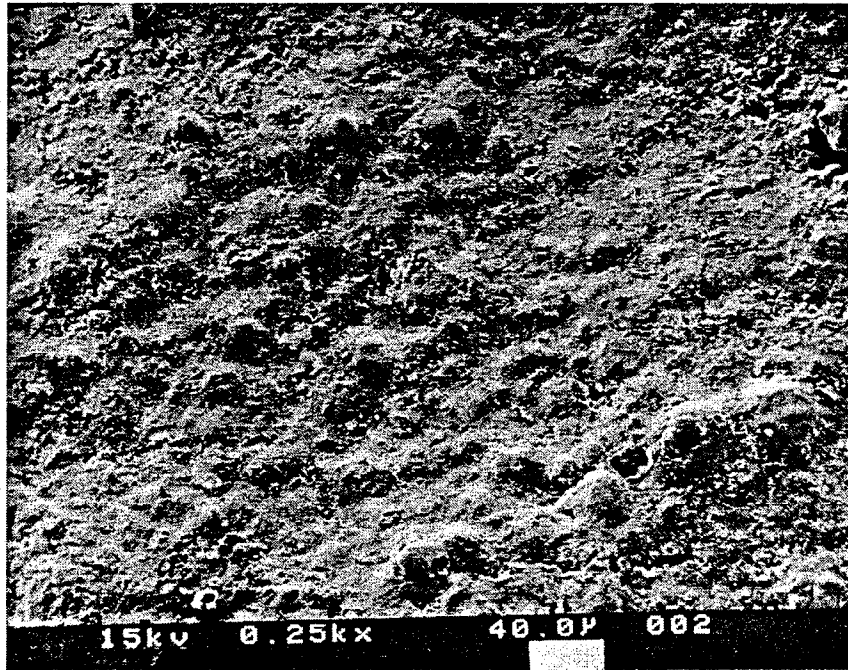
Our industrial partner, Mr. Reed, confirmed that conventional fluidized bed chemical vapor deposition of Si and Ti on rebars would not be economical in large scale operations. He indicated that metallic coatings would be economical only if the chemistry to be done at the coating plant could be minimized. We addressed this requirement by modifying the fluidized bed coating process such that most of the chemistry necessary for the coating process was performed on the metal powders in a fluidized bed reactor to form microcomposites. The prepared powders were then applied on the rebar in a slurry with alcohol or other suitable solvents, followed by rapid heating in an RF furnace to set the coating. In most experiments we used Sn, a metal with a low melting point, to facilitate the metal diffusion and bonding. On an industrial scale, a modified rotary kiln can be used to prepare metal powders. The process in the coating plant could then be just a simple paint-and-heat technique.

We tested numerous powder compositions for paint-and-heat metallization in the vertical RF reactor. Table 1 summarizes the properties and appearance of selected 15-cm (6-inch) rebar specimens coated by paint-and-heat technique. In some of our experiments, we tested metal powder compositions without any preparation other than ball milling to homogenize the mixture. Our objective was to see whether we could skip the fluidized bed CVD step and simplify the coating process considerably. We used metal powders such as Ni, Co, Cr, W, and Mo with Sn and commercial or home-made fluxes. Metals and their compositions were chosen such that the mixture would form an alloy upon dissolution in molten tin.

Figure 4 shows SEM photographs of a coating prepared by paint-and-heat metallization. The coating mixture composition, which contained several as-received metal powders, is given in Table 1, Experiment 9. The morphology of the coating consists of two distinct parts: an easily removable powdery crust and a metallic, shiny gray, hard underlying coating. The easily removable oxide crust was formed by oxidation of metal powders due to insufficient flux and/or high oxygen content in the reactor. The metal powder on the outermost layer was acting as an oxygen scavenger protecting the metal powder below against oxidation and allowing alloys to be formed during heating. The surface of the metallic gray coating is shown in the Figure 4(a).

A close-up of the polished and etched cross section of the coating is shown in Figure 4(b). Because the bulk metal of the rebar etched faster than the coating, the bulk metal surface is lower in the SEM picture. The surface layer and alloyed grains are clearly seen in the photograph. As the temperature was increased, the molten Sn dissolved more of the metals by direct contact with the particles. Molten Sn allows fast interdiffusion of metals and formation of intermetallic compounds of Si, Ni, Ti, and Sn. If only a small amount of Sn had been initially present in the coating, the coating would be very thin (mainly, diffusion from gas phase transport like pack cementation). However, in this case, enough Sn was present that the molten metal could act as transport medium between the powder and grains at the rebar surface. The elemental EDAX analysis of one of the alloy grains showed that it contained 2% Mn, 2% Ni, 3% W, 4% Mo, 4% Cr, 11% Co, 15% Sn, and 59% Fe.

(a)



(b)

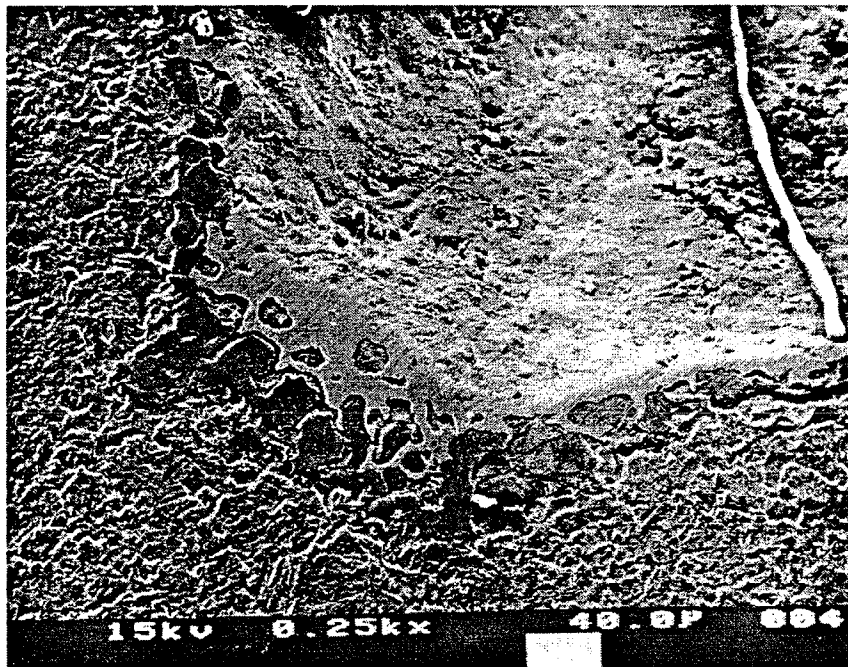


Figure 4. SEM photographs of a coating prepared by paint-and-heat metallization (Table 1, Experiment 9, ID 14).

Figure 5 shows SEM photographs of paint-and-heat metallization using TiNi (70:30) alloy powder (Table 1, Experiment 4). TiNi alloys are well known for their corrosion resistant-Cl and are widely used in high chloride environments. TiNi (70:30) is a eutectic mixture with a fairly low melting point (962°C). The TiNi coating consists of an oxide layer crust with a rough, thin metallic coating underneath. Most of the metal powder in the painted slurry was oxidized during heating, leaving only a thin layer to alloy with the rebar metal. Since TiNi readily undergoes oxidation even at very low concentrations of oxygen, the oxygen partial pressure in the reaction chamber must be very low to prevent the surface crust formation. However, the metallic coating under the crust was very resistant to chloride corrosion. The polished and etched cross section of the coating and bulk rebar is shown in Figure 5 (a). We did not find any rusting after many dips in a 5% NaCl solution except in a few spots where the painted slurry had spalled off during degassing. This problem can be avoided by careful control of the degassing and heating process.

A close-up SEM photograph of the Ti-Ni coating cross section is shown in Figure 5(b). The coating adhered to the rebar surface well with an average thickness of about 5 μm . Thicker coatings could be obtained by using a better flux, more Sn, and/or by lowering the oxygen concentration in the reaction chamber. Alternatively, TiNi (70:30) powder can be coated with a noble metal such as Cu to reduce the reaction with oxygen. Elemental analysis showed that the Ti concentration was higher near the surface and interface and that some Ni diffused across the interface into the rebar.

Even though TiNi (70:30) forms an excellent corrosion resistant coating on steel rebars, this alloy is expensive and it may not be economically feasible to use on an industrial scale. A better approach would be to form an alloy *in situ* during the heating and setting process. Corrosion resistant properties similar to TiNi (70:30) can be obtained by coating Ni powders with Ti and Si in a fluidized bed reactor. These coated powders then could be applied on the rebar with a suitable flux and a low melting metal such as Sn, which would act as the transfer medium to facilitate alloying.

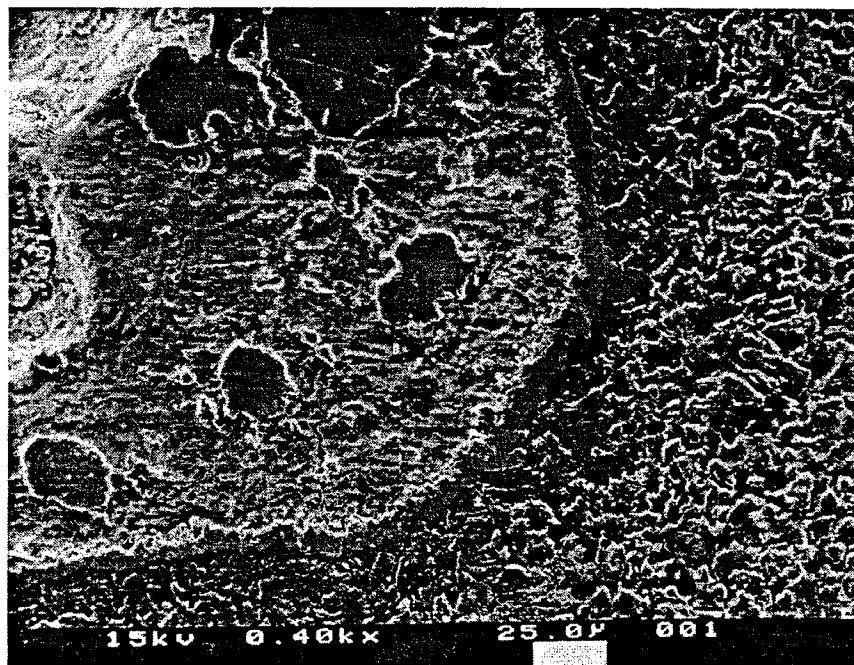
Figure 6 shows SEM photographs of metal powders coated in the fluidized bed reactor for paint-and-heat metallization and plasma spraying. Small amounts of Ti and Si were added to Ni powder and the mixture was fluidized by passing Ar, H₂, and HCl gases through the bed at 750°C. The particles were uniformly coated with an alloy of the metals. As the final step in the coating process, CuCl₂ was introduced to form a passive layer of Cu on the coated particles. Elemental EDAX analysis using the spot mode (penetration depth of 2 to 3 μm) was performed on each kind of particle. The nearly spherical Ni particles shown in Figure 6 (a) had a surface composition of 1% Si, 10% Ti, 35% Cu, and 54% Ni. The much larger angular Si particles were coated with 1% Si, 5% Ti, 8% Ni, and 86% Cu. The sponge-like Ti particles had a composition of 16% Ni, 19% Cu, and 65% Ti. All three types of particles can be seen in Figure 6 (b). The composition of the surface layers can be adjusted by changing the relative amounts of metal powder in the bed, the processing time, and the coating temperature.

Paint-and-heat metallization using fluidized bed prepared powders resulted in a tough, corrosion resistant coating (Table 1, Experiment 8). This coating did not rust in water or salt solutions after cyclic dipping. Surface crust (oxide) formation during heating was considerably minimized by coating the powders with less reactive copper. In addition, the copper surfaces are easily wetted with molten Sn, which then aids the alloying process. Figure 7 is an optical photograph of this polished and etched coating. The coating consists of a dense primary layer on the surface, which has an average thickness of 15 μm , and a much thicker secondary layer containing metallic particles.

Several key experimental parameters need to be carefully controlled to obtain a good corrosion resistant coating by paint-and-heat metallization using as-received metal powders.

Because the metal powders are very reactive toward oxidation, the reactor must be free of oxygen or oxidizing agents. Thus, we use an inert gas such as Ar or N₂. The role of flux is very important in that it removes the surface oxide layer on metal powders to promote wetting and metallic bonding. Water and oxygen in the precoat mixture should be minimized since they mask the effectiveness of the flux and are detrimental to the formation of a thick, adherent, and corrosion resistant coating. In addition, no salt that contains waters of crystallization should be used as a flux in the paint-and-heat metallization. The tin chloride that we initially used as a flux contained two molecules of water per mole of salt (SnCl₂·2H₂O). When heated, it first decomposes to an oxychloride and then to tin oxide. Tin oxide is very stable and difficult to reduce under normal coating conditions and, therefore, does not facilitate wetting and metallic bonding. It was preferable to use NH₄Cl, which decomposes at low temperatures to produce very reactive HCl gas. The HCl can strip off the oxide surface layer from all the metals in the powder mixture (even Si and Ti) and form chlorides such as TiCl₂, SiCl₄, and SnCl₂, which are transported in the gas phase to other areas where they can diffuse into the solid or liquid melt. Another good flux was CuCl₂, which was easily dried in air to form the anhydrous salt at less than 400°C. CuCl₂ is easily reduced at fairly low temperatures, forming HCl gas and pure metallic Cu. Some commercial fluxes such as AllState® Flux also worked reasonably well with the metal powder compositions given in Table 1.

(a)



(b)

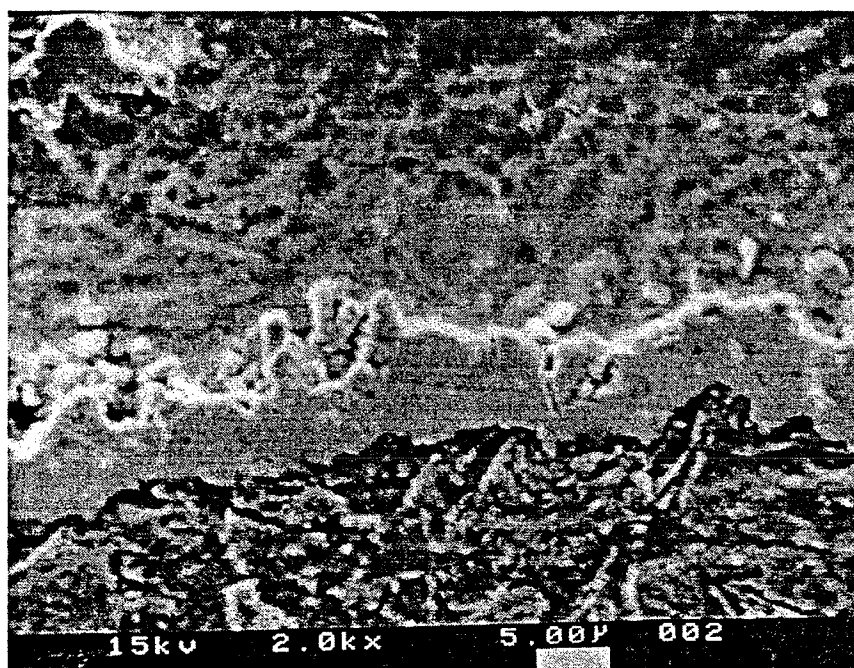
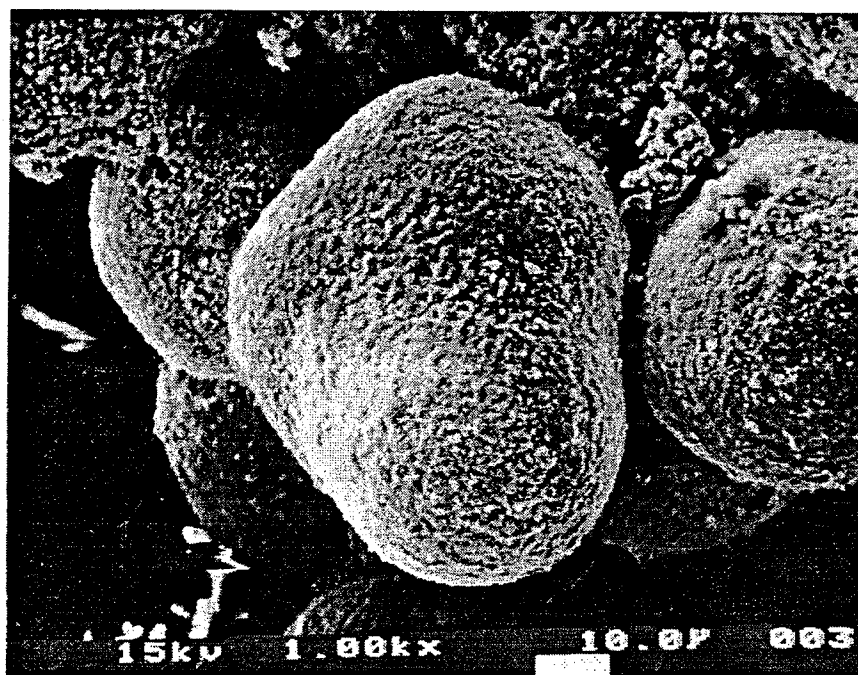


Figure 5. SEM photographs of a coating prepared by paint-and-heat metallization (Table 1, Experiment 4, ID 28).

(a)



(b)

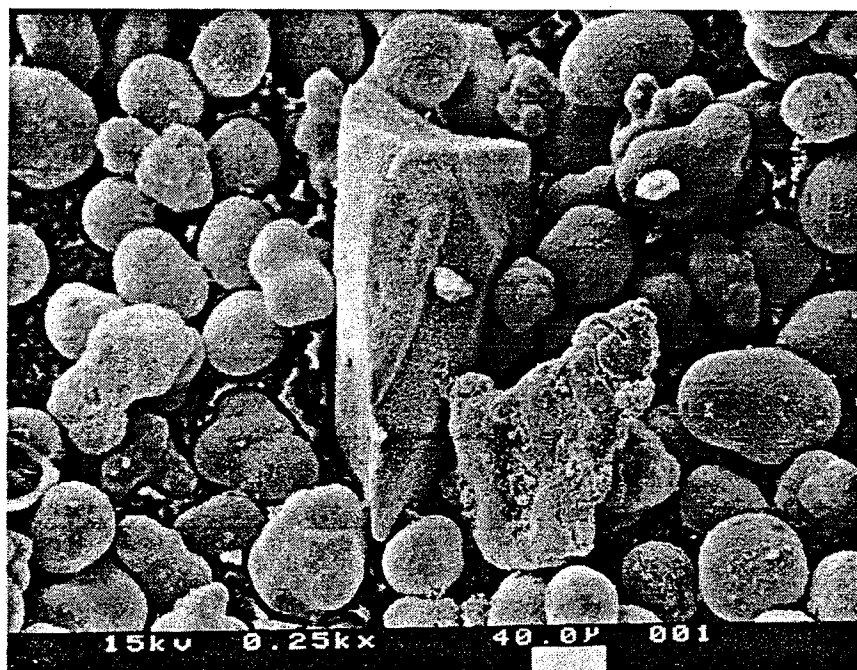


Figure 6. SEM photographs of Ti, Si, and Cu coated Ni powder prepared in a fluidized bed reactor.



Figure 7. Optical photograph at 200X of a coating prepared by paint-and-heat metallization (Table 1, Experiment 8, ID 31).

The amount of flux and other volatile components in the coating should also be minimized to decrease the amount of time required to degas the painted sample before heating. An excessive amount of flux caused the coating to spall off during degassing. According to our calculations, only about 1 g of NH_4Cl was needed to strip off the oxides from 100 g of metal powders. The salt should be completely dissolved in alcohol so that the metal particles are evenly coated with the flux when the powder is dried. The surface can then be degassed and the powder cleaned as the rebar enters the hot zone of the graphite cylinder.

Although it is economical to use as-received metal powders to form coatings on rebars, more research must be performed on suitable fluxes that promote sufficient wetting and metallic bonding. These fluxes should be able to remove the surface oxide layer of metal powders in the presence of air. This may be difficult with reactive metals that form strong oxides. However, if the reactive metal is coated with a noble metal, oxidation in air can be minimized. Therefore, metals such as Si or Ti that form very stable oxides should be coated with a noble metal such as Cu, Sn, or Ni to reduce the reaction with oxygen. Metal powders can be coated in a fluidized bed reactor or, in some cases, in simple salt solutions. For example, Si can be coated with copper from a solution of CuCl_2 in alcohol. Copper plated Si and Ti surfaces are easily wetted with molten Si.

A substantial amount of low melting point metal (Sn) must be present in the coating in order to form a thick continuous surface layer on the rebar. When the Sn melts at 232°C , it wets the surface of the metal particles (Cu, Ni, Ti) around it and flows toward the rebar where it wets the Fe surface. At 340°C , the NH_4Cl begins to sublime/decompose to HCl gas which reacts with and cleans the other metals. The Sn can wet the Ti and some of this will dissolve into the melt. The Sn/Ti melt will wet the rest of the components (even oxides). Unfortunately, the solubility of Si in Sn is very low (only 1 wt.% at 1000°C), so we must rely on diffusion through the melt and gas phase transport by Si halides to get this element into the rebar's surface. We could increase the solubility of Si in the melt by adding Ni or Cu. Other high melting metals such as Ti, Ni, and Fe have substantial solubility (up to 30 wt.%) in Sn and thus form a corrosion resistant alloy on the rebar surface. Figures 8, 9 and 10, respectively show intermetallic solubility and alloy formation in phase diagrams of Ti/Sn, Ni/Sn, and Fe/Sn binary systems. (3)

Plasma Spray Coatings

For plasma spraying or plasma spraying deposition, a heat source such as a combustion flame or nontransferred arc plasma is used to heat a wire or powder feed stock above the melting point of the material. The small, approximately 20- μm molten particles are propelled toward the substrate and freeze on impact at a rate of 10^5 or 10^6°C/s . The spray parameters and rate of material deposited onto the surface are adjusted to maintain the substrate at the desired temperature and obtain the best coating. The substrate temperature ranges from less than 120°C to over 500°C . Plasma spraying is an industrial technique for coating a wide range of components from gas turbines for hot corrosion to steel structures for atmospheric and marine corrosion. Most production coatings are applied with automated systems typically with spray rates ranging from 5.2 kg/hr for ceramics to 18 kg/hr for metals. The practical lower limit thickness for a continuous layer of coating is about 70 μm . This line-of-sight process deposits a coating in layers typically about 10-15 μm with each pass of the spray device, and multiple passes are made to obtain the desired thickness. The porosity of the coating depends on the spray parameters and material and is typically from nonporous to about 10%.

We used plasma spraying with powders coated in a fluidized bed reactor to demonstrate the concept of *in situ* alloying. FeSi, Fe, or Ni powder were coated with Si, Ti, and Cu in a fluidized bed reactor. When the coated powder mixture was thermally sprayed, alloys were formed during the spraying and deposited on the rebar to form a corrosion resistant, metallic alloy coating. Figure 11 shows a simplified plasma spraying process with coated powders.

Table 2 summarizes the combinations of metal powders used for plasma spraying and the morphology of the coatings. Figure 12 shows SEM photographs of a Ni-Ti-Si-Cu-Sn coating prepared by the FBR-plasma spray technique. The thickness of the coating is about 50 μm , including a surface layer of Sn applied using the paint and heat technique. Although the sprayed coating appeared to be thick, dense, and continuous, a surface layer of Sn was added to seal off any possible defects or pinholes. A more practical solution would be to mix some Sn powder with the FBR powder before spraying.

The polished and etched cross section of this sample in the SEM photograph shows that the microstructure of the rebar was not significantly altered. The grain size is fairly small and does not vary with depth from the surface. Elemental analysis of the cross section revealed that the surface consisted mainly of Sn with some Ti and Ni. The coating was mostly Ni with a considerable amount of Si and Ti. Some Ni and Si diffused into the rebar, whereas Ti tended to concentrate near the surface and interface. Cu could not be detected anywhere in the sample.

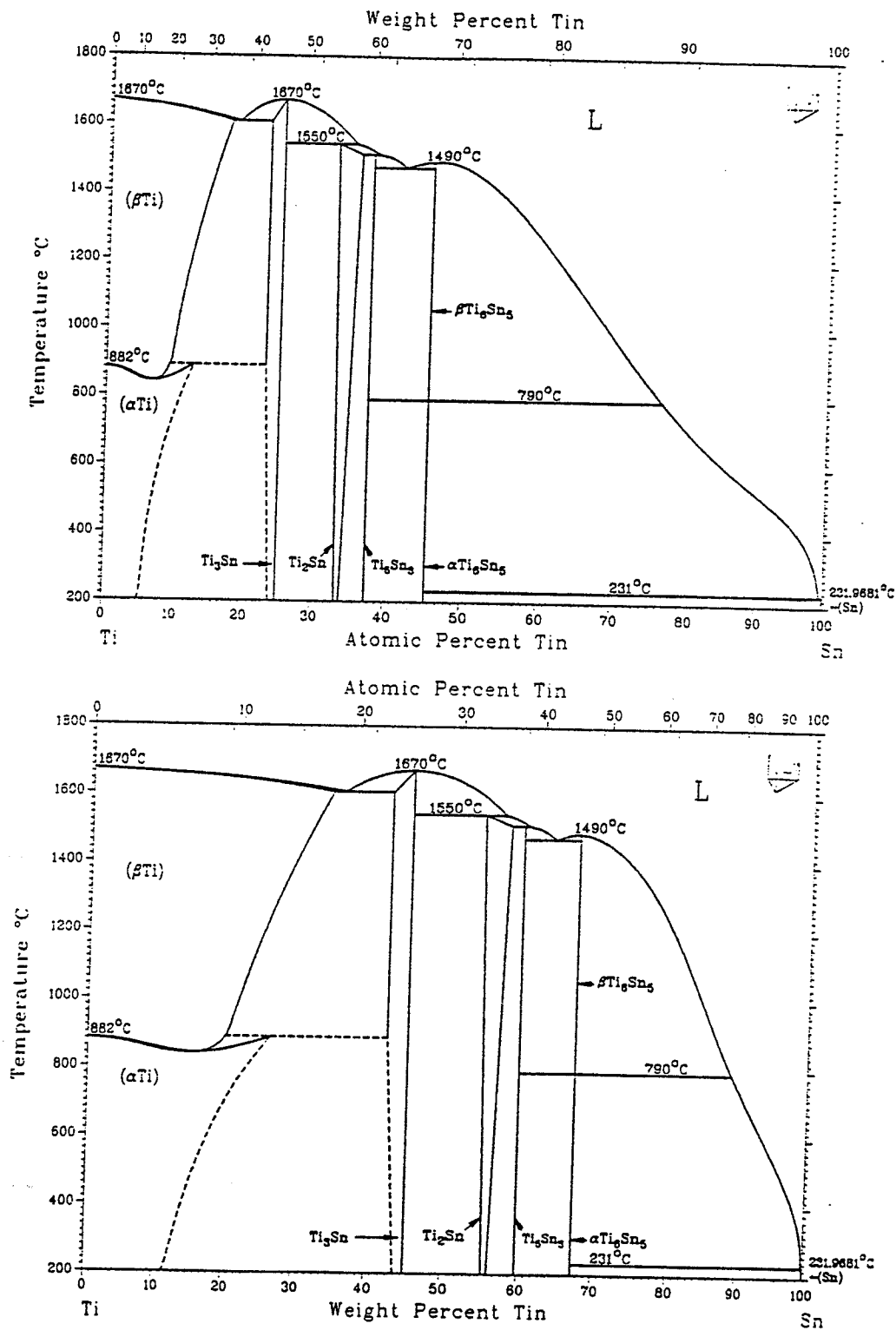


Figure 8. Phase diagram of the Ti-Sn binary system

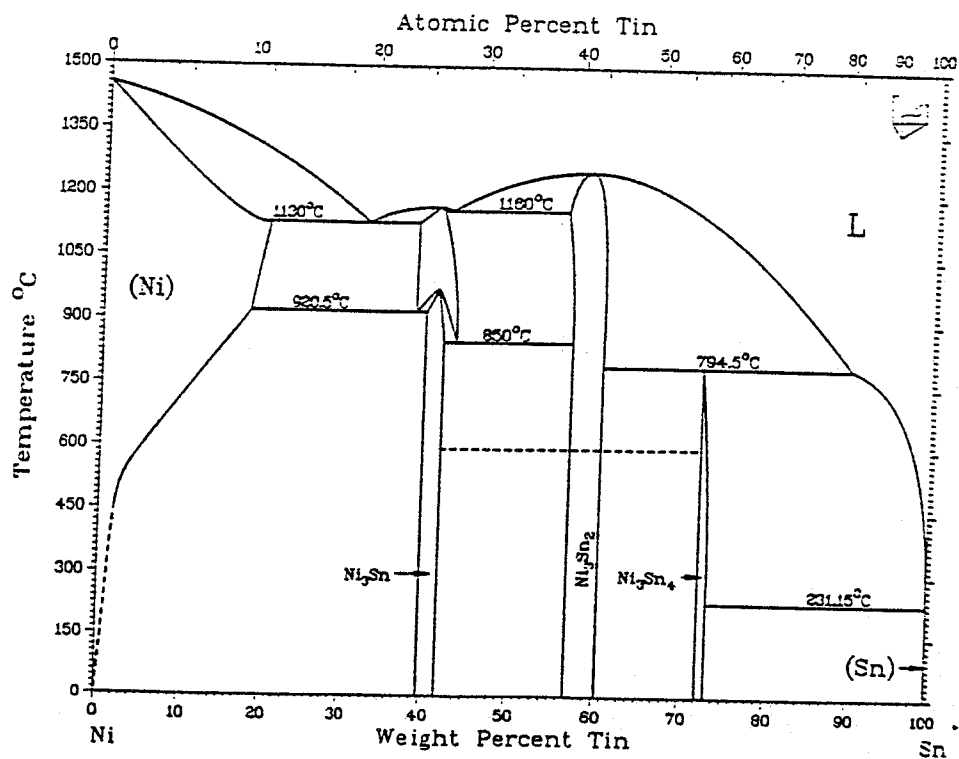
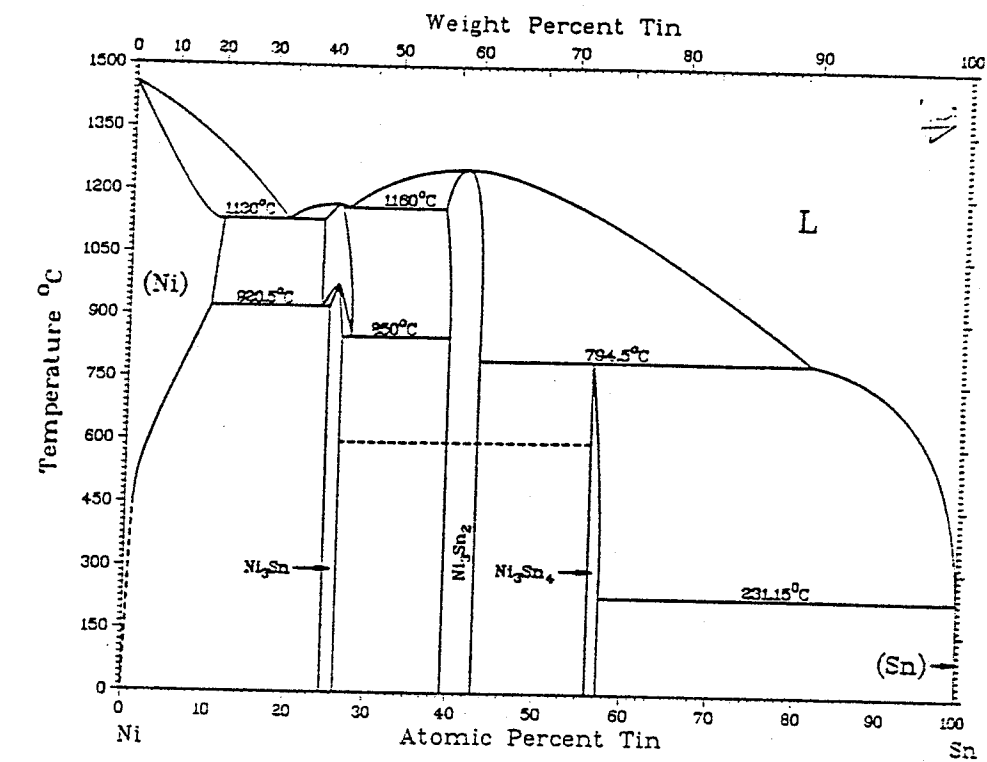


Figure 9. Phase diagram of the Ni-Sn binary system

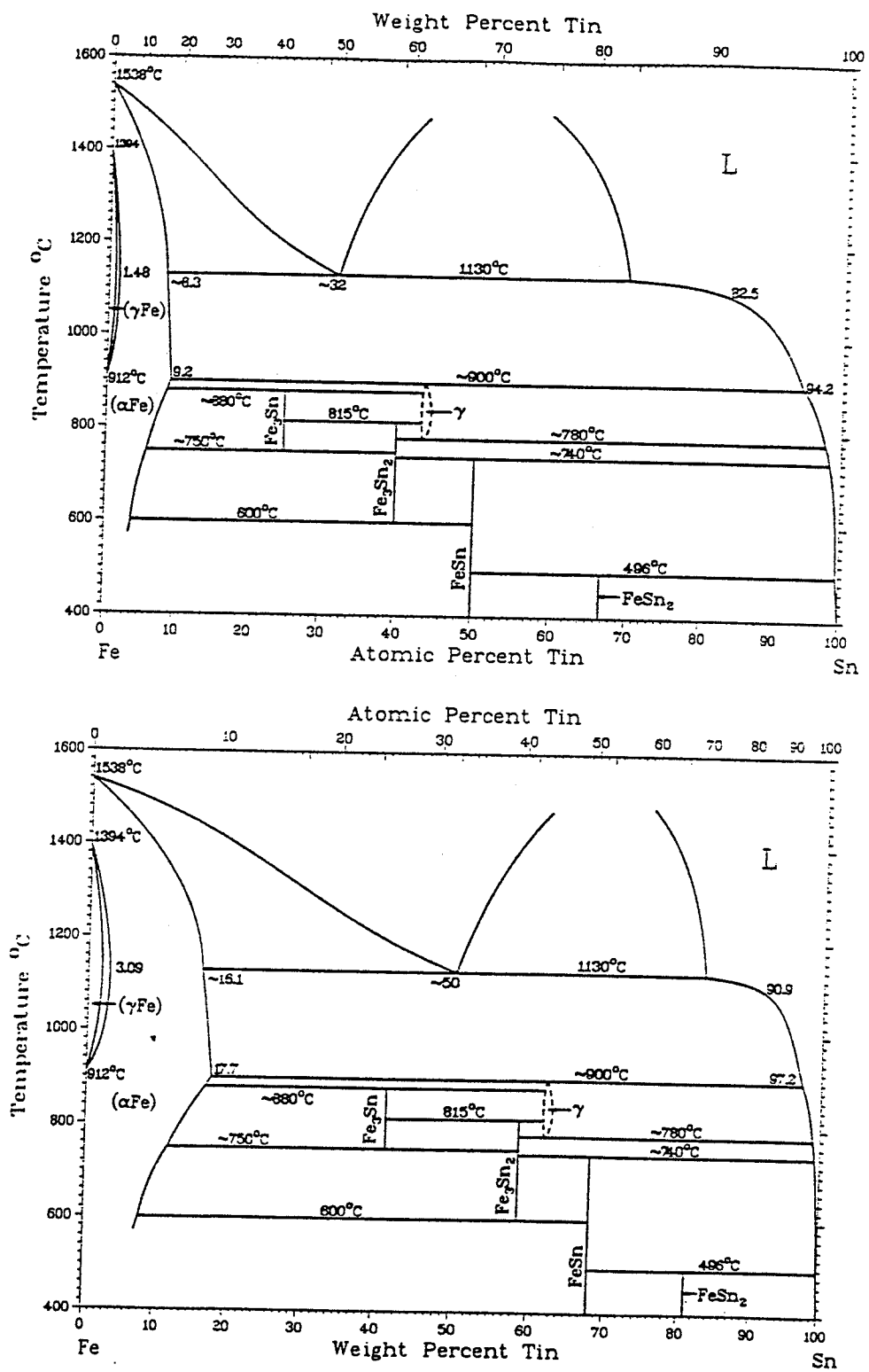


Figure 10. Phase diagram of the Fe-Sn binary system

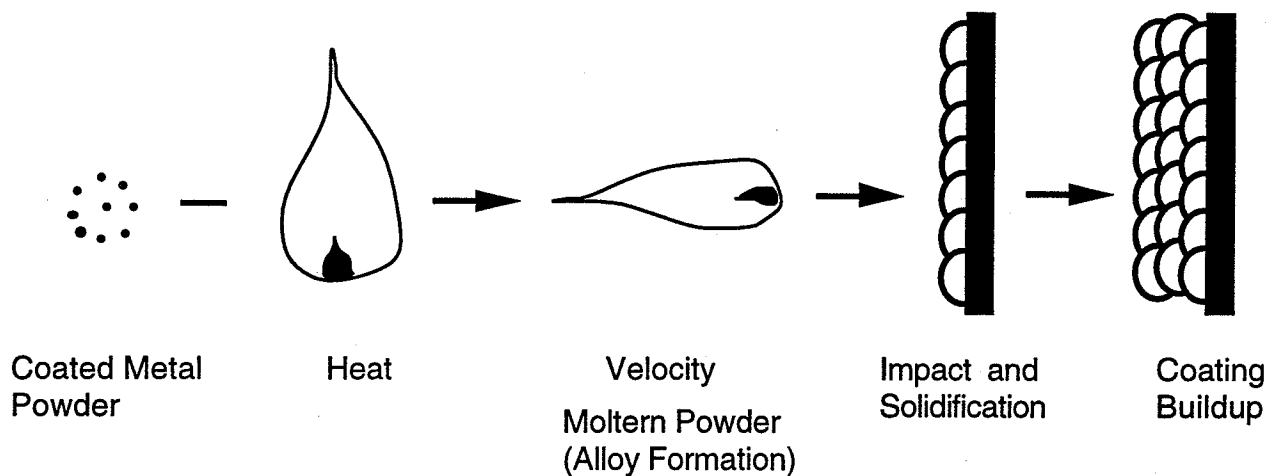


Figure 11. Plasma spraying of coated metal powders.

Table 2. Plasma spray Coatings on 1-m Steel Rebars

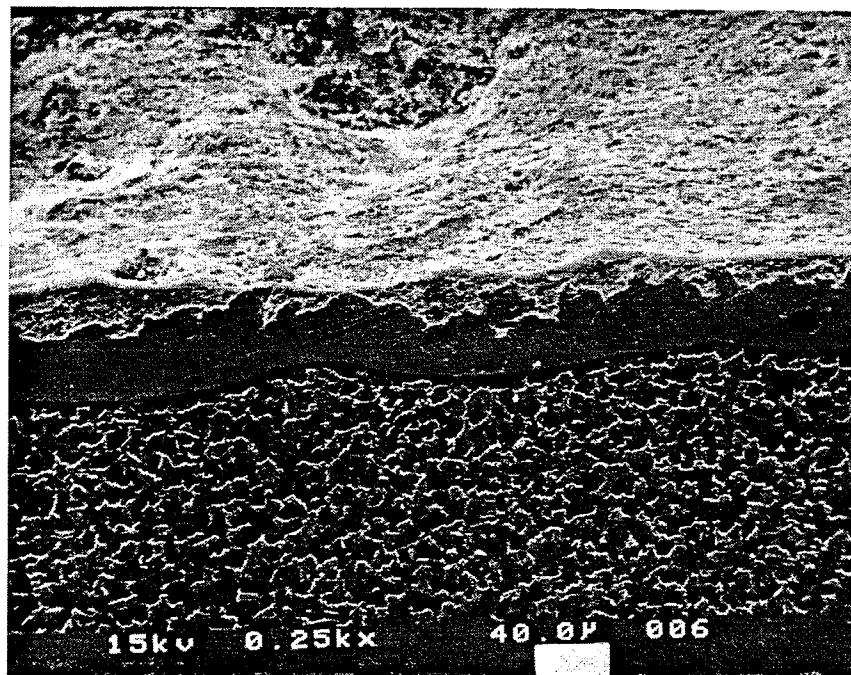
Sample	Powder Characteristics	Coating Description
1. Ti, Ni, Cu on rebar	-120+170 mesh $Ti_{70}Ni_{30}$ coated with Cu in FBR	Rough, thick, golden to shiny metallic
2. Ti, Ni, Fe, Si, Cu on rebar	-120+170 mesh $Ti_{70}Ni_{30}$ 50% -120+170 mesh $TiSi$ 50% coated with each other then Cu in FBR	Rough, thick, golden gray to shiny metallic
3. Ti, Ni, Cu on rebar	-325 mesh $Ti_{70}Ni_{30}$ coated with Cu in FBR	Rough, thick, dark gray to shiny metallic
4. Ti, Ni, Si, Cu on rebar	-60+80 mesh Ni coated with Si and Ti then Cu in FBR	Rough, thick, light gray to shiny metallic
5. Ti, Fe, Si, Cu on rebar	-60+80 mesh Fe coated with Si and Ti then Cu in FBR	Rough, thick, light gray to shiny metallic

The amount of Si, Ti on the base metal powder can be controlled to obtain the optimum metal composition for corrosion protection. Addition of Si, Cr, Ti, and/or Mo metals to steel greatly enhances its corrosion resistance as seen in commercially available alloys such as Hastelloy-C®, E-BRITE®, or Duriron®. However, alloy powders are extremely expensive compared with individual metal powders because of the cost of alloying and crushing. In contrast, coated powders can be prepared in rotary kilns in large quantities very efficiently and economically. For example, inexpensive Fe powders can be coated with Si and Ti. The Fe-Si-Ti ternary phase diagram in Figure 13 shows the liquidus curves and regions of phase stability for this system. (4) In the α region, a Fe-rich single phase alloy such as 6% Ti, 12% Si, and 82% Fe can be obtained with good corrosion resistance and ductility.

CORROSION STUDIES

Corrosion of coated rebars was studied using a conventional salt spray technique and the more advanced electrochemical AC impedance technique. Although the salt spray technique is not quantitative, it gives a general idea of the rate of corrosion in a chloride environment. The salt spray experiments are easily performed, inexpensive, and reasonably accurate in predicting the corrosion resistance of coatings. Thus, this technique was widely used in this project for qualitative evaluation of rebar coatings. The uncoated rebars underwent severe corrosion in 1 to 2 days when exposed to the salt solution. Some coated rebars showed no corrosion, while others corroded at much slower rates. Rebar samples coated with Ti-Ni alloy showed exceptionally good corrosion protection. Observations of the salt test experiments are summarized in Table 1 under Observations Column.

(a)



(b)

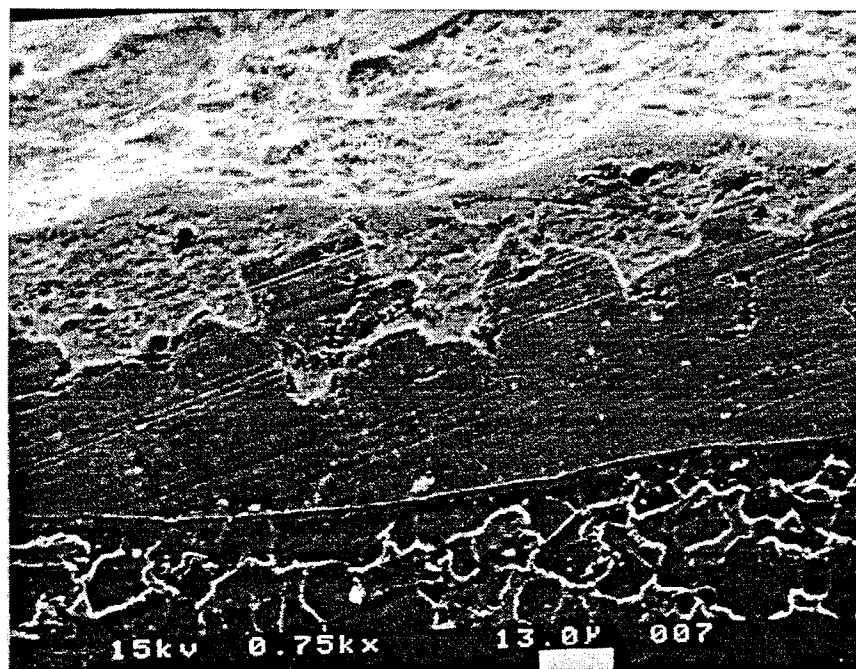


Figure 12. SEM photographs of a coating prepared by thermal spraying of FBR-CVD coated Ni powder (Table 2, Experiment 4).

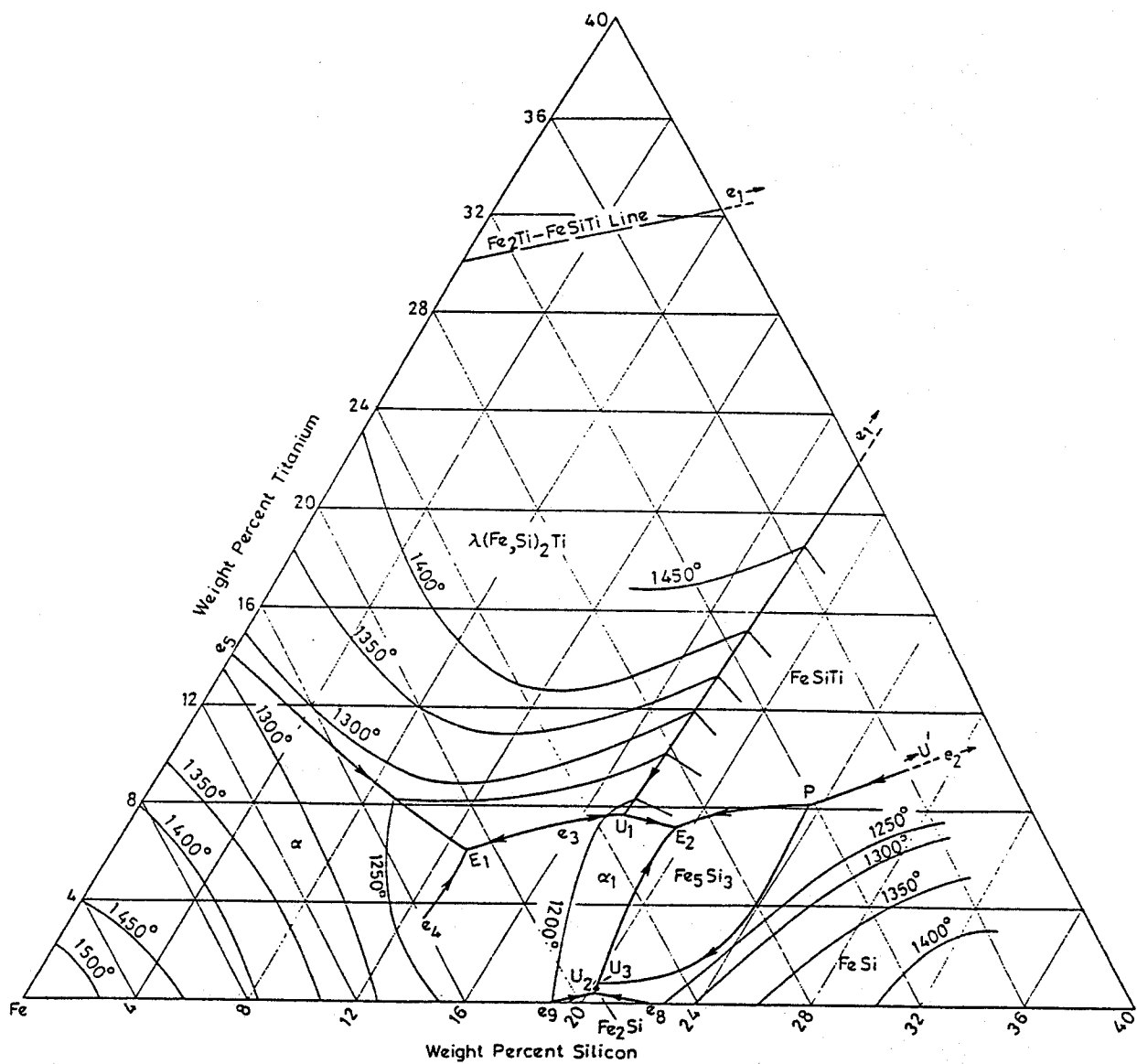


Figure 13. Phase diagram of the Fe-Si-Ti ternary system

In contrast, the electrochemical AC impedance technique can provide a wealth of quantitative and mechanistic information about the corrosion process. It essentially quantifies the degree to which the system resists corrosion attack by the environment. This technique requires a frequency response analyzer and a fast potentiostat, preferably with computer controlled data acquisition and analysis. The experimental data are commonly presented as Nyquist (complex plane) or Bode ($\log \omega$) plots. By applying an AC over a range of frequencies, we can obtain more mechanistic information on the corrosion process than when using a DC technique. The ability to model a corrosion process with electrical elements such as resistors, capacitors, and inductors gives practical utility to the AC impedance technique. Such characterization can lead to more accurate predictions of corrosion behavior. Based on the equivalent circuits for the steel in the chloride solution, the impedance is due to the ohmic or uncompensated resistance at high frequency and to the sum of ohmic resistance and the polarization resistance at low frequencies.

The corrosion rates of selected rebars coated with metal powders were obtained using the AC impedance technique. Both real and imaginary components of the impedance of the coating interface were measured as a function of frequency. From the plot of the real component against the imaginary component (Nyquist plot, Z_{real} vs. $Z_{\text{imaginary}}$), polarization resistance (R_p) is obtained, which is inversely proportional to the rate of corrosion (Figure 14). Polarization resistance itself can be used as a measure of the relative rate of corrosion of various coated and uncoated samples. However, to determine the absolute rate of corrosion, Tafel slopes for steel are needed, which can be obtained by potentiodynamic polarization techniques. For simple salt water systems, published Tafel slope data can be used with reasonably good accuracy. Then the corrosion current can be determined using the Stern-Geary equation. Corrosion data for some of the metal coatings are reported in the Table 3.

$$B = b_a * b_c / 2.303 * (b_a + b_c)$$

Where b_a and b_c are anodic and cathodic Tafel slopes.

$$I_{\text{corrosion}} = B/R_p \quad (\mu\text{A}/\text{cm}^2)$$

$$B = 2 * 10^4 \mu\text{V}; R_p \text{ in } \Omega \text{ cm}^2.$$

$$\text{Corrosion rate} = 0.4595 * I_{\text{corrosion}} \quad (\text{mpy})$$

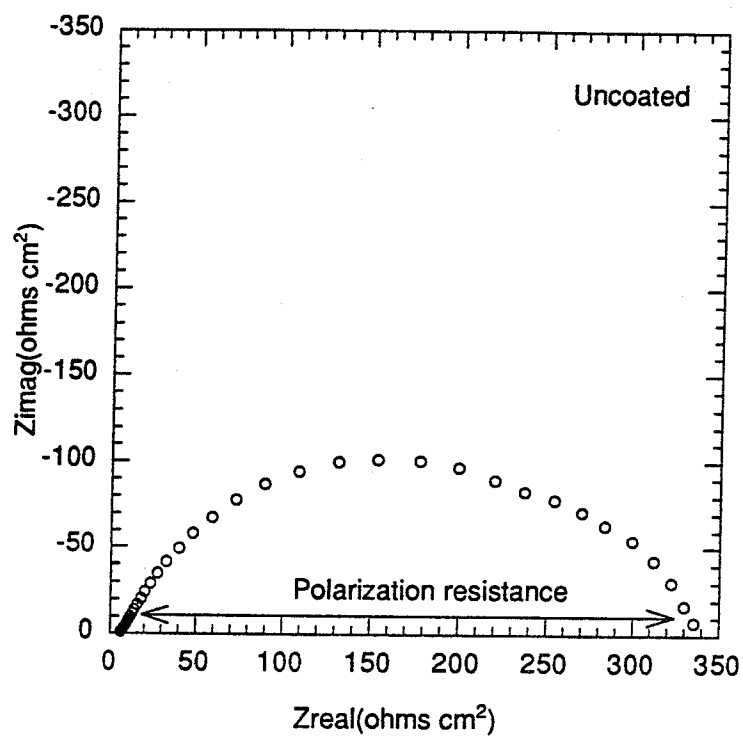
However, the AC impedance technique may sometimes give exaggerated corrosion rates due to slight imperfections or pin holes in the coating. A higher polarization resistance obtained from AC impedance always indicates a lower corrosion rate, but lower polarization resistance does not necessarily mean a higher corrosion rate and less corrosion resistant coating. Table 3 gives the polarization resistance and corrosion rates of selected rebar coatings in a 5% NaCl solution obtained by the electrochemical AC impedance technique. A thin Si coating on a small rebar sample deposited by direct fluidized bed CVD (Table 3, Sample 4) improved the corrosion resistance more than 4-fold compared with the uncoated rebar. A Ti and Sn coating prepared by paint-and-heat metallization with as-received metal powders (Table 3, Sample 13) shows more than a 13-fold improvement of corrosion resistance. A copper coated Si and Sn coating and TiNi (70:30) alloy coating, both prepared by paint-and-heat metallization showed excellent corrosion resistance properties in 5% NaCl solution with more than a 20-fold decrease in the rate of corrosion (Table 3, Samples 9 and 11).

We did not have enough time and funding to complete the corrosion rate measurements of fluidized bed CVD-thermally sprayed coatings. However, salt spray tests indicated that these coatings show excellent resistance to chloride corrosion. As a demonstration our coating concept, 1-m long rebar samples coated with metal powders were shipped to NCHRP, Pacific Gas and Electric Company, and Western Coating, Inc.

Table 3. Corrosion Rates for Some Coated and Uncoated Rebar Specimens

Sample No.	Specimen	Polarization Resistance ($\Omega \text{ cm}^2$)	$I_{\text{corrosion}}$ ($\mu\text{A cm}^{-2}$)	Rate of Corrosion (mpy)
0	Uncoated	333	60.1	27.6
12	Ni:Sn (10:90)	879	22.8	10.5
14	Ti:Al (10:90)	942	21.2	9.8
4	CVD Si	1570	12.7	5.9
13	Ti:Sn (10:90)	4396	4.6	2.1
9	Si(Cu):Sn (50:50)	6908	2.9	1.3
11	TiNi alloy(70:30)	6877	2.9	1.3

(a)



(b)

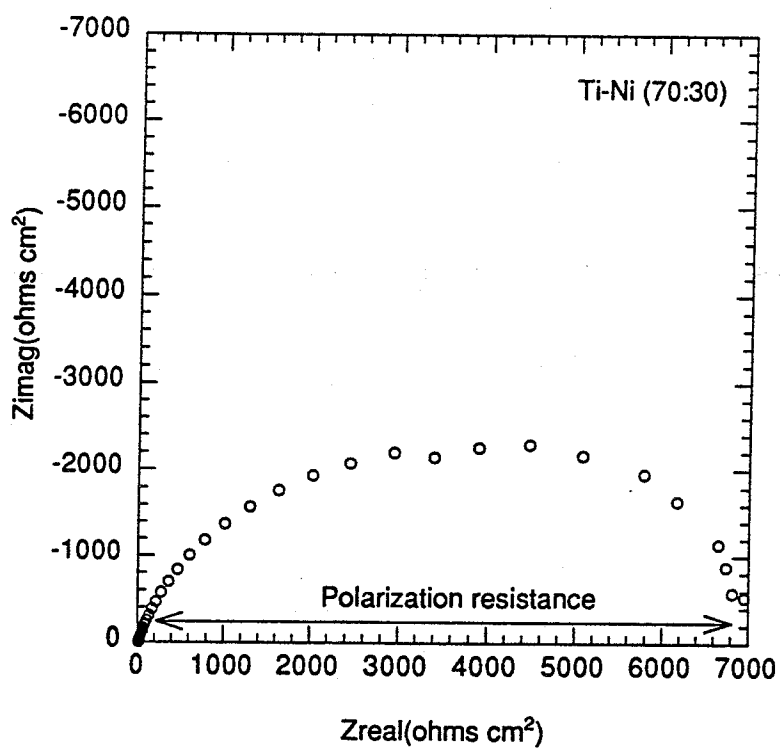


Figure 14. Nyquist plot for uncoated and coated rebar coupons in 5% sodium chloride. 10 mV perturbation, 0.01Hz to 10 kHz frequency scan.

PLANS FOR IMPLEMENTATION

During this study we demonstrated that metallic coatings can improve the corrosion resistance of steel rebar significantly and thereby can increase the service life of concrete and other highway structures. We demonstrated thick coatings of various metals and alloys such as Si, Ti, Ni, and Ti-Ni can be formed on rebars by paint-and-heat or plasma spray techniques. We showed the feasibility of the scale-up process by coating rebars up to 1 m long. These adherent coatings reduced the corrosion rate of steel rebars in chloride environments by over one order of magnitude. The preliminary projected cost for the coating is similar to that of polymer coatings.

Because the paint-and-heat or sprayed coatings are not sacrificial, they will provide much superior corrosion protection for a long time. Our novel powder coatings can be applied easily and economically on new components as well as on existing steel structures such as bridges to decrease the corrosion rate and thus increase the service lifetime. We believe that the potential impact of this corrosion protection coating technique on the highway industry will be tremendous. Therefore, we highly recommend continuing research on these simple coating techniques to transfer the technology to the highway industry.

Accordingly, we recommend the following:

- (1) Using a fluidized bed reactor to prepare various metal powder compositions that are proved to provide corrosion protection for steel in a chloride environment.
- (2) Evaluating commercial and novel fluxes to obtain the best alloying with coated metal powders.
- (3) Coating rebar specimens (up to 1-m long) by paint-and-heat and plasma spray techniques for laboratory and field corrosion testing.
- (4) Simulating field application to demonstrate the feasibility of coating existing structures.
- (5) Participating with industrial partners in testing of coated rebars and technology transfer.

We expect that these coatings will make structural parts of steel behave as if they were alloys such as Hastelloy-C or Duriron® from the corrosion point of view. Coatings will be fairly thick, 50-100 μm ; thus damage from scratches and erosion will be minimal. The alloy coatings can be made more ductile by increasing the soft metal content and thus coatings will not crack during bending and shaping of coated steel rods. In a Fe-Si-Ti coating, the Fe-rich, malleable layer will provide protection when rebars are bent. In the unlikely event of cracks in the coating, we expect that the protection will be provided by the oxidation of Si and Ti when exposed to the aqueous environment, which will reduce the exposure of the base metal. We expect that these oxides will form an impervious protective layer, unlike the porous layers of Fe hydroxides and oxychlorides generated in uncoated bars. These alloy coatings will significantly increase the corrosion resistance and lifetime of rebars and other steel structures.

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