

A Thesis
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MULTI LAYER COATINGS FOR CARBON STEELS

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TABLE OF CONTENTS

	Page
I. Introduction	10
II. Literature Survey	11
A. Silica Sol-gel Layer	11
B. Gallium Layer	12
C. Sodium silicate Layer	12
D. Iron phosphate	13
E. Corrosion Tests	14
III. Experimental Procedure	15
A. Sample Preparation	15
1. Drilling and Polishing	15
2. Cleaning and Chemical Pretreatment	15
B. Sample 1	16
C. Sample 2	16
D. Sample 3	16
E. Sample 4	17
F. Sample 5	17
G. Sample 6	17
H. Sample 7	18
I. Corrosion Testing	19
IV. Results and Discussion	20
A. Chemical Pretreatment, Sample 1	20

B. Chemical Pretreatment, Sample 2	20
C. Silica Sol-gel on Steel, Sample 3	20
D. Gallium on Steel, Sample 4	21
E. Gallium on Silica Sol-gel, Sample 5	22
F. Sodium silicate on Sample 6	24
G. Sodium silicate on Sample 7	25
H. Corrosion Testing	26
V. Conclusions	28
VI. Suggestions for Future Work	29
VII. Appendix	30
VIII. References	54

IX. List of Equations

- | | |
|--|-----------|
| 1. The Sodium silicate Reacts | 12 |
| 2. The Phosphoric acid Reacts with the Iron | 13 |

X. List of Figures

Figure 1. Cross Section of the Multi-Layer Coating.....	13
Figure 2. Schematic of the steel disc eight holes used for Samples 3 through 7.....	16
Figure 3. The schedule for the heat treatment of the Samples 3, 4, and 5.....	17
Figure 4. The schematic diagram of water glass mixtures distribution for Samples 6 and 7...18	
Figure 5. The heat treatment schedule for Samples 6, 7, 8, 9, and 10.....	18
Figure 6. Sample 1, steel pretreated by Method 3.....	30
Figure 7. Sample 1, steel polished and pretreated by method 3.....	30
Figure 8. Sample 2, steel pretreated with Method 1 and Method 2.....	31
Figure 9. Sample 2, steel pretreated by method 1.....	31
Figure 10. Sample2, steel pretreated by method 2.....	32
Figure 11. Sample 3, steel pretreated by method 3 and coated with silica sol-gel.....	32
Figure 12. Sample 3, steel pretreated by method 1 and coated with silica sol-gel.....	33
Figure 13. Sample 3, steel pretreated by method 2 and coated with silica sol-gel.....	33
Figure 14. Sample 3, steel pretreated with Methods 1, 2, 3 and coated with silica sol-gel.....	33
Figure 15. Sample 3, steel pretreated with method 3, coated with silica sol-gel and fired.....	34
Figure 16. Sample 3, steel pretreated with method 1, coated with silica sol-gel and fired.....	34
Figure 17. Sample 3, steel pretreated with method 2, coated with silica sol-gel and fired.....	35
Figure 18. Sample 3, steel pretreated with Methods 1, 2, 3 and coated with silica sol-gel and fired...35	
Figure 19. Sample 4, steel pretreated with method 3, coated with gallium.....	35
Figure 20. Sample 4, steel pretreated with method 1, coated with gallium.....	36
Figure 21. Sample 4, steel pretreated with method 2, coated with gallium.....	36
Figure 22. Sample 4, steel pretreated with Methods 1, 2, 3, coated with gallium.....	36
Figure 23. Sample 4, steel pretreated with method 3, coated with gallium and fired.....	37
Figure 24. Sample 4, steel pretreated with method 1, coated with gallium and fired.....	37
Figure 25. Sample 4, steel pretreated with method 2, coated with gallium and fired.....	38
Figure 26. Sample 4, steel pretreated with Methods 1, 2, 3, coated with gallium and fired.....	38

Figure 27. Sample 5, steel pretreated by method 3 was coated with silica sol-gel, fired, and coated with gallium.....	38
Figure 28. Sample 5, steel pretreated by method 1 was coated with silica sol-gel, fired, and coated with gallium.....	39
Figure 29. Sample 5, steel pretreated by method 2 was coated with silica sol-gel, fired, and coated with gallium.....	39
Figure 30. Sample 5, steel pretreated with Methods 1, 2, 3, coated with silica sol-gel, fired, coated with gallium.	39
Figure 31. Sample 5 where the steel pretreated by method 3 was coated with silica sol-gel, fired, coated with gallium and fired.....	40
Figure 32. Sample 5 where the steel pretreated by method 1 was coated with silica sol-gel, fired, coated with gallium, and fired.....	40
Figure 33. Sample 5 where the steel pretreated by method 2 was coated with silica sol-gel, fired, coated with gallium, and fired.....	41
Figure 34. Sample 5 where the steel pretreated with Methods 1, 2, 3. Coated with silica sol-gel, fired, coated with gallium and fired.....	41
Figure 35. Sample 6. Sodium silicate with a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 1.....	41
Figure 36. Sample 6. Sodium silicate with a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 2.....	42
Figure 37. Sample 6. Sodium silicate with a 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 1.....	42
Figure 38. Sample 6. Sodium silicate with a 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 2.....	43
Figure 39. Sample 6. Sodium silicate with a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 3.....	43
Figure 40. Sample 6. Sodium silicate with a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 1.....	44
Figure 41. Sample 6. Sodium silicate with a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel pretreated with method 2.....	44
Figure 42. Sample 7. Sodium silicate with a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on Gallium oxide, silica sol-gel, and steel pretreated with method 3.....	45
Figure 43. Sample 7. Sodium silicate with a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on Gallium oxide, silica sol-gel, and steel pretreated with method 1.....	45
Figure 44. Sample 7. Sodium silicate with a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on Gallium oxide, silica sol-gel, and steel pretreated with method 2.....	46

Figure 45. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 3.....46

Figure 46. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 1.....47

Figure 47. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 2.....47

Figure 48. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 3.....48

Figure 49. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 1.....48

Figure 50. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na₂SiO₃ to Na₂SiF₆ coated on Gallium oxide, silica sol-gel, and steel pretreated with method 2.....49

Figure 51. The SE and BSE images of Sample 8 before it was submitted to the corrosion test....49

Figure 52. The SE and BSE image of Sample 8 after it has been submitted to the corrosion test....50

Figure 53. The EDS spectra collected from Sample 8 after the corrosion test.....50

Figure 54. The SE and BSE images of the surface of Sample 9 before it was submitted to the corrosion test.....51

Figure 55. The SE and BSE images of Sample 9 after the corrosion test.....51

Figure 56. The EDS gathered from Sample 9 after the corrosion test.....52

Figure 57. The SE and BSE images of Sample 10 before the corrosion test.....52

Figure 58. The SE and BSE images of Sample 10 after the corrosion test.....53

Figure 59. The EDS spectra of Sample 10 after the corrosion test.....53

ABSTRACT

In this thesis, an attempt is made to develop a three layer coating structures to protect steel against corrosion. The first layer is a silica sol-gel thin film, the second layer is a gallium thin film, and the third layer is a mixture of Na_2SiO_3 and Na_2SiF_6 . The coatings are applied onto carbon steel substrates, with several types of chemical pretreatments. The samples were examined by SEM/EDS for the coatings' interaction between each other and the pretreated steel. Three samples of multi-layer coatings with specifically selected pretreatments were coated with the three layers and subjected to 12 M Hydrochloric acid, and observed to fail the test.

I. Introduction

Carbon steel used in medical and utility applications needs to be protected from corrosion by chemicals such as acid. Corrosion leads to a compromise of the structural integrity and the sterility of steels. Methods have been researched and experimented with to achieve an adequate coating for steels: requiring: the coating material to be chemically inert, able to adhere to the steel, provide full coverage, have mechanical compatibility with the steel at different temperatures, and be feasibly constructed.

A new method of coating steels with multiple layers of glass and ceramic materials to provide corrosion-protection has never been tried before. Multiple layers of different materials can be applied and heat treated to produce a composite covering. Materials that were chosen include silica sol-gel, gallium, and mixtures of Sodium silicate and Sodium hexafluorosilicate. To improve adhesion of the coatings, the samples of steel were selectively polished and treated with Phosphoric acid to produce topography for the enhancement of this interaction.

II. Literature survey

A. Sol-gel Layer

In the past, silica sol-gel methods have been explored as a method of protecting steel from corrosion. Silica sol-gel is a feasible repair material in that it can be consolidated into chemically-inert glass at temperatures below 605°C, the point at which the subject porcelain enamel begins to deform. Silica sol-gel consists of a solution of alcohol, water, acid, and Tetraethyl Orthosilicate (TEOS). Upon evaporation of the alcohols, the silica sol-gel becomes a Xerogel.¹ The surface area of the glass particles in the Xerogel allows for solid glass to be formed from consolidation at 500°C, a much lower temperature than most glasses.²

Methods used for the application of silica sol-gel are dip-coating, spin coating, and roll coating. These methods however are not universally applicable for two reasons. Dip, spin, and rolling coatings are used to produce nanometer-thin coatings of silica sol-gel: applications for silica sol-gel such as process equipment need at least two millimeters of coating.³ The protective coatings for steel would be susceptible to corrosion over long periods of time; a coating nanometers thick would not last numerous lifetimes. The most practical method for the purpose of this paper was to apply the silica sol-gel manually using a pipette.

Silica sol-gel has a problem with cracking due to warping from drying. This is primarily due to volumetric change, and rate of evaporation between the surface and the bulk of the silica sol-gel films.⁴ These cracks make the structure permeable and compromise the repair's integrity. This cracked silica sol-gel cannot be sealed by multiple layers since the cracks only intensify in size with an increase in layers..

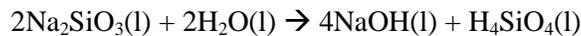
B. Gallium Layer

Different materials can be employed to fill the cracks, making the multi-layer coating impermeable, therefore protecting the underlying steel from corrosion. It is shown in Figure 1 that Gallium metal was chosen to fill the cracks in the silica sol-gel since gallium is a metal which melts at 29°C and may wet the sol-gel. At elevated temperatures the gallium will form a surface layer of Gallium (III) oxide and an FeGa₃ alloy with the steel.^{5 6} Gallium(III) oxide has chemically inert properties, being able to provide some anti-corrosive protection against acid.

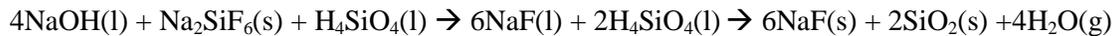
C. Sodium silicate Layer

To further increase corrosion resistance, a layer of Sodium silicate (Na₂SiO₃) mixed with Na₂SiF₆ will be coated on top of the gallium and sol-gel layers, illustrated in Figure 2.⁸ Na₂SiO₃ can react with Na₂SiF₆ hardening agent to create a strong glass according to the chemical reaction in Equation 1.

Eq(1). The Sodium silicate solution begins to React:



The Sodium hexafluorosilicate is added:



The NaF becomes locked within the SiO₂ structure and strengthens the SiO₂ bonds while the water vapor becomes expelled through bubbles. The Na₂SiO₃ and Na₂SiF₆ must be mixed in a weight ratio of 1:0.289 grams to achieve the 2:1 molar ratio. Two other ratios: 1:0.28 and 1:0.30 grams should be produced and experimented with to see if too much or too little Sodium hexafluorosilicate hardening agent would aid the Sodium silicate's corrosion resistance. Adding too much Na₂SiF₆ might increase the chemical bond

strength in the Sodium silicate or accelerate the reaction in Equation 1 detrimentally; and too little Na_2SiF_6 would avoid accelerated chemical reaction but a weaker Sodium silicate might result.^{9 10}

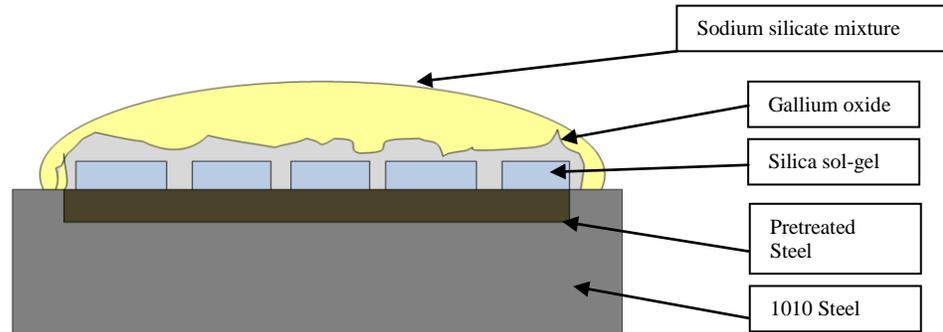


Figure 1. is a cross-sectional schematic of the steel substrate with chemical pretreatment and coatings.

D. Iron phosphate

Silica sol-gel exhibits the behavior to delaminate from the metal's surface upon drying due to volumetric changes; liquid gallium and Sodium silicate exhibit difficulty in adhering to metal surfaces as well. To improve the adhesion of these materials, the steel can be polished using a pneumatic grinder, cleaned with ultrasonication and chemically-treated with phosphoric acid. Phosphoric acid creates holes in steel and Iron phosphate is formed by the reaction of the phosphoric acid with the steel as seen in Equation 2.

Eq(2). The Phosphoric acid reacts with the Iron



Iron phosphate crystals can provide an anti-corrosive layer on the steel and create an environment to enable the silica sol-gel and gallium to bond to the steel.¹¹

E. Corrosion Tests

Corrosion tests were conducted to observe the performance of the three layers of material together as repair technique. The corrosion tests were in conformance with ASTM G48.1.1.2.¹² This method employs 12 M HCl to test the pitting and corrosion resistance of steel at room temperature in a ferric chloride environment. The coatings applied for the repair must be able to withstand this test.

III. Experimental Procedure

A. Sample Preparation

1. Drilling and Polishing

1010 steel discs 12.5 centimeters in diameter were drilled with resulting in areas on the steel free of rust 12.5 millimeters in diameter. To create a flat topography these holes were polished with a 3M alumina pneumatic die grinder with 22,000 grit, at a 45° angle.

2. Cleaning and Chemical Pretreatment

Figure 3 is a schematic which shows how the discs are pre-treated in different locations with the three pre-treatment methods. After being drilled and polished, the discs were cleaned by ultrasonicated them for 10 minutes in 70% Isopropyl alcohol (IPA) and dried using compressed air. In Figure 3, the drilled and polished spots designated as those pretreated by method 1 were covered with 4 vol% Phosphoric acid for 10 minutes, ultrasonicated in 70% IPA for ten minutes, and dried with compressed air. The spots pretreated by method 2 were coated with 4 vol% Phosphoric acid for five minutes, ultrasonicated in 70% IPA for ten minutes, dried with compressed air, coated with 4 vol% Phosphoric acid for 20 minutes, rinsed with deionized water, and dried with compressed air. The areas designated as pretreated with method 3 had no exposure to Phosphoric acid but were ultrasonicated in 70% IPA for ten minutes a second time.

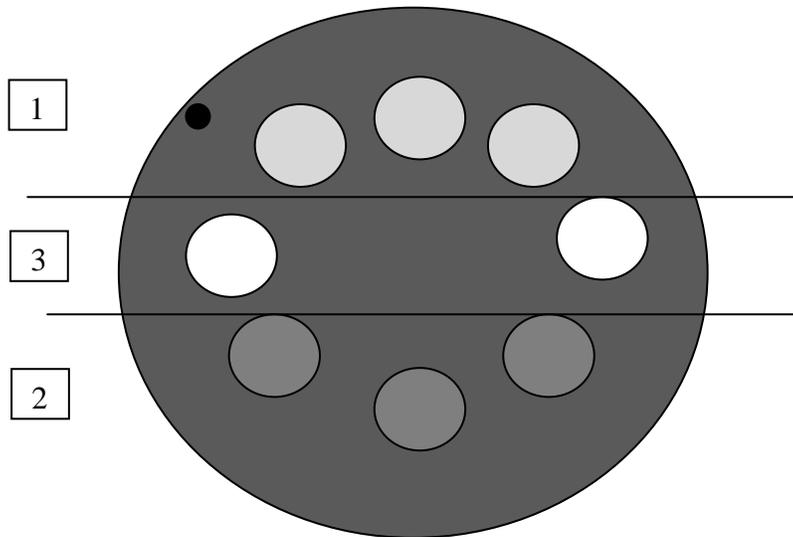


Figure 2. Is a schematic of the steel disc with eight spots used for Samples 3 through 7. The top spots are chemically pre-treated with method 1. The middle two spots are treated with method 3. The bottom three spots are treated with method 2.

B. Sample 1.

Sample 1 was drilled and polished and received chemical pretreatment method 3.

C. Sample 2.

Sample 2 was given the chemical pretreatment methods 1 and 2.

D. Sample 3.

Sample 3 was a disc given the chemical pretreatment and each spot was given a drop of silica sol-gel via pipette. After drying, the disc was fired at 500°C for one hour according to the heat treatment schedule seen in Figure 1.

The silica sol-gel was purchased from Chemat Technology, Inc. under the product name SIO 03 (SiO₂ coating solution). Its composition consisted of 39.4 wt% TEOS (Si(OC₂H₅)₄), 46.5 wt% Isopropanol (C₃H₈O), 13.4 wt% Water (H₂O), and 0.7 wt% Hydrochloric acid (HCl) obtaining a pH ranging from 7 to 7.5.

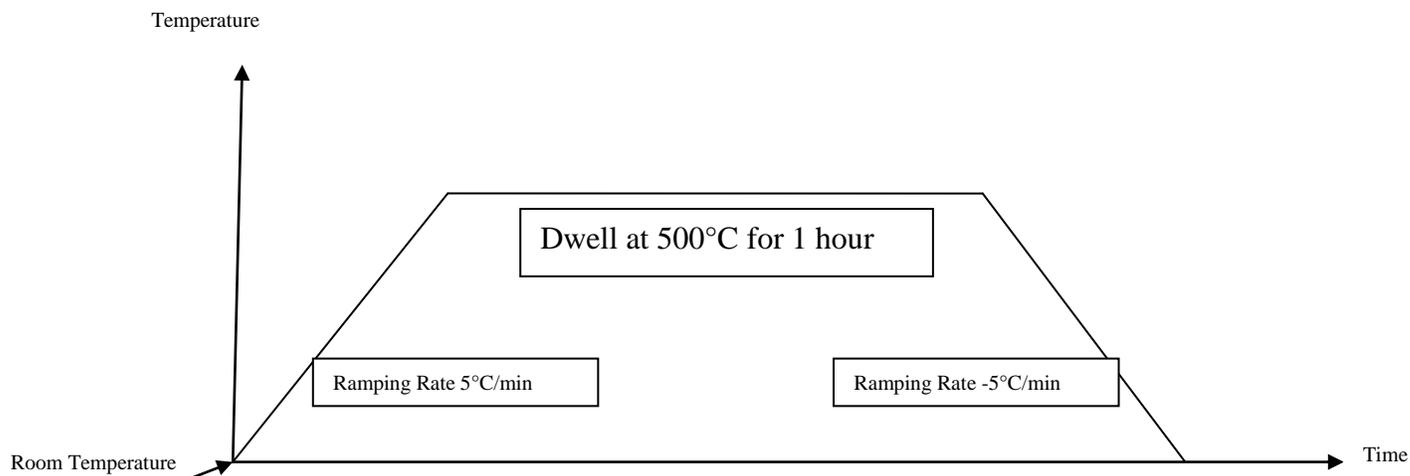


Figure 3. is the schedule for the heat treatment of the Samples 3, 4, and 5.

E. Sample 4.

Sample 4 was a disc given chemical pretreatment and each hole was administered liquid gallium metal with a cotton cloth, smeared in a circular motion for three seconds. The gallium-covered disc was fired at 500°C for one hour according to the same heat treatment schedule used in Figure 3.

The gallium used was an ingot purchased from Alfa Aesar with a purity of 99.99% gallium.

F. Sample 5.

Sample 5 was a disc given chemical pretreatment and each hole was given one drop of silica sol-gel via pipette. After drying, the disc was fired according to the schedule in Figure 3. Upon reaching room temperature the disc was given liquid gallium via cotton cloth by a similar circular rubbing motion used on Sample 4. The disc was fired according to the heat treatment schedule in Figure 3.

G. Sample 6.

Sample 6 was a disc given chemical pretreatment then coated with the mixture of Na_2SiO_3 and Na_2SiF_6 in ratios of 1:0.28, 1:0.289, and 1:0.3 distributed in single drops

according to the design in Figure 4. After heat treatment according to the heat treatment schedule in Figure 5, the sample was observed through the ESEM to witness how the Sodium silicate interacted with the untreated and chemically-treated steel.

The Na_2SiO_3 was purchased from The Science Company and the Na_2SiF_6 was purchased from Aldrich.

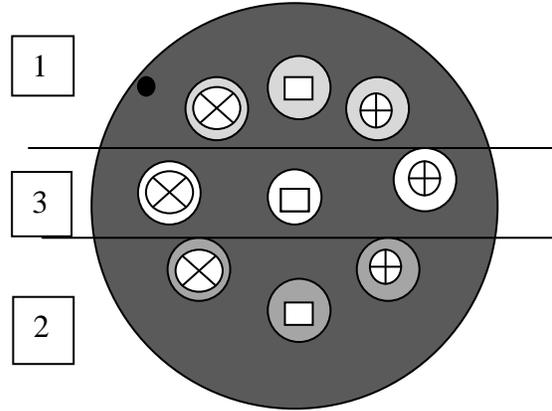


Figure 4. Is the schematic diagram of how the Sodium silicate mixtures were distributed in Samples 6 and 7. The spots marked with “X” are coated with a Na_2SiO_3 to Na_2SiF_6 ratio of 1:0.28. The spots marked with squares are coated with a ratio of 1:0.289, and the spots marked with crosses are coated with a ratio of 1:0.3.

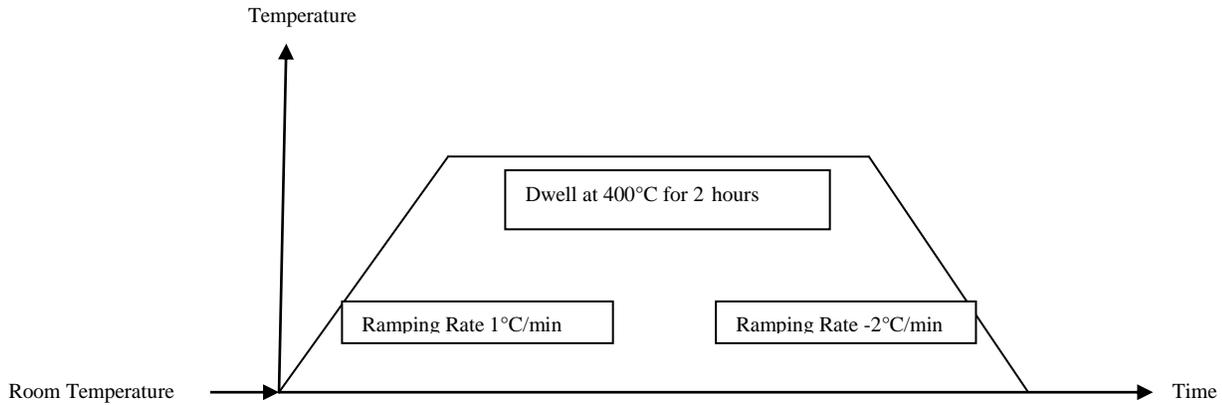


Figure 5. is the heat treatment schedule for Samples 6, 7, as well as the heat treatment for the water glass coatings on Samples 8, 9, and 10.

H. Sample 7.

Sample 7 was a disc given the chemical pretreatment, and heat treated layers of silica sol-gel and gallium consecutively. Mixtures of Sodium silicate with ratios of Na_2SiO_3 to

Na_2SiF_6 being 1:0.28, 1:0.289, and 1:0.30 were distributed in single drops across the sample according to Figure 5. After being cured at 55°C for 24 hours on a hotplate, the samples were heat treated in a furnace according to the schedule in Figure 5 and observed with the ESEM to record how Sodium silicate interacts with silica sol-gel and gallium.

I. Corrosion Testing

After Samples 1-7 were observed, the optimum chemical-pretreatment method was chosen for Samples 8-10. These next samples were polished, cleaned, and the target spots were pretreated with Method 2. The treated samples were then given heat-treated layers of silica sol-gel and gallium, and then given coatings of Sodium silicate two millimeters thick, entirely covering the holes in the enamel. Sample 8 was given a Sodium silicate mixture of Na_2SiO_3 and Na_2SiF_6 in a ratio of 1:0.28, Sample 9 was given a ratio of 1:0.289, and Sample 10 was given a ratio of 1:0.30. The samples were then fired again according to the heat treatment schedule in Figure 3, further explained in the Results section of this paper. The samples were photographed using the ESEM to record their status before the corrosion test was conducted.

The corrosion test consisted of using Silicone rubber to seal hollow tubes of polyurethane to the coated holes in the three discs. The silicone was left to cure for the prescribed 24 hours and then 1mL of 12 M HCl was poured into each of the tubes which were sealed with plastic caps. The tubes remained this way for four hours until the acid was extracted using pipette and the opened tubes on the samples were left to dry under the chemical hood for 12 hours. The samples were then observed again with the ESEM.

The Hydrochloric acid was purchased from Alfa Aesar and the Silicone was purchased from DAP Products Incorporated.

IV. Results and Discussion

A. Chemical Pretreatment, Sample 1

The pneumatic polisher created a mostly flat topography on the exposed steel surface of Sample 1 seen in Figure 6. Microscopic scratches (1-3 μm wide) covered the surface, with embedded grains of alumina particles (1 μm in diameter as seen in Figure 7) from the alumina grinder. The steel, however, did contain trenches from the drill, which were millimeters in width and unable to be removed by polishing.

B. Chemical Pretreatment, Sample 2

Chemical pretreatment methods 1 and 2 create holes in the polished metal and deposit crystals of Iron phosphate within them, presented in Figure 8. A comparison of Figures 9 and 10 shows how pretreatment method 1 creates more shallow pits and smaller colonies of phosphate crystals than pretreatment method 2 which allowed greater time for the Phosphoric acid to react with the steel and not be removed by ultrasonication with IPA.

C. Silica Sol-gel on Steel, Sample 3

Before Firing

On polished and clean steel from pretreatment method 3, the silica sol-gel cracks and delaminates extensively. The silica sol-gel does conform to the steel's surface upon drying and some pieces of steel do adhere to the sol-gel, observed on upside down flakes of which broke off in Figure 11. However, the flat surface does not provide suitable anchorage to prevent significant amount of sol-gel loss.

For steel that is polished and chemically pretreated by both methods 1 and 2, the silica sol-gel cracking is observably much more extensive but the delamination and loss

of the coating is significantly less than steel that was not pretreated: the comparison of the three methods can be seen in Figure 14. The cracking is more frequent due to the sol-gel anchoring itself to the microscopic holes and Iron phosphate crystals in the surface of the steel, visible in Figures 12 and 13, during the volume change which occurs during drying. It is observed that in deep crevices from cold-working the silica sol-gel adheres less due to possible contamination. In the recesses of the steel, contamination is harder to remove by ultrasonication.

After Firing

After the sample was fired, the silica sol-gel on the steel pretreated by method 3 delaminated considerably. At the microscopic level, the sol-gel was observed to have difficulty adhering to the steel deformed from the 500°C temperature of firing, seen in Figure 15. For the steel pretreated by methods 1 and 2 in Figures 16 and 17, the delamination was less but the sol-gel still deformed considerably. The silica sol-gel applied and fired on the metal treated by method 2 deformed and delaminated less than on the steel pretreated by the other two methods. From Figure 18, pretreatment method 2 proves to be the most effective in adhering the sol-gel to steel after it has been fired, due to the increased amounts of holes and phosphate crystals present in the steel, the interaction of which is seen in Figure 17.

D. Gallium on Steel, Sample 4

Before Firing

The gallium metal exhibits wetting behavior when applied to the steel after it has been pre-treated by methods 1, 2, and 3. A comparison of Figure 19 (pretreatment method 3) with Figure 20 and 21 show that the steel that was not treated with Phosphoric

acid has less capability for gallium to adhere to it. The holes and Iron phosphate crystals from pre-treatment methods 1 and 2 enhance the wetting of the gallium (Figure 22). However all three methods fail to obtain gallium adhesion to recesses produced by the grinding process (ranging from 0.05 to 1mm in width) because the bottoms and sides of these recesses could not be contacted by the gallium during its application of gallium with a cotton cloth.

After Firing

Evident in all three pretreatment methods in Figures 23, 24, and 25, after firing the discs at 500°C for 1 hour the gallium on the steel was converted into Gallium (III) oxide, with grains 0.5 to 3 μm in diameter. More Gallium oxide can be detected by backscatter electrons for steel pretreated by methods 1 and 2 than method 3 (Figure 26). In the SE and BSE images of the steel pretreated with all three methods, the gallium oxide is thinner on the peaks created by the polishing method and thicker in the troughs. This behavior is due to the sideways motion of the cotton cloth when it applied the liquid gallium metal; the microscopic troughs captured the wetting gallium while the tips of the peaks didn't have enough flat surface area for much gallium to adhere to.

E. Gallium applied on Sol-gel, Sample 5

Before Firing

The gallium coated on sample 5 adheres to the silica sol-gel coatings at microscopic levels. Entire coverage of the silica sol-gel by the gallium metal was not obtained for any of the three pre-treatment methods. This was a result of the application of the liquid gallium, the force of which detached the fired sol-gel coating from the steel. Much of the silica sol-gel coated on metal pre-treated by method 3 was broken off by the

gallium being applied. This case was less severe for method 1 and 2 with much greater adhesion by the sol-gel withstanding the gallium application.

When the gallium had silica sol-gel to be applied upon it adhered considerably to the steel pretreated by methods 1 and 2 in comparison with the steel pretreated by method 3, in Figure 30. The gallium is capable of filling some of the cracks present in the layer of sol-gel. Topography was previously observed to provide adhesion problems for the liquid gallium. Similar to the deep recesses in the steel, some of the cracks in the silica sol-gel prove to be difficult for the liquid gallium to reach during its application. In some places on Sample 5 where detached chips laid upside down upon the surface in Figures 27, 28, and 29, the underside of the silica sol-gel was covered even more by the gallium from pieces of steel and Iron phosphate crystals clinging to the underside of the sol-gel and/or these broken flakes remained stuck to gallium-covered cloth for longer periods of time before being deposited on the surface.

After Firing

The gallium converted into Gallium oxide after firing just like Sample 4. Figure 31 shows how one of the spots pretreated by method 3 and coated with silica sol-gel had Gallium oxide along with bits of gallium which did not oxidize, while some of the cracks remained unfilled. Figures 32 and 33 of the spots where pretreatment methods 1 and 2 were used in conjunction with sol-gel had gallium which melted during the firing process and filled the cracks. This was the case much more with steel pretreated by method 2: In Figure 33, the gallium that was sitting on top of the plates of silica sol-gel melted and spilled into the micrometer-wide cracks and oxidized. Figure 34 shows the improvement

in coverage of Gallium oxide for steel that was pretreated by methods 1 and 2 as opposed to method 3.

F. Sodium silicate on Sample 6

Structure

The Sodium silicate on Sample 6 has the same bubbled and cracked structure with the three different compositions and the three differently pretreated steel surfaces beneath them. The only difference between the nine cases was their adhesion to the steel, as a result of the pretreatment methods 1, 2, and 3.

1:0.28

The Sodium silicate with composition ratio 1:0.28 of Na_2SiO_3 to Na_2SiF_6 adhered well to steel that was pretreated by methods 1 and 2, as seen in Figures 35 and 36. However the Sodium silicate did not adhere to the steel that had no Phosphoric acid pretreatment and it detached before an ESEM picture could be taken.

1:0.289

The Sodium silicate with composition ratio 1:0.289 of Na_2SiO_3 to Na_2SiF_6 adhered to the steel pretreated by methods 1 and 2 (in Figures 30 and 31) similarly to the 1:0.28 ratio Sodium silicate mixture. This batch of Sodium silicate did not adhere to the steel pretreated by method 3 and fell off before an ESEM picture was taken.

1:0.30

The Sodium silicate with composition ratio 1:0.30 of Na_2SiO_3 to Na_2SiF_6 adhered to the steel pretreated by methods 1 and 2, in Figures 40 and 41. This is similar to the other two batches of Sodium silicate pretreated by these methods. The Sodium silicate does not adhere to steel pretreated by method 3 in Figure 39. The Sodium silicate only

remained resting on the surface of the steel long enough for it to be analyzed by the ESEM.

G. Sodium silicate on Sample 7

Structure

The three Sodium silicate compositions on Sample 7 have the same bubbled and cracked structures over all three differently treated steel surfaces by methods 1, 2, and 3. The three separate Sodium silicate compositions on the pretreated steel surfaces also bear resemblance to the Sodium silicate coatings on Sample 6. The only difference noted was that all the Sodium silicate coatings adhered to the steel surfaces pretreated by method 3 on Sample 7 whereas this wasn't the case for Sample 6. The coatings of silica sol-gel and Gallium oxide were adhered to by the Sodium silicates on the pretreated steel spots.

1.0:0.28

The Sodium silicate with a composition ratio 1:0.28 of Na_2SiO_3 to Na_2SiF_6 adhered well to steel that was pretreated by methods 1, 2, and 3 as seen in Figures 42, 43, and 44, respectively. The Sodium silicate covered and even conformed to the structure of the exposed silica sol-gel and the gallium oxide. The sodium silicate was wetted by the excess gallium which had been pushed out from underneath the coating due to its liquid expansion during firing at 400°C.

1.0:0.289

The Sodium silicate with a composition ratio 1:0.289 of Na_2SiO_3 to Na_2SiF_6 adhered well to steel that was pretreated by methods 3, 1, and 2 as seen in Figures 45, 46, and 47. Similar to the 1.0:0.289 Sodium silicates, these coatings conformed and adhered

to the structure of the exposed silica sol-gel and Gallium oxide. The Sodium silicate also experience excess gallium metal forced out from beneath the coatings.

1.0:0.30

The Sodium silicate with a composition ratio 1:0.289 of Na_2SiO_3 to Na_2SiF_6 adhered to the pretreated steel shown in Figures 48, 49, and 50. Similar to the 1.0:0.289 and 1.0:0.30 mixtures of Sodium silicate, these coatings conformed and attached to the structure of the exposed silica sol-gel and Gallium oxide. Excess gallium metal didn't remain underneath this layer, similar to the other two sodium silicate compositions, on Sample 7.

H. Corrosion Testing

Choosing the Optimum Chemical Pretreatment

Based on the results from Samples 1-7, the pretreatment method for Samples 8, 9 and 10 was chosen to be method 2 to obtain the greatest adhesion and uniform coverage of silica sol-gel, gallium, and Sodium silicate. Pretreatment method 2 obtained the highest amount of sol-gel adhesion before and after gallium was applied in Samples 3 and 5; it enabled gallium to adhere to steel before and after it was oxidized by firing in samples 4 and 5. Parts of steel remaining uncovered by silica sol-gel and Gallium oxide on steel pretreated by method 2 (for Samples 6 and 7) allowed adhesion by all three batches of the Sodium silicate.

Once the Samples were coated with silica sol-gel, gallium, and Sodium silicate then heat treated, it was observed in the case of Samples 8, 9, and 10 that excess gallium metal (which hadn't oxidized) tried to come up from beneath the foamed Sodium silicate, through capillary action in pre-existing holes within the Sodium silicate. The state of the

multilayer coatings in Samples 8, 9, and 10 are presented in Figures 51, 54, and 57 after they were fired according to the heat treatment schedule in Figure 3 which was meant to oxidize the excess gallium.

After Corrosion Tests

Samples 8, 9, and 10 all failed to stop corrosion of the metal. Gallium chloride, Sodium chloride, and Iron chloride became present on the multi-layer coating surface after the Hydrochloric acid test took place. For example, Sample 9 reacted with the acid producing a Chloride surface layer (Figure 55), the EDS spectra in Figures 56 and 59 indicate that the layer found on this Sample 9 and Sample 10 is composed of Gallium chloride, Iron chloride, and cube-like crystals of Sodium chloride. The Sodium chloride was produced by the sodium in the Sodium silicate reacting with the HCl, depositing the cubic crystals on the surface. The dissolving of the Sodium silicate in Samples 8, 9, and 10 caused the collapse of areas in the Sodium silicate where there were previously large concentrations of bubbles (hundreds of microns in diameter) as a result of heat treatment at 400°C. One of these collapsed structures can be seen from Sample 10 in Figure 58. The Gallium chloride originated from the HCl reacting with gallium that had been underneath the thinner parts of the Sodium silicate. The HCl had reached down to the steel and created Iron chloride, which is present in the spectra from Figure 56. Sample 8 (Figure 45) reacted similarly with the Hydrochloric acid but the EDS spectra in Figure 53 did not indicate any presence of iron. The gallium veins present in the Sodium silicate layer reacted with the acid, and it is unknown if the acid made contact with the steel while not producing enough iron to be detected.

V. Conclusions

Chemical pretreatment method 2 performed optimally for preparing the steel substrate to be adhered to by silica sol-gel, gallium and Sodium silicate, creating a composite coating for the steel. The multi-layer method did not prevent corrosion of the steel that was meant to be protected by the porcelain enamel. The concentrated structures of bubbles in the Sodium silicate partially dissolved in the corrosion test allowing for gallium (present in veins throughout the Sodium silicate) to make contact with the Hydrochloric acid. The application of too much gallium resulted in these veins of excess gallium which were not turned into Gallium oxide upon firing, before the Sodium silicate was applied and heat treated. The acid reacted with the gallium and then the steel itself, creating a contaminated surface on the multi-layer coating, unsuitable for use. The greatest contributing factor to the failure of the multi-layer method was the excess gallium in between the silica sol-gel and Sodium silicate layers.

VI. Suggestions for Future Work

Other methods which should be explored to optimize the multi-layer coating are diluting the silica sol-gel with IPA to create thinner layers, which may crack less. The amount of cracking may also be reduced by modifying the drilling and polishing process to produce shallower recesses. The application process for the gallium metal should be changed to produce a thinner layer of gallium (in the range of microns) that can easily be entirely oxidized. This can be accomplished by preheating the samples to 29.8°C (gallium's melting point) and gently applying the gallium to the warm metal in order to reduce the amount of delaminated silica sol-gel and prevent millimeter wide beads of gallium from remaining on the surface.

More compositions of Sodium silicate should be created and tested in conjunction with the preliminary coatings, using higher amount of Sodium hexafluorosilicate to strengthen the Sodium silicate. The heat treatment must also be modified to minimize the amount of bubbles created in the structure.

More tests should be conducted to determine if the multi-layer coating would adequate for different applications. Tests for qualities such as thermal shock resistance, elastic modulus, compressive strength, and corrosion tests involving salt-spraying and boiling Hydrochloric acid would attest to the performance of the coating in the field.

VII. APPENDIX

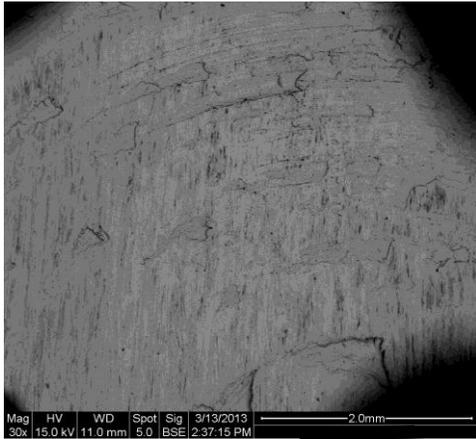


Figure 6. is the BSE image of Sample 1, the surface has been polished and prepared using pretreatment Method 3.

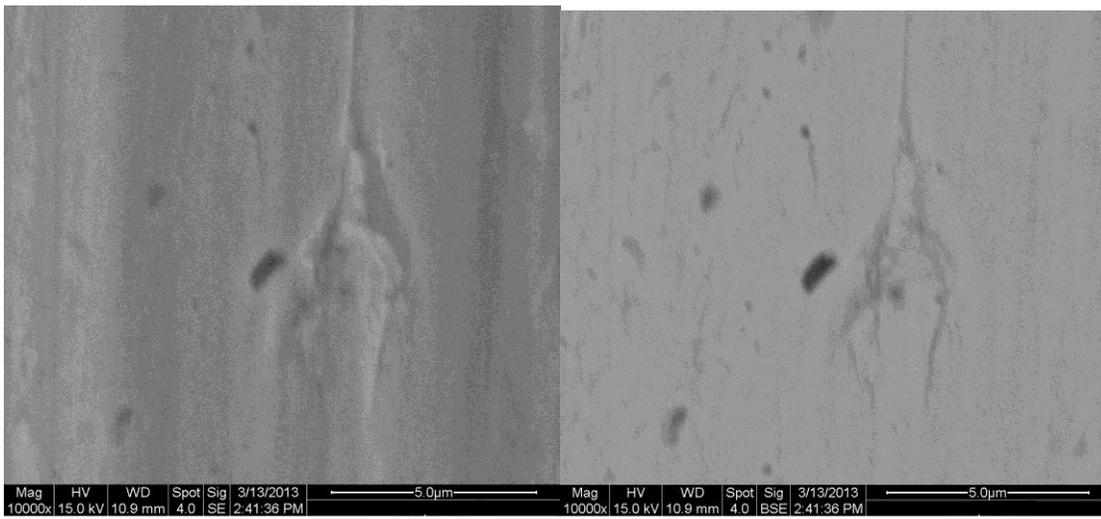


Figure 7. The SE and BSE images of Sample 1 where the steel has been polished and cleaned with pretreatment method 3. The dark crystals present are left from the pneumatic grinder which used alumina crystals.

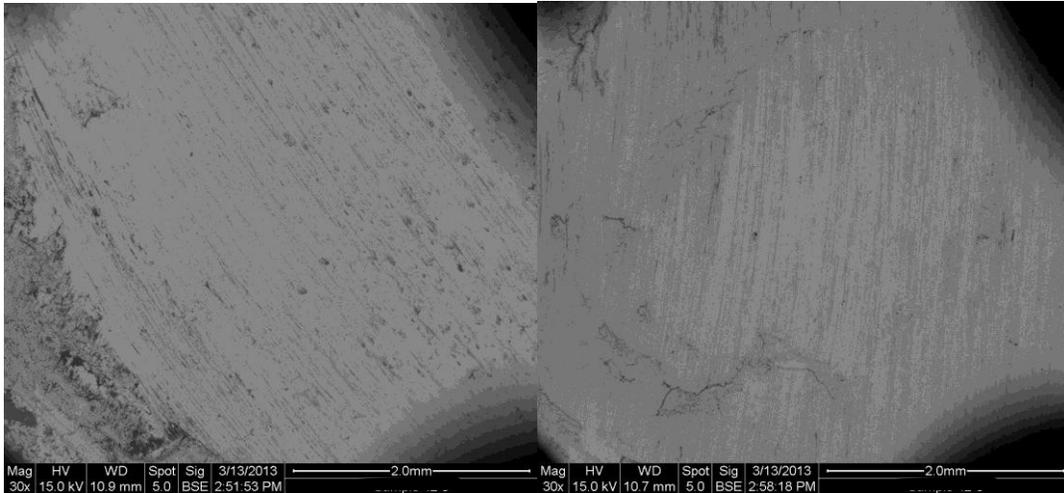


Figure 8. is the BSE images of Sample 2. The Left image is of steel that was pretreated with Method 1 and the right image is of steel pretreated by Method 2.

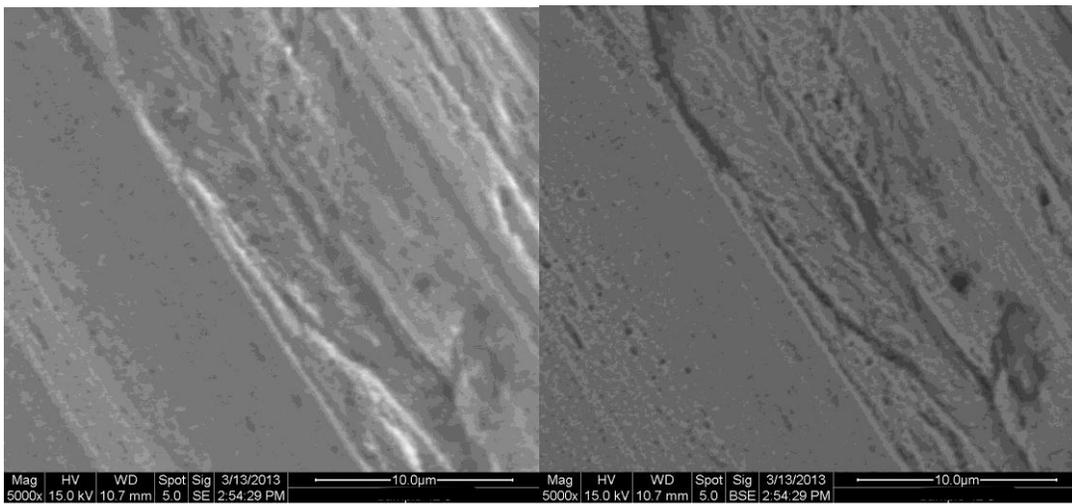


Figure 9. The SE and BSE images of Sample 2 where the steel has been polished, cleaned, and chemically pretreated by method 1. Crystals of iron phosphate coat the surface from the phosphoric acid.

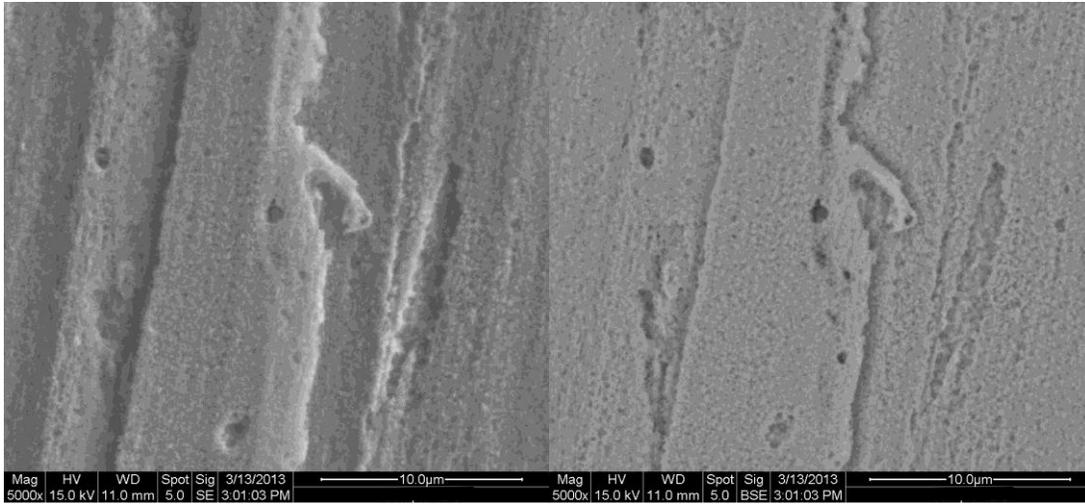


Figure 10. The SE and BSE images of Sample 2 where the steel has been polished, cleaned, and chemically pretreated by method 2. Crystals of iron phosphate coat the surface from the phosphoric acid.

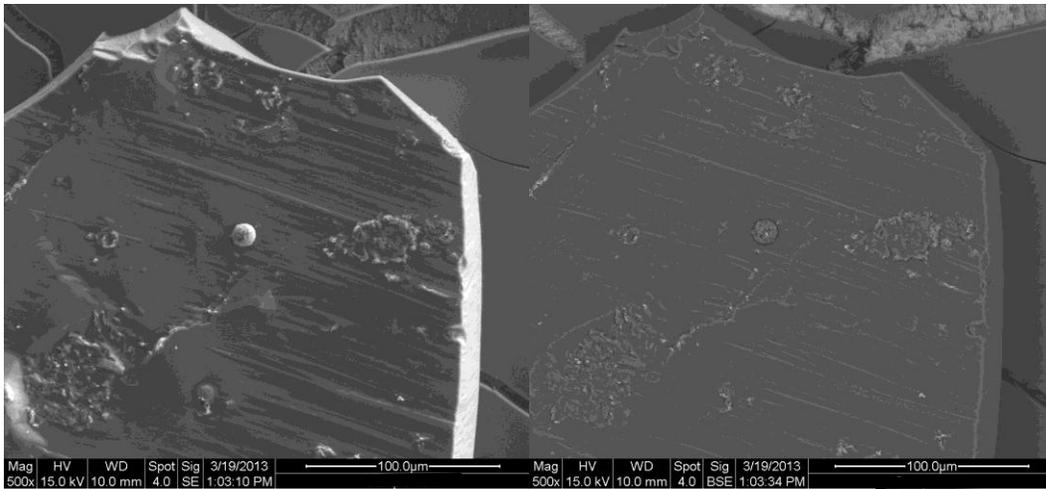


Figure 11. The SE and BSE images of Sample 3 where the steel has been chemically pretreated by method 3. The silica sol-gel on the sample is cracked and adheres to the steel. A flipped over piece of sol-gel shows the adherence of the sol-gel to the steel, pieces of which still cling to it.

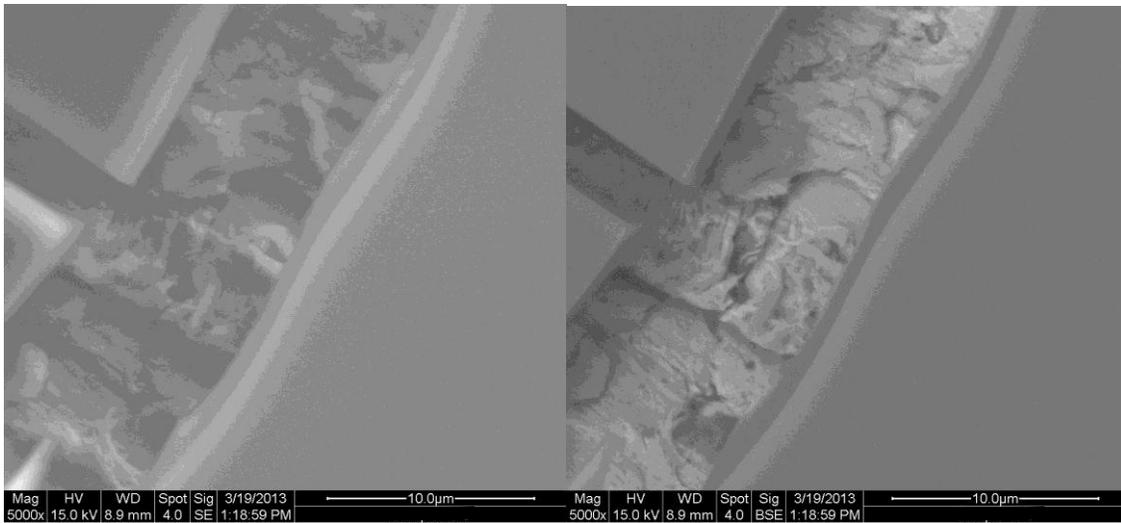


Figure 12. The SE and BSE images of Sample 3 where the steel has been pretreated by method 1. Silica sol-gel adheres to the steel and phosphate crystals.

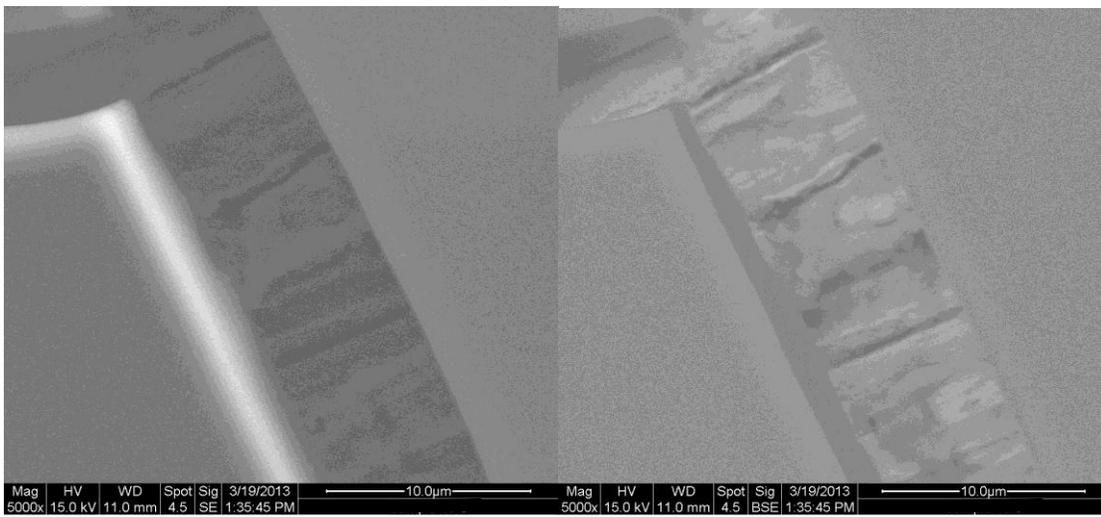


Figure 13. The SE and BSE images of Sample 3 where the steel has been pretreated by method 2. Silica sol-gel adheres to the steel and phosphate crystals.

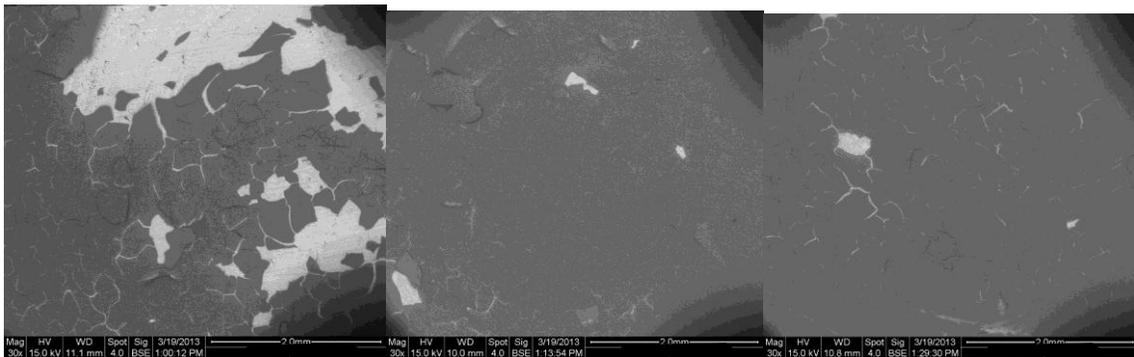


Figure 14. is the BSE images of Sample 3 where the steel was pretreated with Method 3 (Left), 2 (Middle), 1 (Right). The steel was then coated with silica sol-gel.

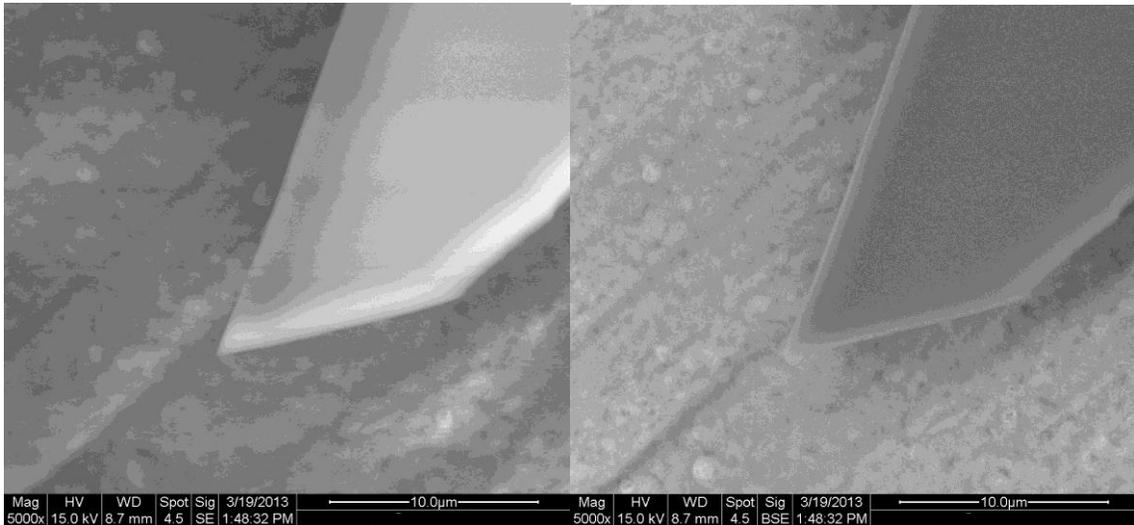


Figure 15. The SE and BSE images of Sample 3 where the steel has been pretreated with method 3. The silica sol-gel remains partially adhered to the steel after it has been fired.

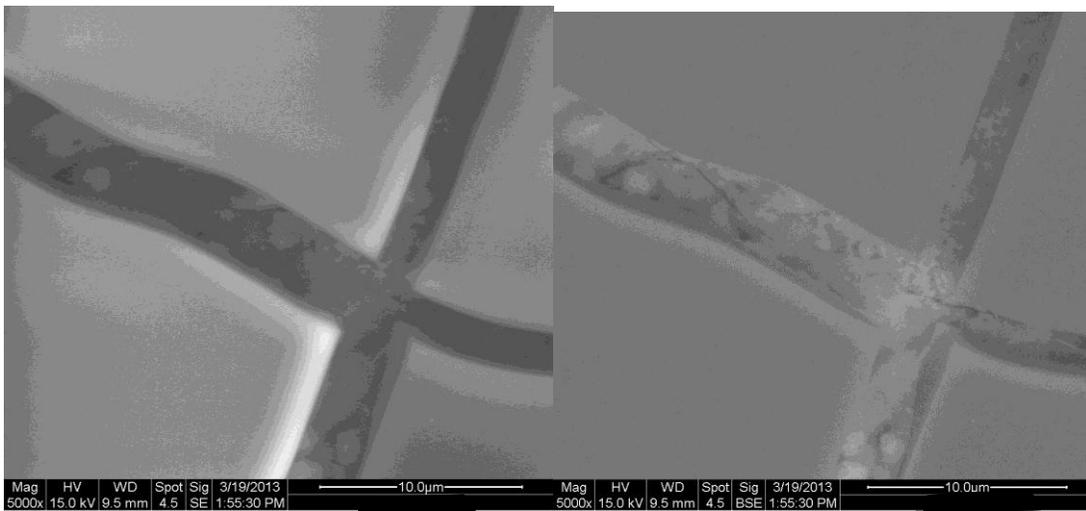


Figure 16. The SE and BSE images of Sample 3 where the steel has been pretreated with method 1. The silica sol-gel remains adhered to the steel and crystals of Iron phosphate after it has been fired.

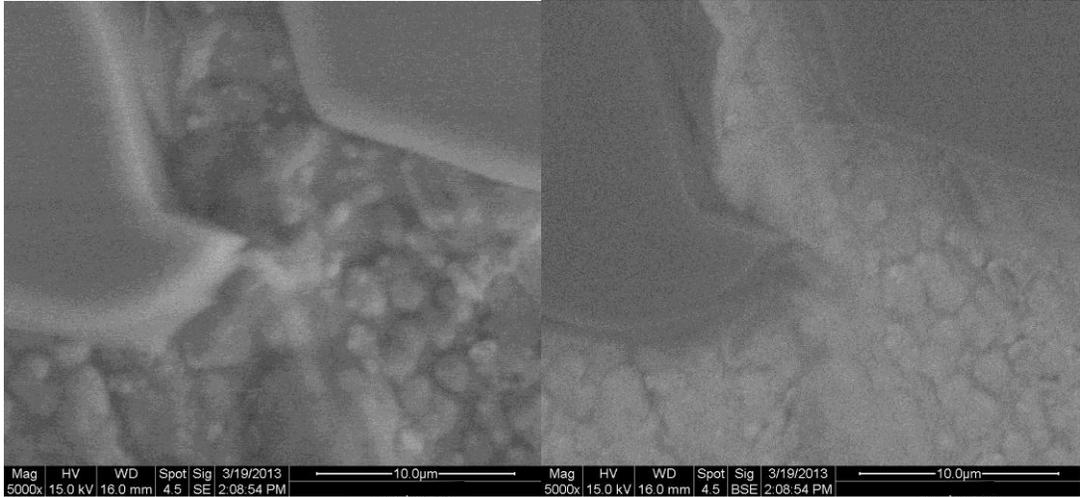


Figure 17. The SE and BSE images of Sample 3 where the steel has been pretreated with method 2. The silica sol-gel remains adhered to the steel and crystals of Iron phosphate after it has been fired.

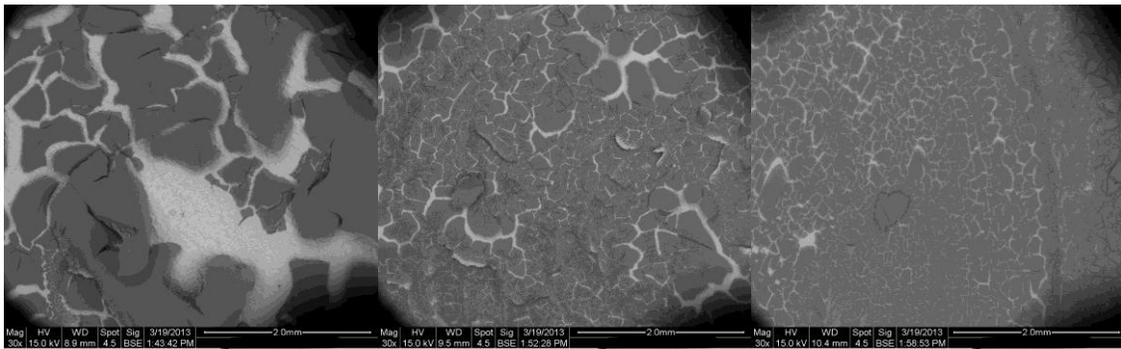


Figure 18. is the BSE images of Sample 3 where the steel had been pretreated with Method 3 (Left), 2 (Middle), 1 (Right). After the steel was then coated with silica sol-gel it was fired at 500°C.

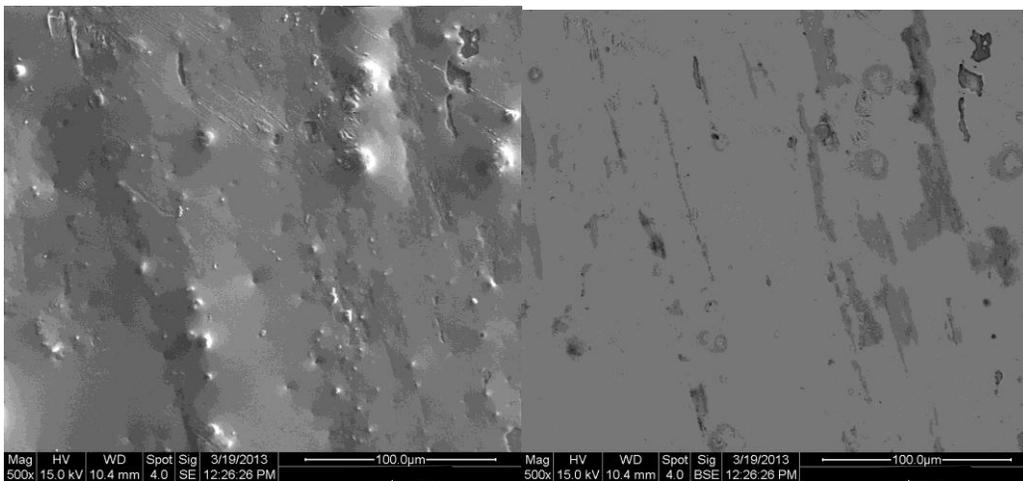


Figure 19. The SE and BSE images of Sample 4 where the steel was chemically pretreated with method 3. Gallium was coated on the surface with chunks of gallium metal that partially solidified during the application of the liquid metal.

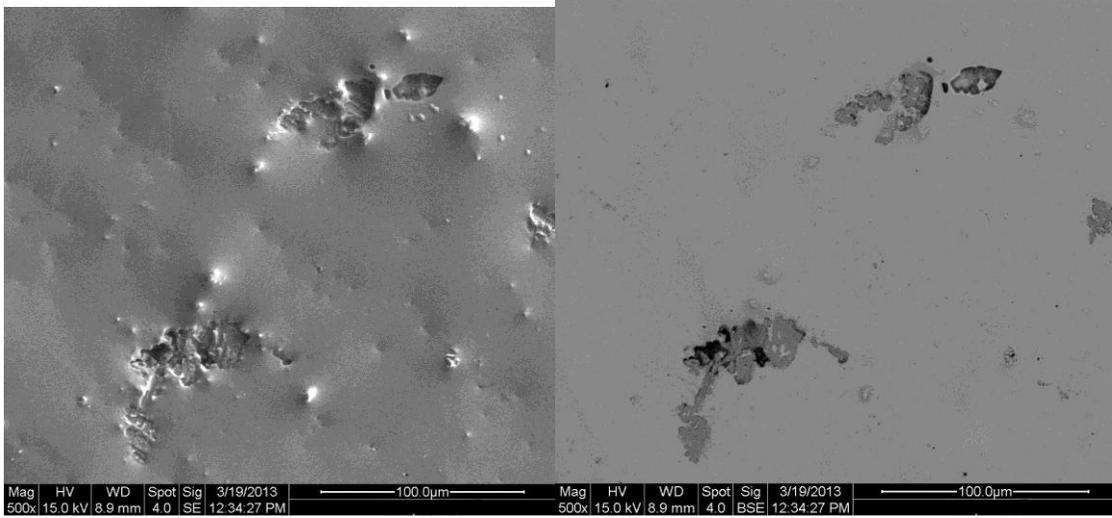


Figure 20. The SE and BSE images of Sample 4 where the steel was chemically pretreated with method 1. Gallium was coated on the surface and it is seen here adhering to the surface.

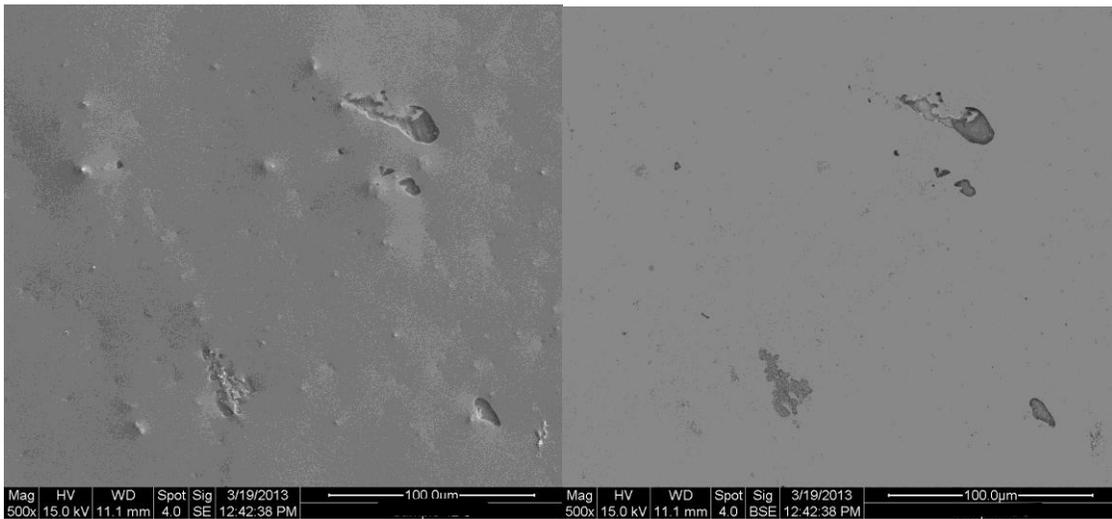


Figure 21. The SE and BSE images of Sample 4 where the steel was chemically pretreated with method 2. Gallium was coated on the surface and it is seen here adhering to the surface.

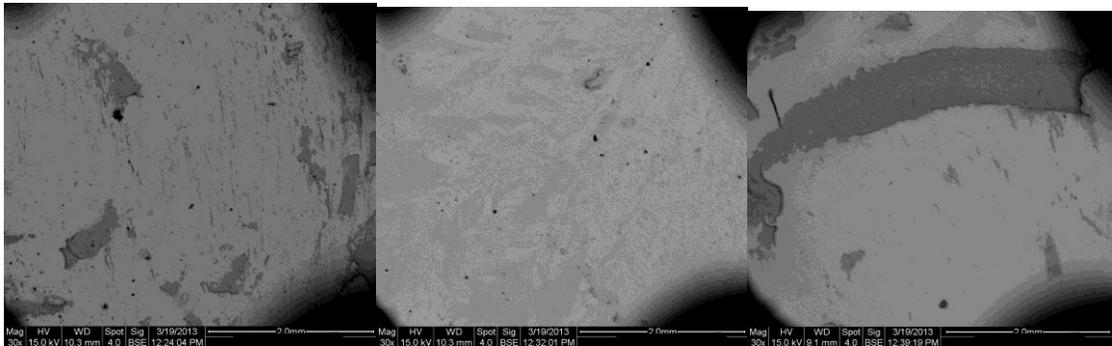


Figure 22. is the BSE images of Sample 4 where the steel was pretreated with Method 3 (Left), 2 (Middle), 1 (Right). The steel was then coated with liquid gallium metal.

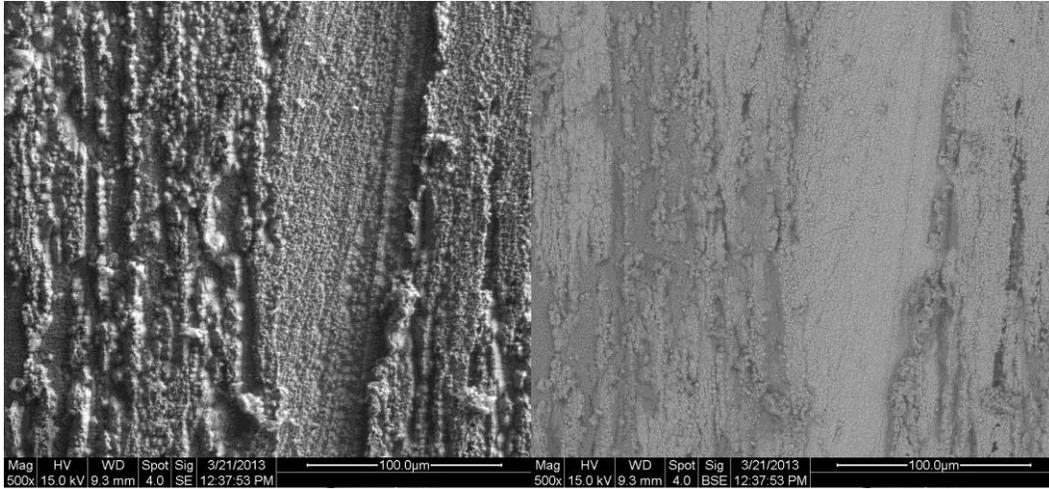


Figure 23. The SE and BSE images of Sample 4 where the steel has been pretreated with method 3. The gallium coated on the surface was fired, creating Gallium oxide.

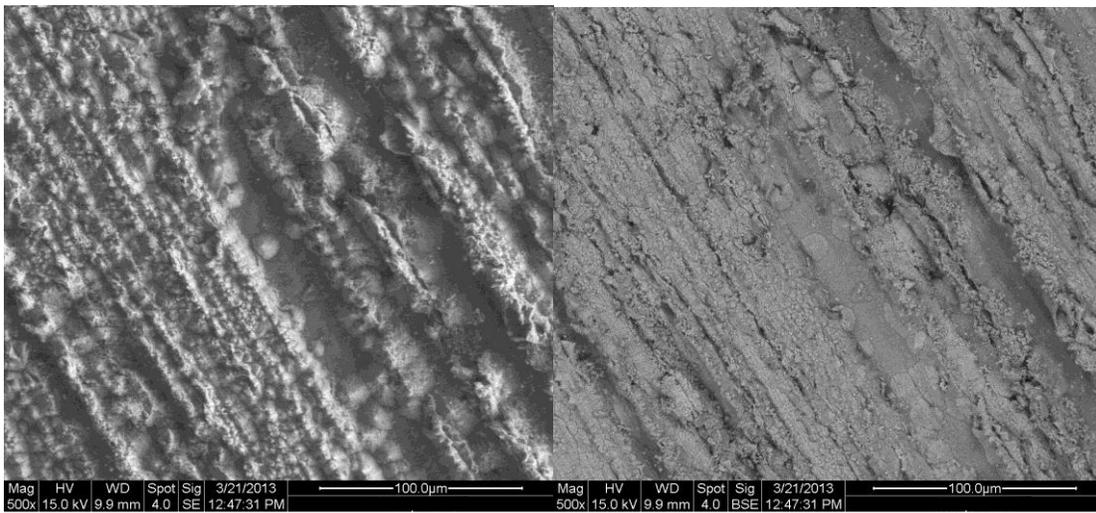


Figure 24. The SE and BSE images of Sample 4 where the steel has been pretreated with method 1. The gallium coated on the surface was fired, creating Gallium oxide.

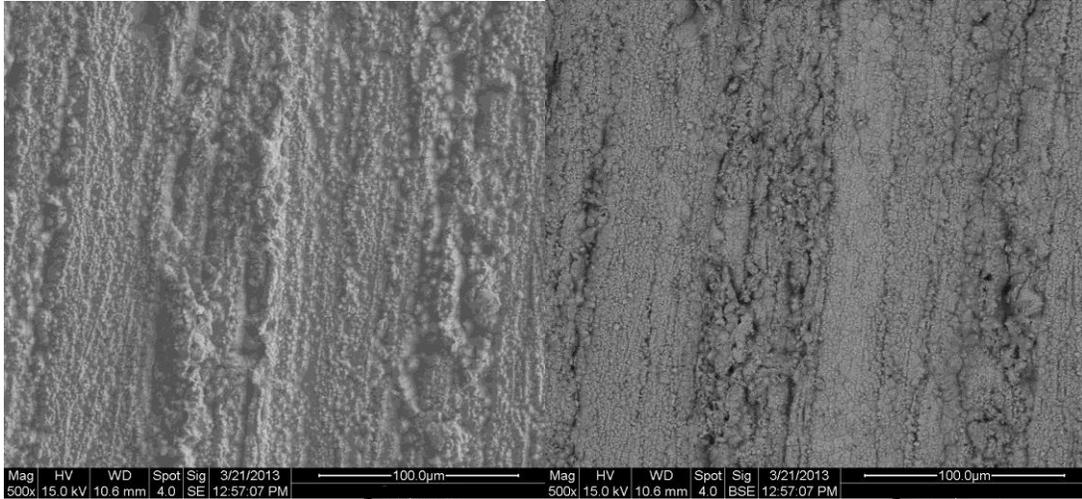


Figure 25. The SE and BSE images of Sample 4 where the steel has been pretreated with method 2. The gallium coated on the surface was fired, creating Gallium oxide.

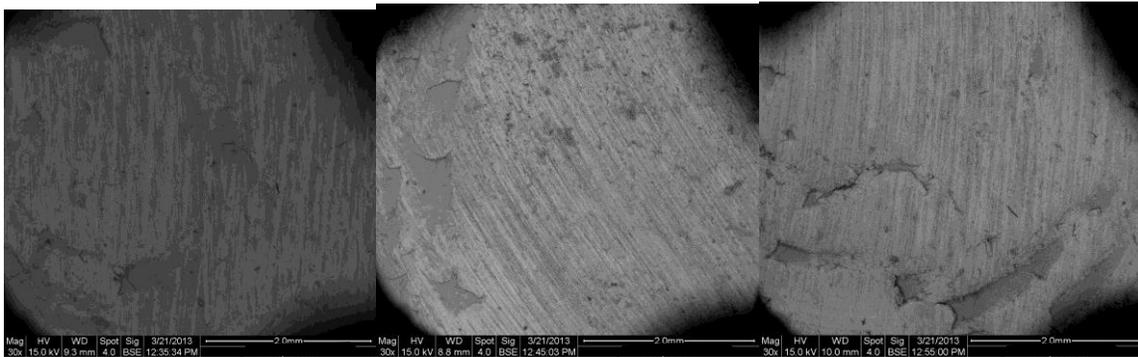


Figure 26. is the BSE images of Sample 4 where the steel had been pretreated with Method 3 (Left), 2 (Middle), 1 (Right). After the steel was then coated with gallium metal it was fired at 500°C.

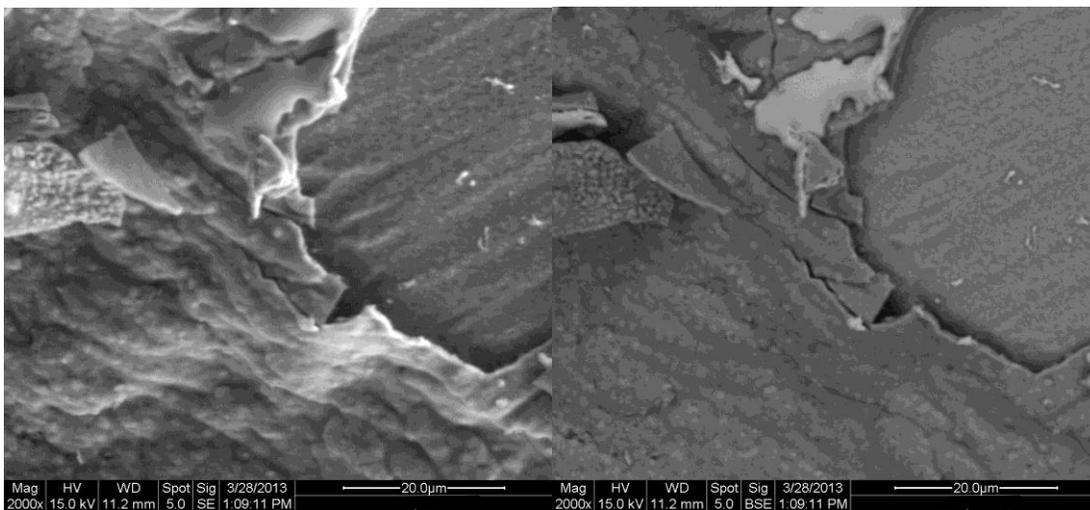


Figure 27. The SE and BSE images of Sample 5 where the steel pretreated by method 3 was coated with silica sol-gel, fired, and coated with gallium. The application of gallium fractured much of the silica sol-gel and some of what was remaining is shown here, coated by gallium.

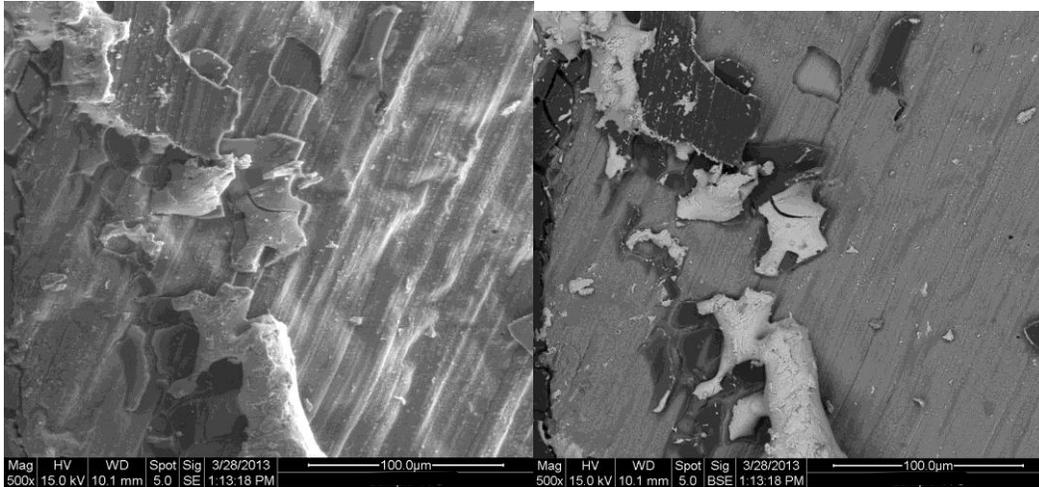


Figure 28. The SE and BSE images of Sample 5 where the steel penetrated by method 1 was coated with silica sol-gel, fired, and coated with gallium. Fragments of silica sol-gel broken by the application of gallium are seen in these images, overlaying silica sol-gel that was coated and its cracks were sealed by gallium.

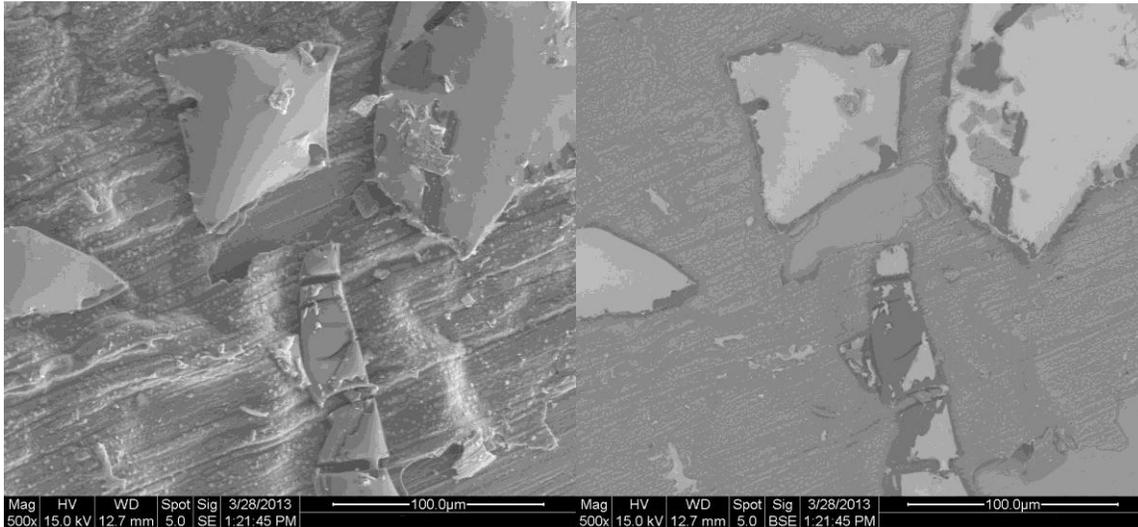


Figure 29. The SE and BSE images of Sample 5 where the steel penetrated by method 2 was coated with silica sol-gel, fired, and coated with gallium. The gallium has coated and sealed the cracks in the silica sol-gel layer and even the fragments of silica sol-gel broken off by the application of gallium.

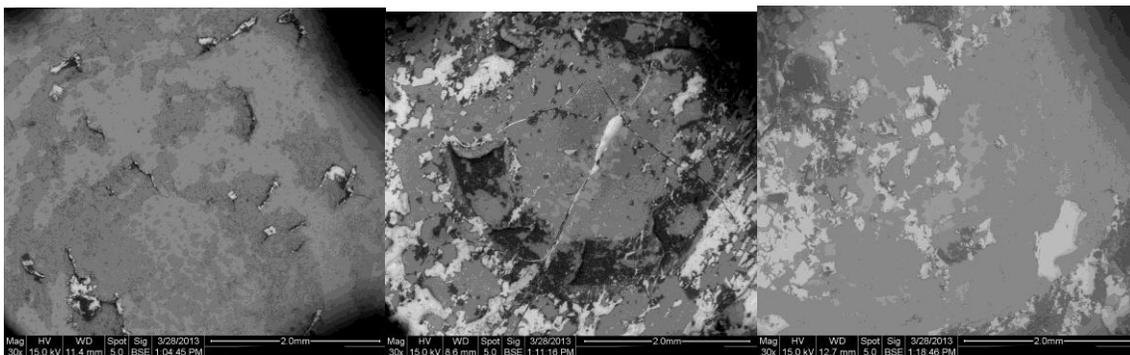


Figure 30. is the BSE images of Sample 5 where the steel had been pretreated with Method 3 (Left), 2

(Middle), 1 (Right). After the steel was coated with silica sol-gel and fired at 500°C, it was coated with liquid gallium metal.

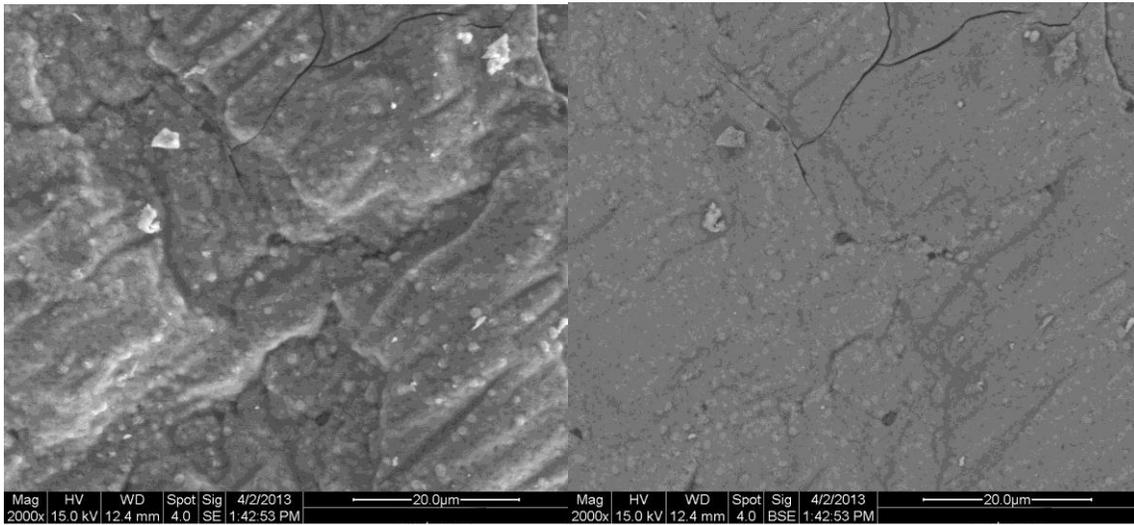


Figure 31. The SE and BSE images Sample 5 where the steel pretreated by method 3 was coated with silica sol-gel, fired, coated with gallium and then fired. The remaining flakes of silica sol-gel that survived the process in which liquid gallium was applied, was coated with gallium and transformed into Gallium oxide after firing.

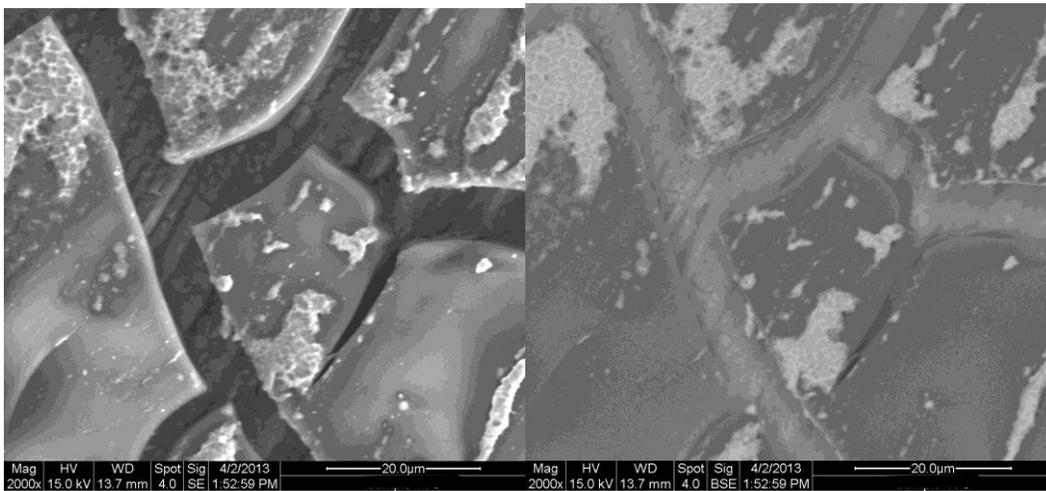


Figure 32. The SE and BSE images Sample 5 where the steel pretreated by method 1 was coated with silica sol-gel, fired, coated with gallium, and then fired. Some gallium metal remains on the surface, while Gallium oxide formed on these surfaces and in between the platelets of silica sol-gel.

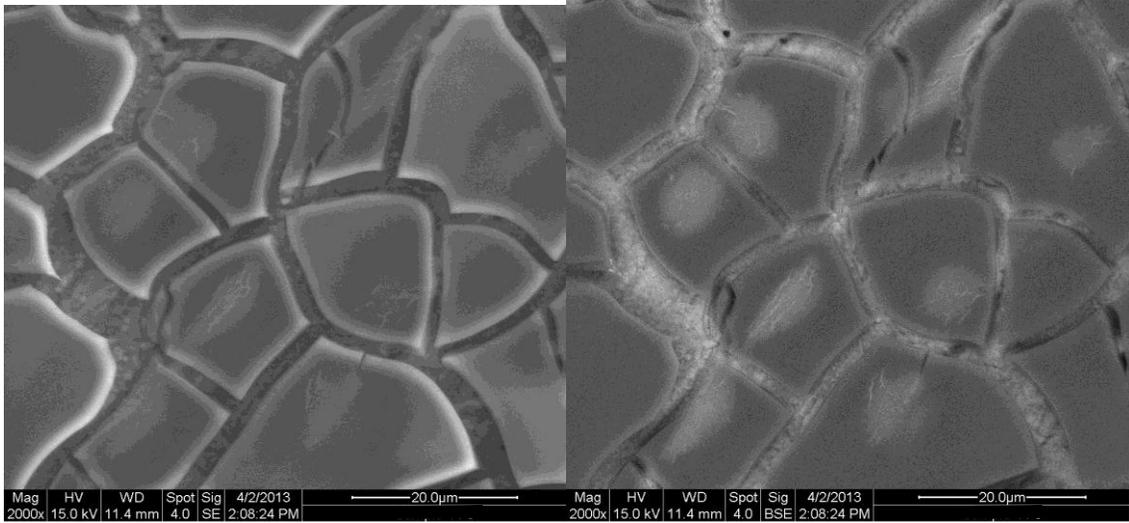


Figure 33. The SE and BSE images Sample 5 where the steel pretreated by method 2 was coated with silica sol-gel, fired, coated with gallium, and then fired. Some gallium metal remains on the surface and Gallium oxide formed on these surfaces and in between the platelets of silica sol-gel.

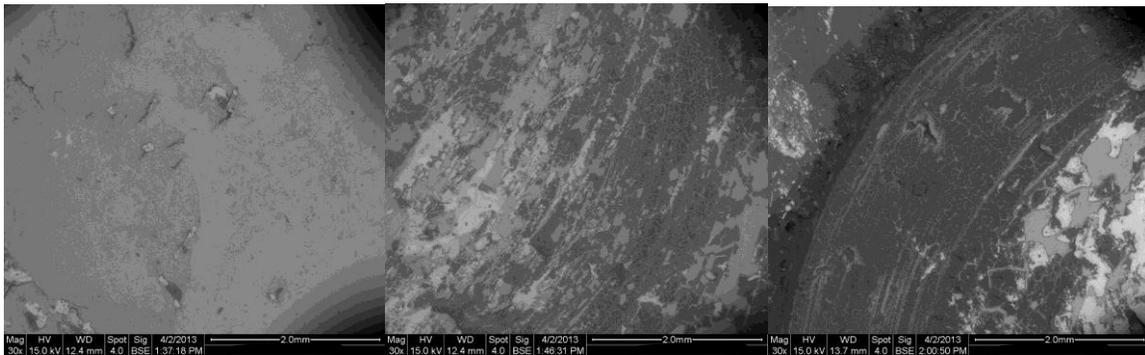


Figure 34. is the BSE images of Sample 5 where the steel had been pretreated with Method 3 (Left), 2 (Middle), 1 (Right). After the steel was with silica sol-gel and fired at 500°C it was coated with liquid gallium metal and fired at 500°C.

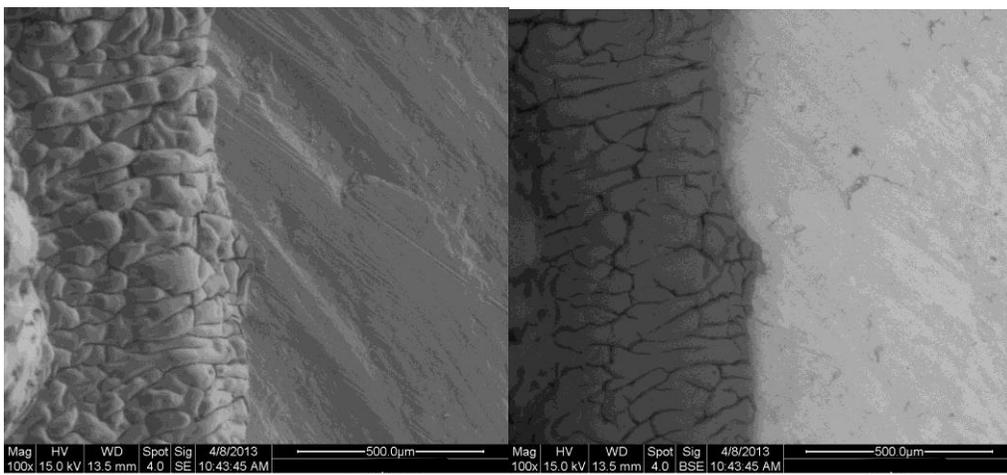


Figure 35. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel chemically treated with method 1.

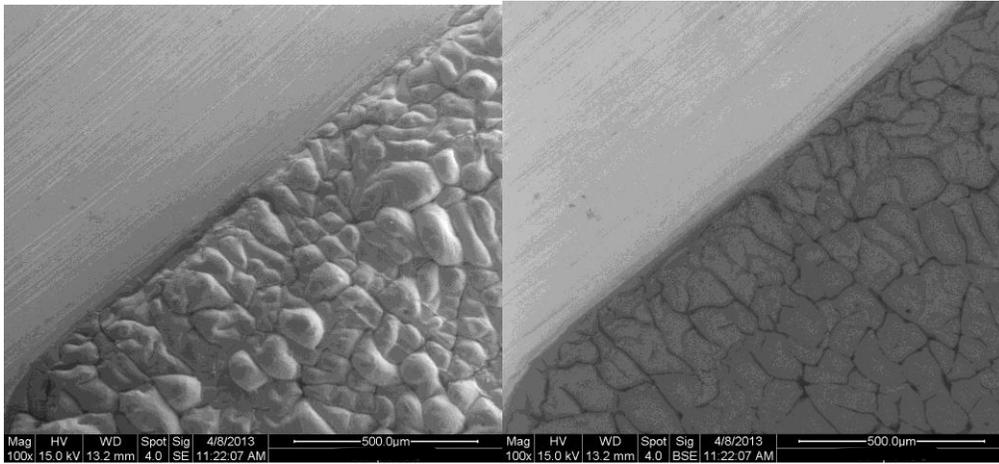


Figure 36. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 2.

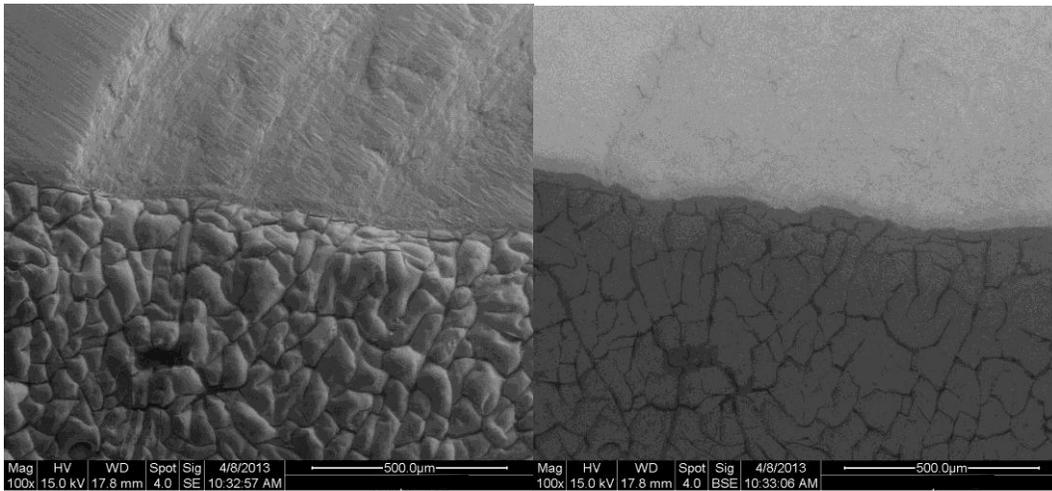


Figure 37. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 1.

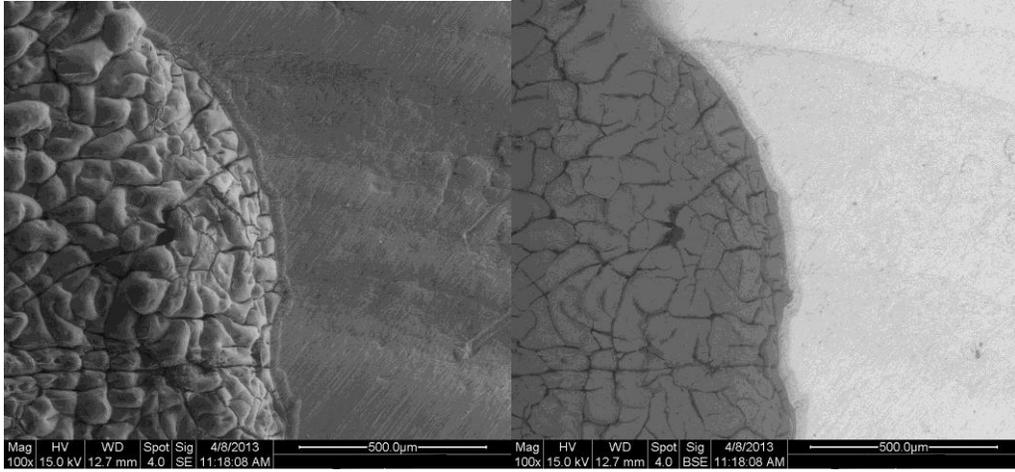


Figure 38. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 2.

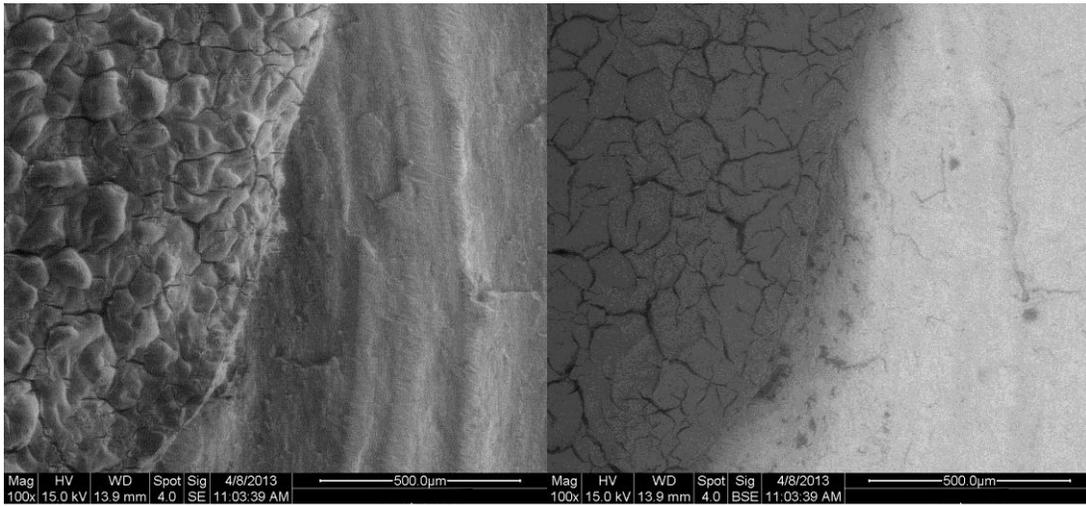


Figure 39. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 3.

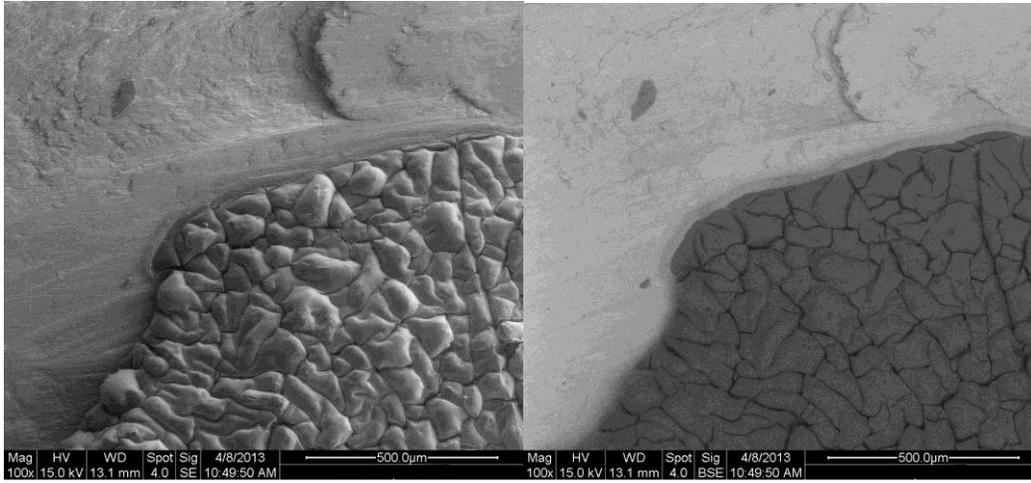


Figure 40. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 1.

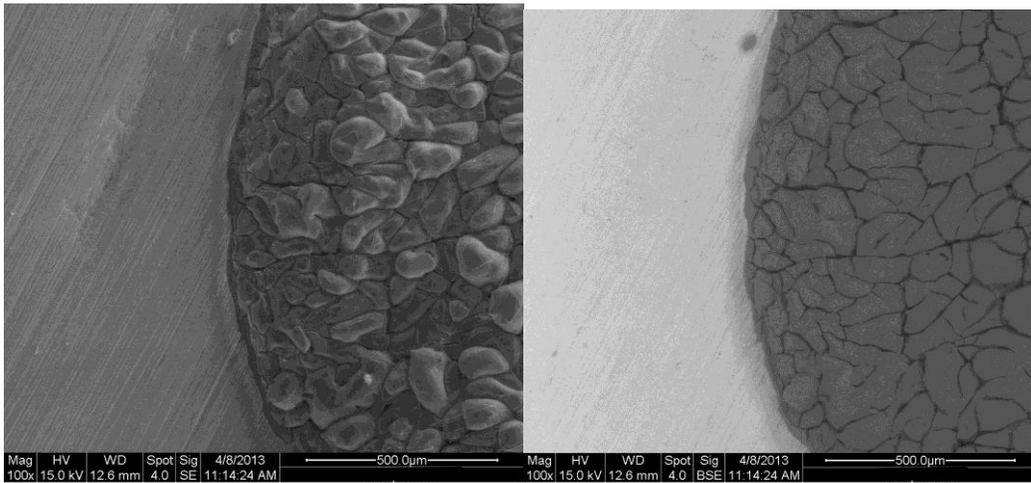


Figure 41. The SE and BSE images of Sample 6. Sodium silicate containing a 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on steel that was chemically treated with method 2.

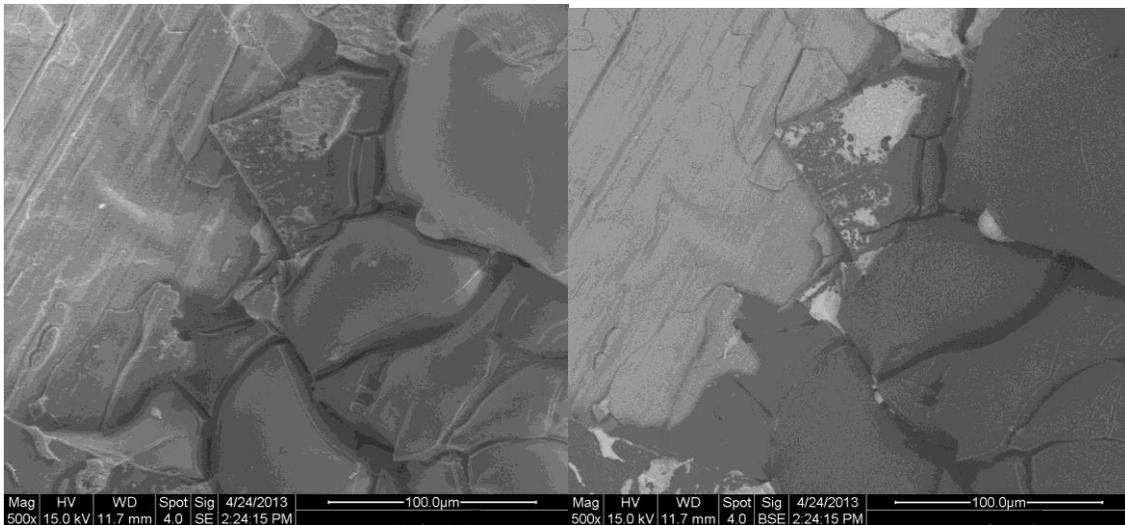


Figure 42. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 3.

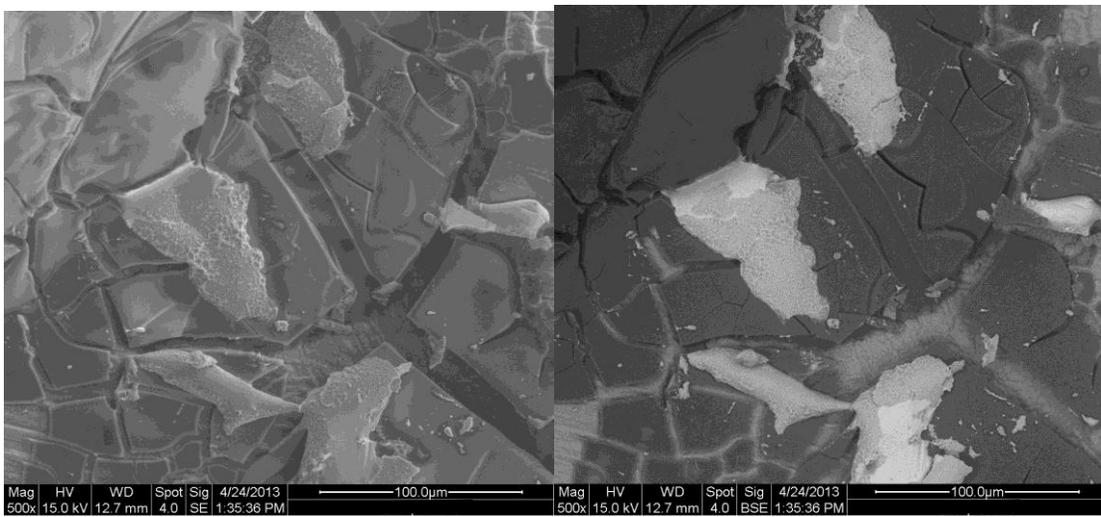


Figure 43. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 1.

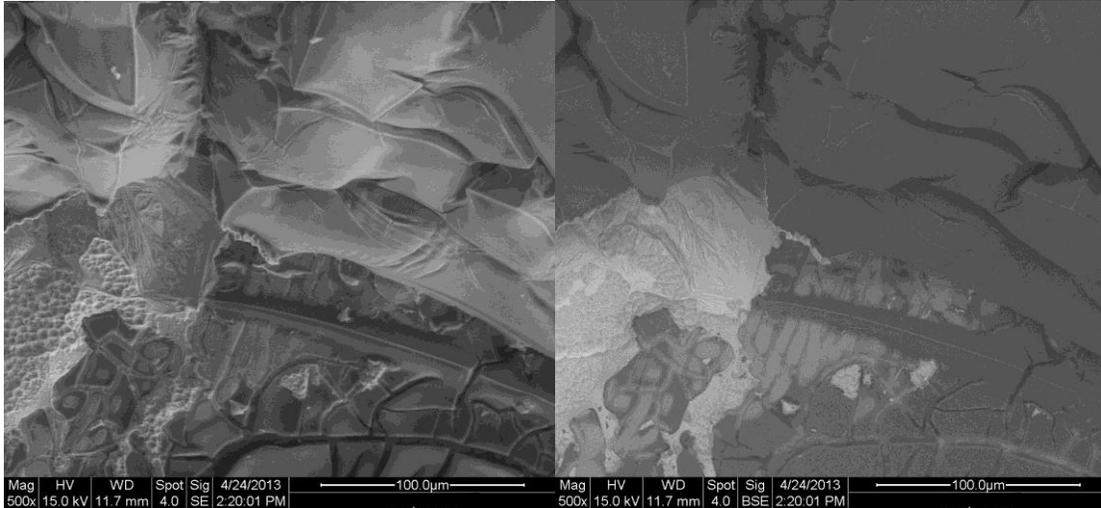


Figure 44. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.28 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 2.

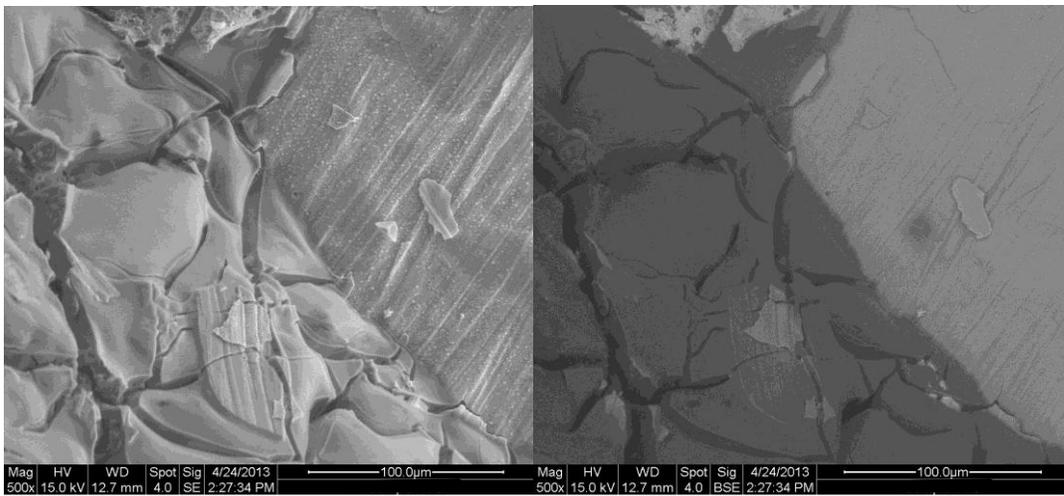


Figure 45. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 3.

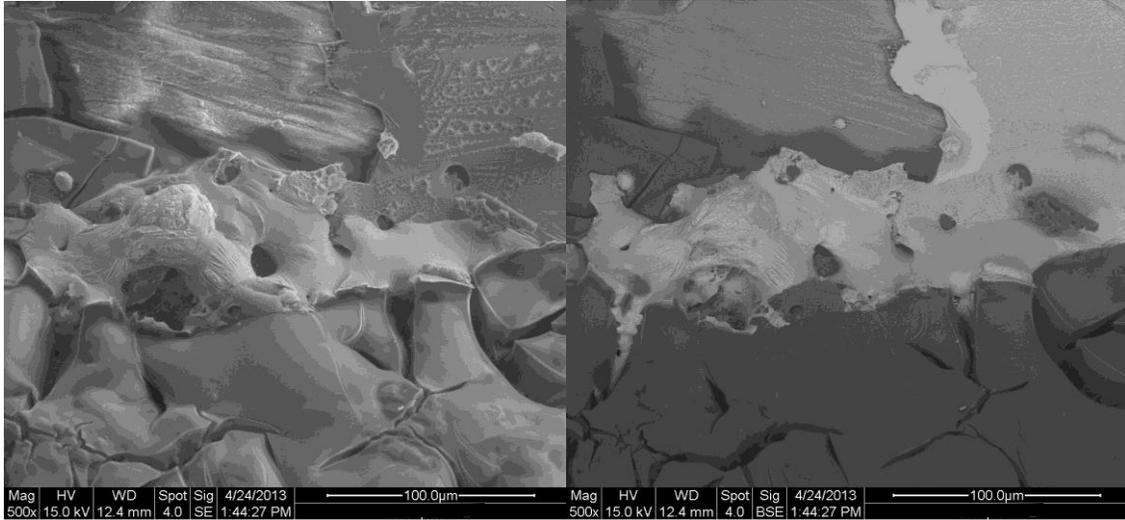


Figure 46. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 1.

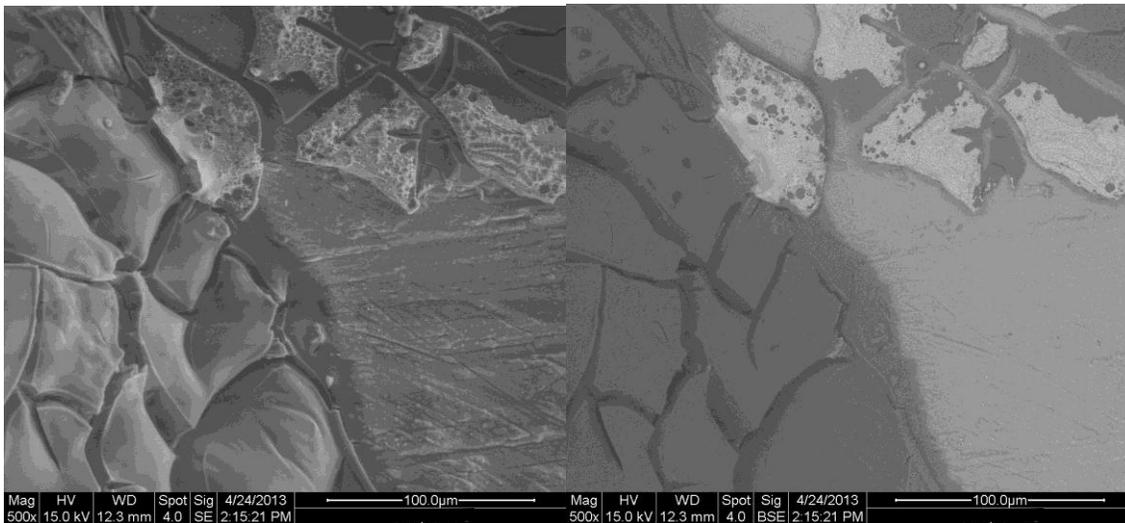


Figure 47. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.289 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 2.

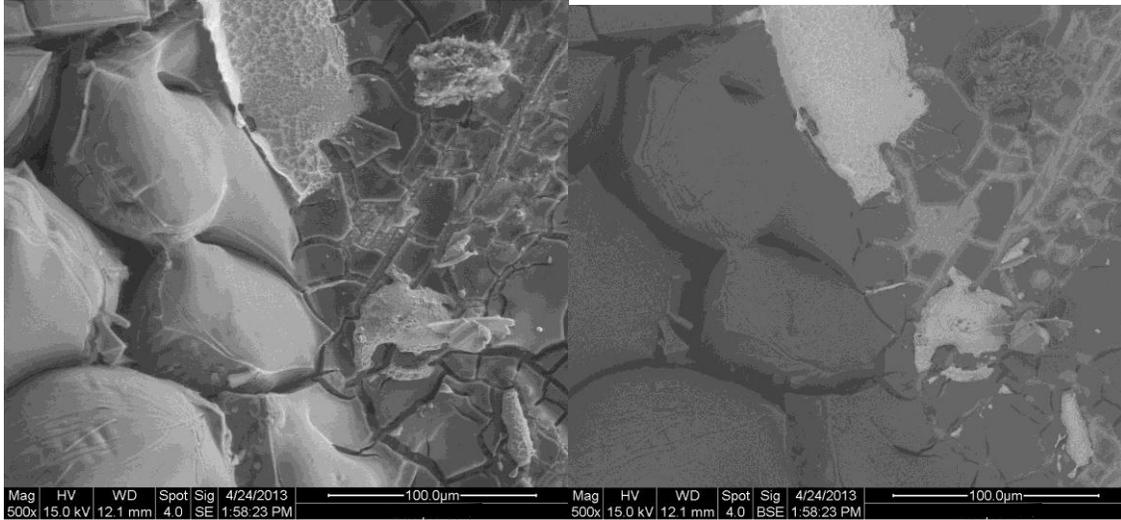


Figure 48. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 3.

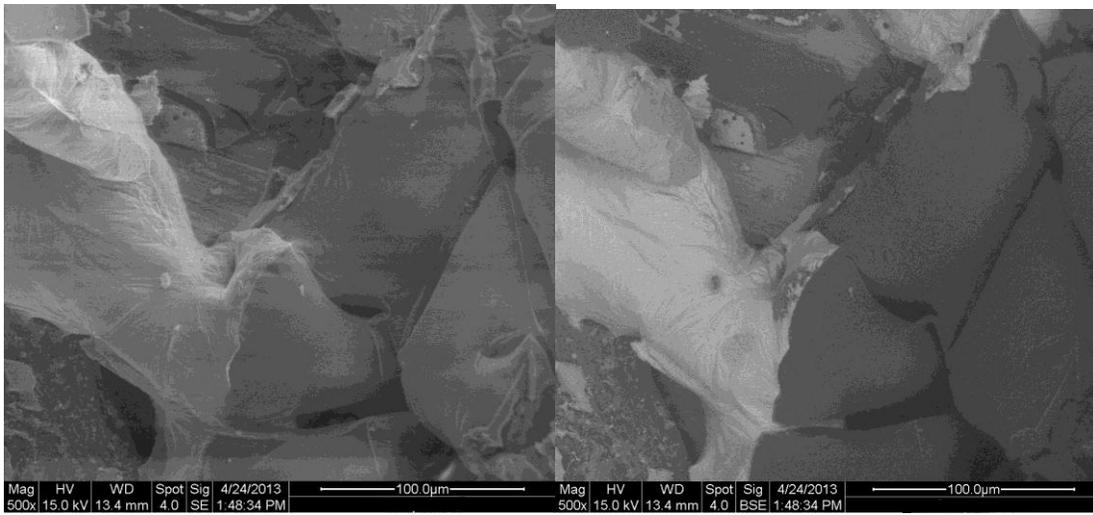


Figure 49. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 1.

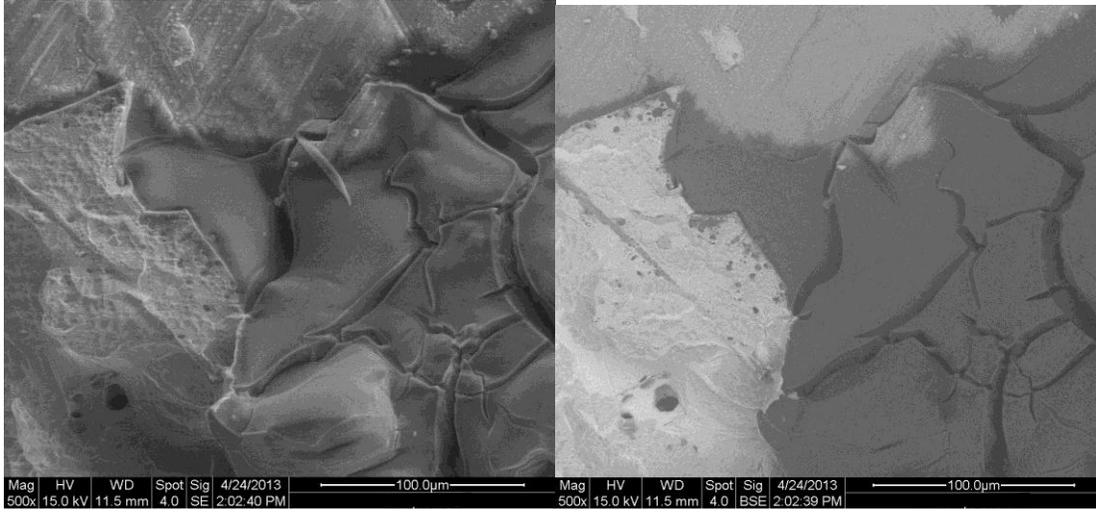


Figure 50. The SE and BSE images of Sample 7. Sodium silicate containing 1:0.30 ratio of Na_2SiO_3 to Na_2SiF_6 coated on gallium, Gallium oxide, silica sol-gel, and steel that was chemically treated with method 2.

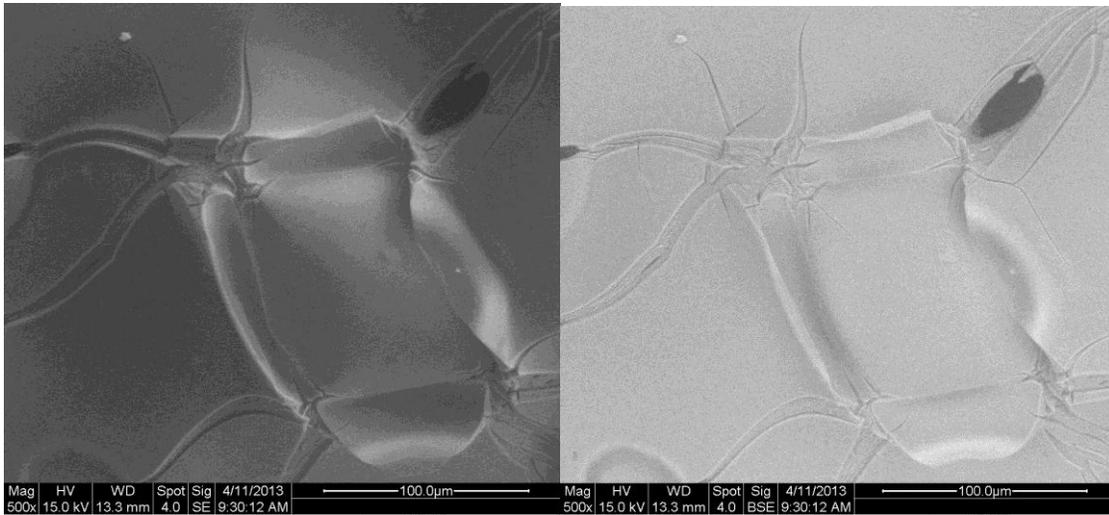


Figure 51. The SE and BSE images of Sample 8 before it was submitted to the corrosion test.

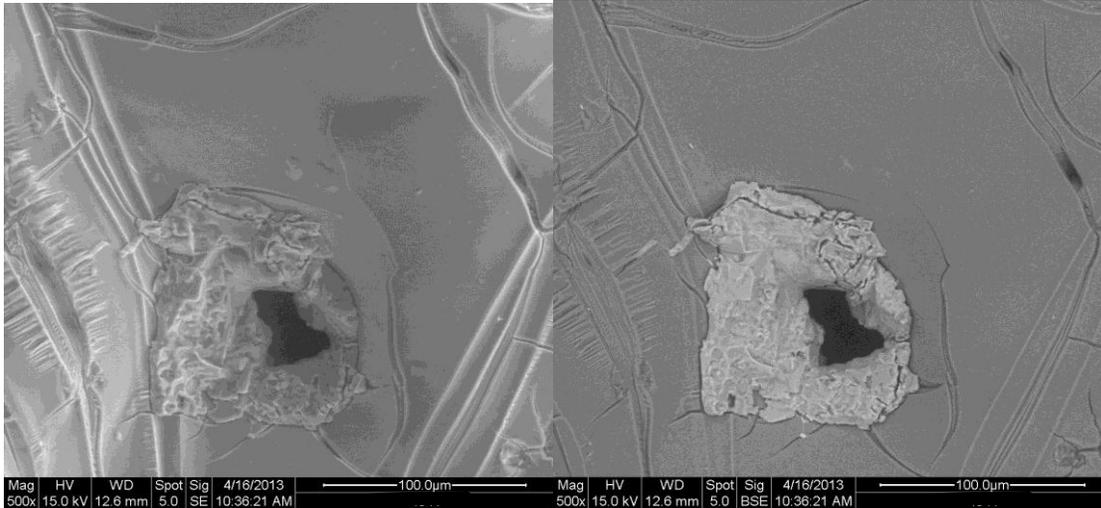


Figure 52. The SE and BSE image of Sample 8 after it has been submitted to the corrosion test. A hole in the Sodium silicate layer is filled mostly with gallium was turned into Gallium chloride.

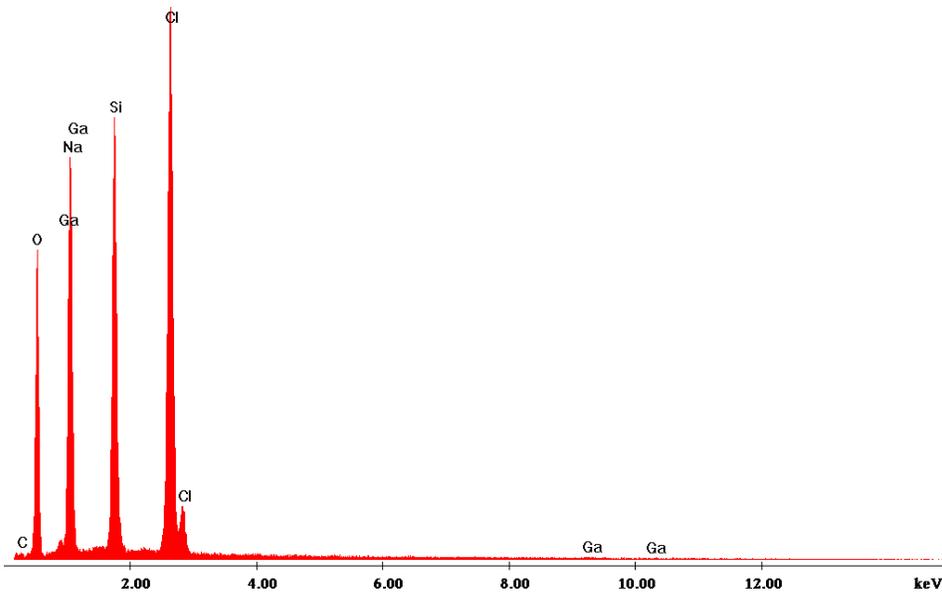


Figure 53. The EDS spectra collected from the hole in Sample 8. The acid had corroded the gallium and produced Gallium chloride as well as Sodium chloride from the Sodium silicate.

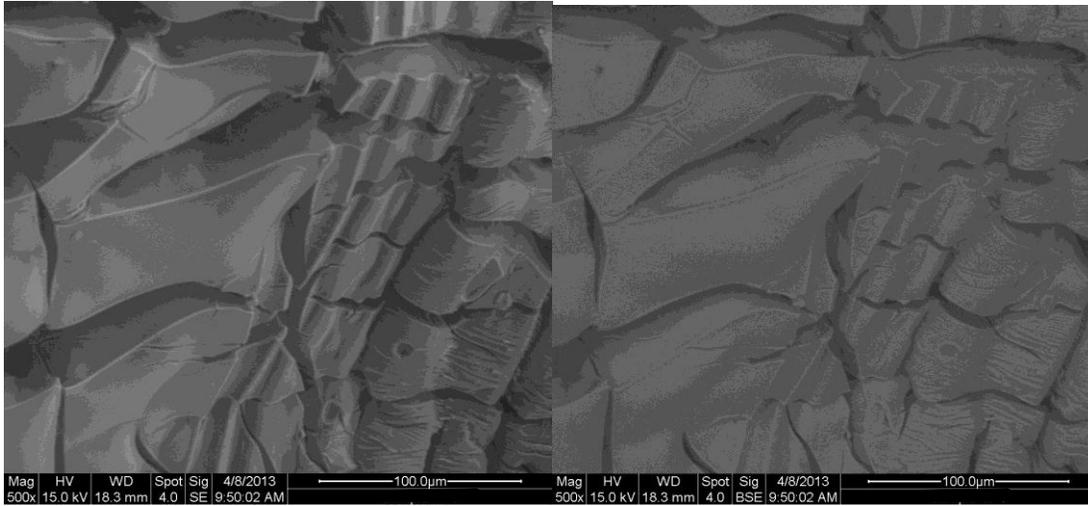


Figure 54. The SE and BSE images of the surface of Sample 9 before it was submitted to the corrosion test.

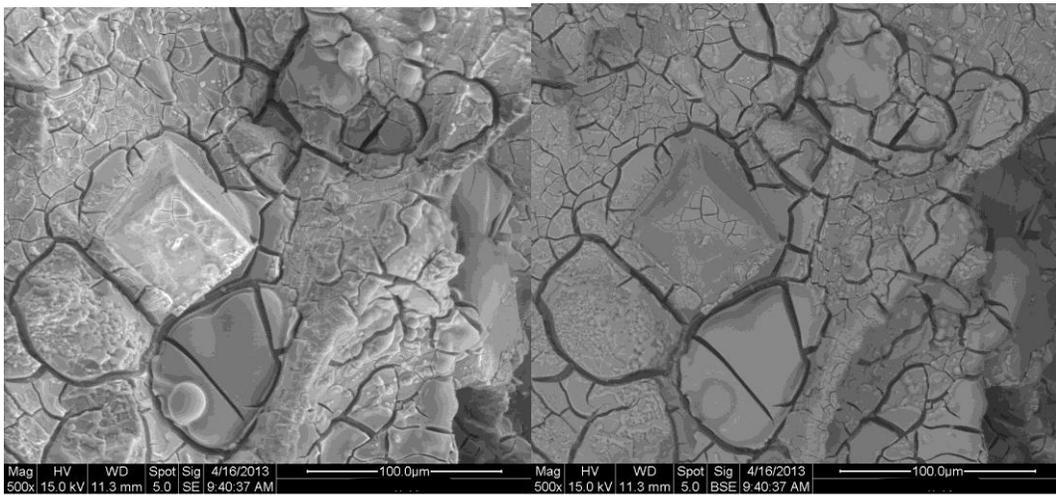


Figure 55. The SE and BSE images of Sample 9 after the corrosion test. Patches of Gallium chloride and cubic crystals of Sodium chloride are deposited on the surface. The holes seen here are from the bubbled structures in the Sodium silicate which collapsed during the corrosion test.

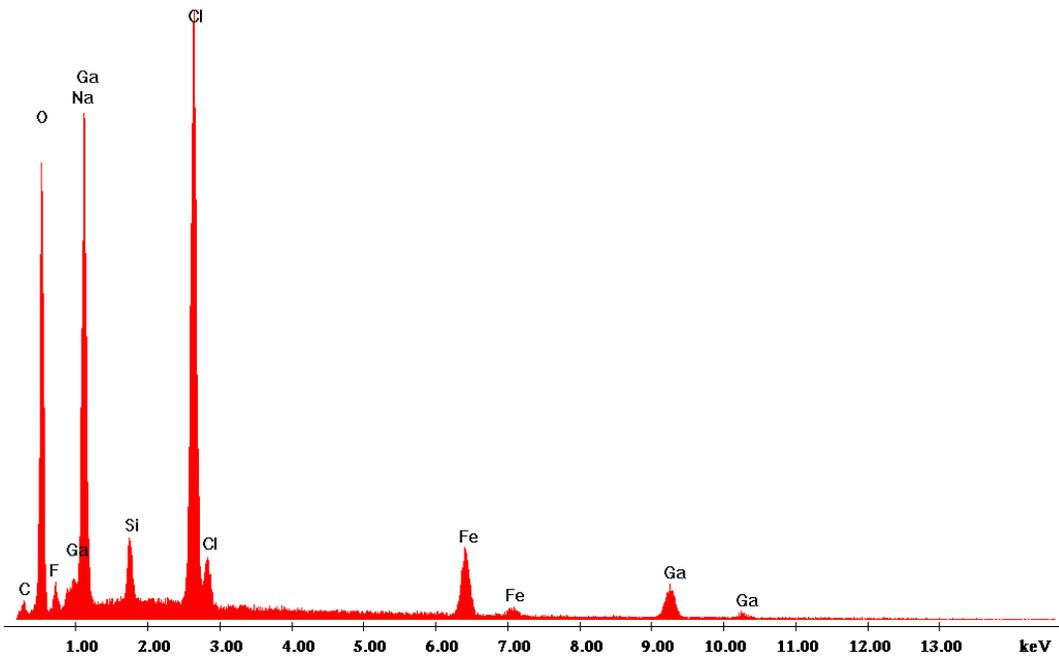


Figure 56. The EDS gathered from Sample 9, indicating the presence of steel that was corroded and deposited on the surface of the coatings in the form of Iron chloride. Sodium chloride and Gallium chloride are also indicated by this EDS as well.

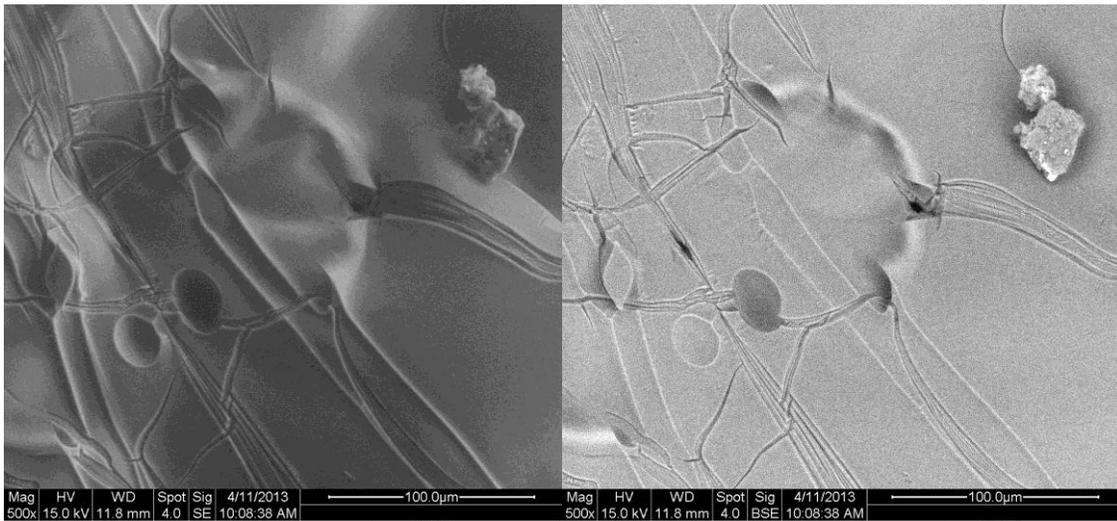


Figure 57. The SE and BSE images of Sample 10 before the corrosion test.

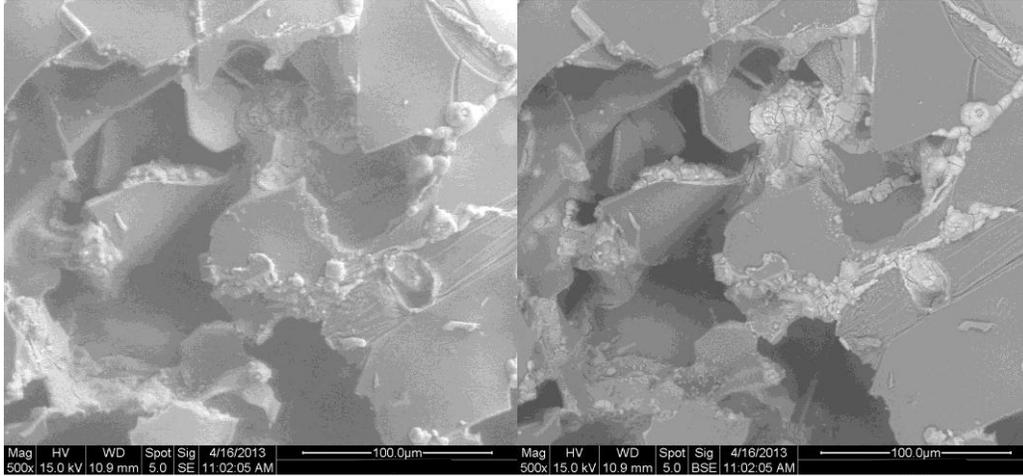


Figure 58. The SE and BSE images of Sample 10 after the corrosion test. Collapsed bubbled structures in the water glass contained gallium which reacted with the Hydrochloric acid to form Gallium chloride.

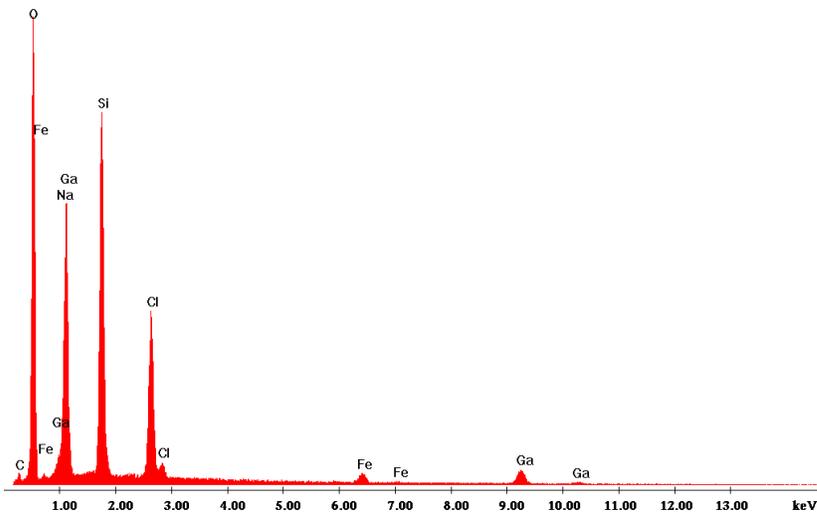


Figure 59. The EDS spectra of Sample 10 where Gallium chloride patches were observed.

VIII. REFERENCES

- ¹Chemat. (2009, June 15). *Sol-Gel Technology*. Retrieved February 24, 2013, from www.chemat.com: <http://www.chemat.com/chemattechnology/SolGel.aspx>
- ²Mellot, N. (2013, February 15). Assistant Professor Materials Science and Engineering. (E. Wake, Interviewer)
- ³Huang, Yuhong, et al. (December 2001). *Advances in Sol-Gel Technology*. Retrieved March 10, 2013, from http://www.chemat.com/chematscientific/docs/Sol-Gel_Dip_Coater_Processes_and_Equipment.pdf
- ⁴Brinker, C. Jeffrey, Scherer, George W. (1990). *Sol Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press Inc., San Diego California Pgs 444-508.
- ⁵H. Okamoto: "The Fe-Ga (Iron-Gallium) System," *Bull. Alloy Phase Diagrams*, 1990, 11(6), pp. 576-81.
- ⁶O. Ikeda, R. Kainuma, I. Ohnuma, K. Fukamichi, and K. Ishida. *Phase Equilibria and Stability of Ordered b.c.c. Phases in the Fe-Rich Portion of the Fe-Ga System, J. Alloys Compd.*, 2002, 347, pp. 198-205.
- ⁷READE. (2013). *Gallium Oxide G2O3) from READE*. Retrieved March 13, 2013, from <http://www.reade.com/supersite>
- ⁸Gengying Li, Guangjing Xiong, Yunhai lü, Yegao Yin. *The physical and chemical effects of long-term sulphuric acid exposure on hybrid modified cement mortar*. *Cement & Concrete Composites* 31 (2009) 325–330.
- ⁹Liu, M. (2013, March 30). Bachelors of Materials Science and Engineering. (E. Wake, Interviewer)
- ¹⁰Liu, J. (2013, April 3). Professor in Chemistry and Materials Science. (E. Wake, Interviewer)
- ¹¹Milanco Industrial Chemicals. (1997). *Iron Phosphate Coatings*. Retrieved on April 22, 2013, from <http://www.milanco.com/training/iron.htm>
- ¹²ASTM International. (2013). *ASTM G48 - 11 : Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*. Retrieved on April 21, 2013, from <http://www.astm.org/Standards/G48.htm>