ORIGINAL ARTICLE

Sealing of thermally-sprayed stainless steel coatings against corrosion using nickel electroplating technique

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Abstract

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Electric arc spraying (EAS) is one of the thermal spray techniques used for restoration and to provide corrosion resistance. It can be utilized to build up coatings to thicknesses of several millimeters, It is easy to use on-site. Most importantly, the cost of this technique is lower than other thermal spraying techniques that may be suitable for part restoration. A major disadvantage associated with the electric arc sprayed coating is its high porosity, which can be as high as 3-8% making it not appropriate for use in immersion condition. This work was carried out around the idea of using electroplating to seal off the pore of the EAS coating, with an aim to improve the corrosion resistance of the coating in immersion condition.

This research compared the corrosion behavior of a stainless steel 316 electric arc sprayed coating in 2M NaOH solution at 25°C. It was found that the Ni plating used as sealant can improve the corrosion resistance of the EAS coating. Furthermore, the smoothened and plated stainless steel 316 coating has a better corrosion resistance than the plated EAS coating that was not ground to smoothen the surface before plating.

Key words : thermal sprayed coating, coating sealants, electroplating, electrochemical, corrosion

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บทคัดย่อ

หทัยพัฒน์ ค่อยประเสริฐ และ ปนัดดา นิรนาทล้ำพงศ์

การปิดรูพรุนของผิวเคลือบเหล็กกล้าไร้สนิมที่พ่นเคลือบด้วยเปลวความร้อนเพื่อต้านทานการกัดกร่อนโดยใช้เทคนิคการชุบเคลือบนิกเกิลด้วยไฟฟ้า

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การพ่นเคลือบด้วยอาร์กไฟฟ้าเป็นเทคนิคหนึ่งของการพ่นเคลือบด้วยเปลวความร้อนใช้ในพ่นเคลือบเพื่อเพิ่มเนื้อวัสดุทดแทนส่วนที่เสียไปและใช้ในการเตรียมผิวให้มีความต้านทานการกัดกร่อน การพ่นเคลือบด้วยอาร์กไฟฟ้าสามารถพ่นเพิ่มเนื้อวัสดุได้หนาหลายมิลลิเมตร อีกทั้งง่ายต่อการนำไปพ่นเคลือบชิ้นงานนอกสถานที่ ที่สำคัญคือค่าใช้จ่ายในการพ่นเคลือบมีราคาถูกกว่าเทคนิคพ่นเคลือบด้วยเปลวความร้อนเทคนิคอื่น ๆ จึงทำให้การพ่นเคลือบด้วยอาร์กไฟฟ้าเหมาะที่จะใช้ในการซ่อมแซมชิ้นส่วนต่าง ๆ เพื่อนำชิ้นส่วนดังกล่าวกลับมาใช้ใหม่ ส่วนใหญ่ข้อจำกัดที่พบในการใช้งานผิวเคลือบที่พ่นเคลือบด้วยอาร์กไฟฟ้าคือ ผิวเคลือบที่ได้มีรูพรุนสูง 3-8% ทำให้ไม่เหมาะที่จะใช้เป็นชิ้นส่วนที่ใช้งานแช่อยู่ในสารละลาย งานวิจัยนี้ทำขึ้นภายใต้แนวความคิดที่จะใช้การชุบเคลือบด้วยไฟฟ้าในการปิดรูพรุนของผิวเคลือบอาร์กไฟฟ้า วัตถุประสงค์เพื่อป้องกันการกัดกร่อนของผิวเคลือบที่ได้จากการพ่นเคลือบด้วยเปลวความร้อนสำหรับใช้งานในสารละลาย

งานวิจัยนี้ได้ทำการเปรียบเทียบพฤติกรรมการกัดกร่อนของผิวเคลือบเหล็กกล้าไร้สนิมเกรด 316 ที่พ่นเคลือบด้วยอาร์กไฟฟ้า ทดสอบในสารละลายโซเดียมไฮดรอกไซด์ความเข้มข้น 2 โมล/ลิตร ที่อุณหภูมิ $25^{\circ}C$ พบว่า การอุดรูพรุนด้วยการชุบเคลือบด้วยนิกเกิลช่วยปรับปรุงสมบัติด้านความต้านทานการกัดกร่อนของผิวเคลือบอาร์กไฟฟ้าให้ดีขึ้น นอกจากนี้เมื่อขัดผิวเคลือบที่ได้จากการเคลือบอาร์กไฟฟ้าให้เรียบแล้วชุบเคลือบด้วยนิกเกิลจะทำให้มีความต้านทานการกัดกร่อนดีกว่าผิวเคลือบที่ขรุขระแม้ว่าจะชุบเคลือบนิกเกิลแล้วก็ตาม

กลุ่มวิจัยและพัฒนาเทคโนโลยีเซรามิกส์ ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ สำนักงานพัฒนาวิทยาศาสตร์และเทคโนโลยีแห่งชาติ อำเภอคลองหลวง จังหวัดปทุมธานี 12120

Equipment such as tank, pipeline, impeller and pump, are affected by corrosion and corrosive wear that consume natural resources and energy in part replacements. Electric arc spraying (EAS) is a thermal spraying technique used for protection of parts and components from corrosion and corrosive wear in many industries due to an ability to build up several millimeters of coating rapidly and at a reasonable cost. Therefore, the EAS is widely used in restoration for reusing of the equipments. The principle of EAS involves two current carrying, electrically conductive wires fed into a common arc point, creating a temperature of up to the melting point of the wire material at which melting occurs. The temperature at the wire tips can be as high as 1,500°C (Cramer, 2003). The molten material is continuously atomized and the droplets are accelerated toward the substrate by a compressed air jet. The EAS process schematic diagram is shown in Figure 1. Nevertheless porosity of the EAS coating of about 3-8% (Unger, 1998) limits the use of the coating in some corrosive conditions such as immersion conditions and high humidity conditions, in which corrosive media can penetrate through the coating porosity to the underlying substrate. This can accelerate the corrosion and the corrosive wear, leading to failure of the coating.

Electroplating of nickel is widely used for protection from corrosion in many industries, and the facility is easily accessed in Thailand due to its low price. However, the electroplating of nickel limits the thickness to be not more than 0.1 mm (Tucker, 2002), which is not sufficient for part restoration where a large bulk of material is damaged.

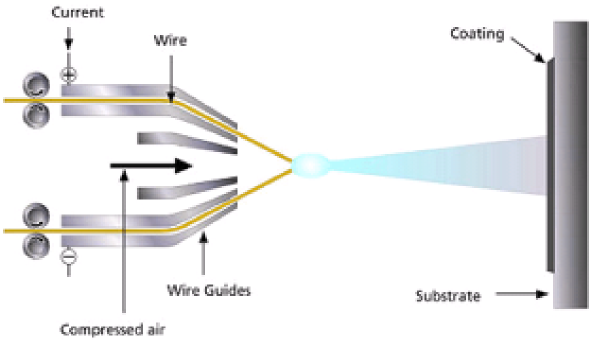

Figure 1. Schematic diagram showing the electric arc spraying process. (www.advanced-coating.com, 2005)

In this project, specimens were coated with a stainless steel 316 (TAFA 85T) using the EAS technique to a thickness of approximately 500 µm. and plated with Ni to seal off the porosity. Using the Ni plating to seal off thermal sprayed coating pores is a novel technique for improving the corrosion resistance of the thermal sprayed coating in immersion condition. The corrosion behaviors of the specimens were studied using the potentiostat equipment, comparing various coating conditions.

Materials and Methods

The substrates and reference samples were made by cutting a flat stainless steel 304 bar into specimen of dimension 20x20x3 mm. The sample group 1, which was a reference sample, was surface ground to achieve a surface roughness of 0.07 µm Ra and left to stand for 24 hours to allow for the build-up of passive films before the electrochemical test. The sample groups 2-5 were roughened by grit blasting using a 740 micron alumina grit to obtain a sharp peaked surface contour with the substrate surface roughness of approximately 4.57 µm Ra to promote a good coating adhesion, the air pressure used for grit blasting was 7 bars. The blasting nozzle was held perpendicular to the sample surface at a distance of 80 mm. for 30 seconds. After the grit blasting process, the samples were cleaned in acetone using an ultrasonic bath for 15 minutes. The samples were then ready for electric arc spraying using TAFA 9000 system to produce coatings of approximately 500 µm thickness, using TAFA 85T stainless steel 316 wire (nominal composition of 12Ni-17Cr-2.5Mo-0.08C-2Mn-1Si-Fe(bal.), in wt. %) as the coating material. The spray parameters used in this experiment were optimized for the coating to obtain a uniform, high-density, good adhesion coatings with a low oxide content. These parameters are shown in Table 1. The average surface roughness after spraying is 10.4 Ra. The sample groups 3 and 5 were ground using wet SiC papers after the coating process to achieve a coating surface roughness of 0.2 µm Ra, and still leaving a coating thickness of 400 µm on the substrate. The specified sample groups were then electroplated with nickel using an in-house electroplating equipment. The samples were electroplated using Watt's solution (Shreir, 1994), with the power supply voltage of 2.5V and the current of 0.1A, with the plating time of 10 min. for nickel layer of 10 µm thickness. The as-plated samples were cross-sectioned to study the sealing ability of the nickel plating using a scanning electron microscope. The sample group 6 was the TAFA 85T stainless steel 316 wire.

The corrosion resistance of the samples was investigated in an electrochemical polarization experiment using potentiodynamic method, which was set up as shown in Figure 2. The test utilized a preset program called "General propose electrochemistry system" (GPES) by Autolab potentiostat equipment. The electrolyte was 2M NaOH solution (pH 12.5), the test sample was set up as the working electrode, and Ag/AgCl was used as the

Table1. Spray parameters for the electric arc spraying technique.

	Stainless steel 316 coating.
Air pressure (bar)	4
Arc load (Volt)	30
Arc current (Amp.)	165-170
Spray distance (mm.)	178

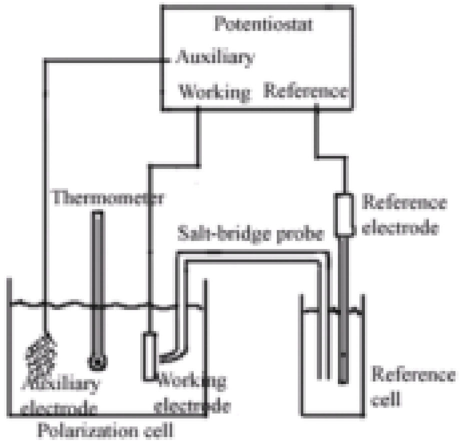

Figure 2. Experimental setup of the potentiostat.

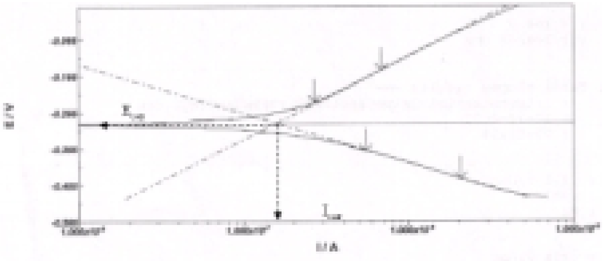

Figure 3. Tafel extrapolation of the bulk stainless steel 304 in NaOH solution.

reference electrode. The platinum mesh auxiliary electrode supplied the current to the working electrode in order to polarize it. The potential between the working and the reference electrodes was measured and controlled to increase in fixed intervals while the current flow was measured. The testing temperature was 25°C. Testing was done at a scan rate of 0.01 V/sec. The test result is be presented in the form of the polarization curve, which is the plot of the electrode potential (E) versus the log of the current density (I). At least 3 specimens per each group of samples were tested using the potentiodynamic technique and Tafel extrapolation method in order to calculate the average corrosion potentials (E_{corr}) and corrosion rates of the test samples.

Figure 3 shows a section of the polarization curve of the bulk stainless steel 304 in NaOH solution. The Tafel curves were extrapolated to the corrosion potential at which the rate of hydrogen evolution is equal to the rate of metal dissolution. This point corresponds to the corrosion rate of the system expressed in terms of current density. Equation 1 is used to determine the corrosion rate in terms of millimeters/year.

Results and Discussion

1. Corrosion behavior of the substrate and the coating material.

The polarization curves of a bulk stainless steel 304 sample and a stainless steel 316 wire, which was used for EAS coating, are shown in Figure 4. Both of these materials show similar corrosion behavior in 2M NaOH solution. The E_{corr} value of the bulk stainless steel 304 sample is lower than that of the stainless steel 316 wire, which indicates that the bulk stainless steel 304 corrodes more easily than the stainless steel 316 wire. However, from Equation 1, it was found that the stainless steel 316 wire has slightly higher corrosion rate than the bulk stainless steel 304 at E_{corr} of -0.420 V and corrosion rate of 0.013 millimeters/year respectively. During the test, $Fe(OH)_2$, $Ni(OH)_2$, $Cr(OH)_3$ and possibly other oxides and spinels can form on the surface as a passive layer. Figure 4 indicates the formation of a protective oxide film at the potential range from 0.125V to 0.5V after which the film starts to break down. The potential range of this drop overlaps the chromium oxidation peak (Marijan, 1999). Corrosion rates of each coating are later presented in Figure 12.

$$CR = K\ Icorr\ EW / d$$

(Equation 1) (Lawrence, 1987)

CR	is the corrosion rate (mm/year)
I_{corr}	is the corrosion current density in microamps/cm^2
K	is a constant that defines the units for the corrosion rate (3.27×10^{-3})
EW	is the equivalent weight in grams
d	is density in grams/cm^3

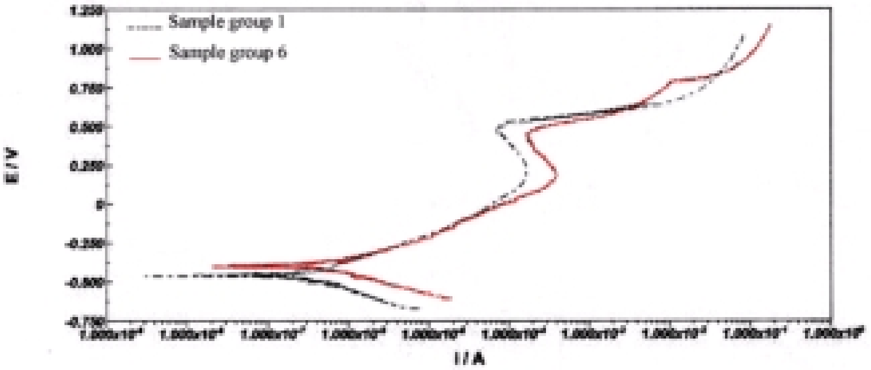

Figure 4. Polarization curves of the bulk stainless steel 304 substrate(sample 1) and the stainless steel 316 wire (sample 6) tested in 2M NaOH.

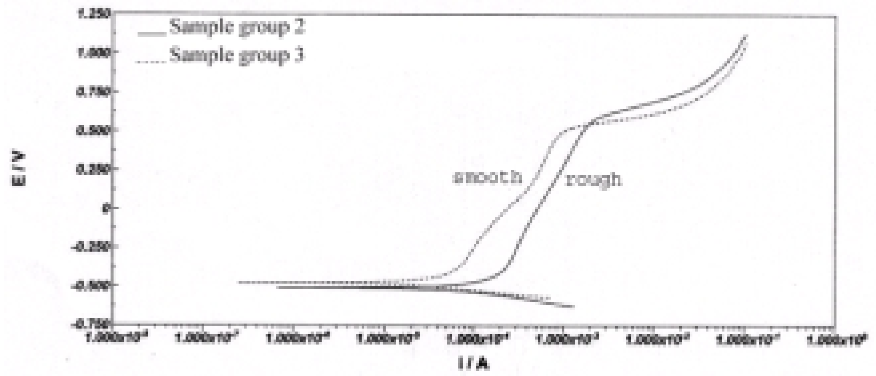

Figure 5 Polarization curves of sample group 2 (as-sprayed stainless steel 316 coating) and group 3 (ground stainless steel 316 coating) tested in 2M NaOH.

2. Effect of the coating on the corrosion behavior

After spraying, the polarization curves of sample group 2 (as-sprayed stainless steel 316 coating) and sample group 3 (ground stainless steel 316 coating) are shown in Figure 5. Values of the surface roughness of specimens are shown in Table 2. The formation of passive films is now not evidenced. This is thought to be because the arc sprayed coating is formed by individual splat depositions, the intersplat pores are common. These pores cause the discontinuity in the formation of the protective oxide film, which leads to a decrease in the ability to hinder the oxidation of the surface coating. Moreover, thermal effect from the arc temperature of around 1,500°C resulted in the reduction of chromium content. The EDS analysis shows that the chromium content of the stainless steel 316 wire (18.41%Cr) is higher than that of the as-sprayed stainless steel 316 coating (12.67%

Table 2. Surface roughness of the samples

Sample group	Surface roughness (µm Ra)
1 (Bulk stainless steel 304 substrate)	0.07
2 (as-sprayed stainless steel 316 coating)	10.38
3 (ground stainless steel 316 coating)	0.17
4 (Ni plated on as sprayed stainless steel 316 coating)	10.62
5 (Ni plated on ground stainless steel 316 coating)	0.17

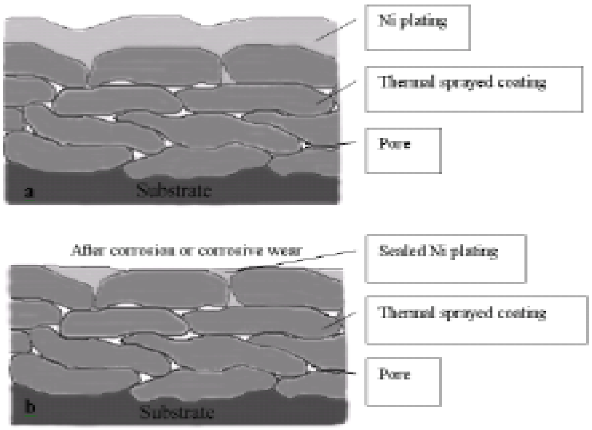

Figure 6. Thermal sprayed coating sealed by Ni plating.

Cr). The reduction of the chromium contents suggests that some chromium was used in the oxide film formation process. Corrosion rates of the as-sprayed and ground stainless steel 316 coating are later presented in Figure 12. The corrosion rate of the ground coating is shown to be lower than the as-sprayed coating because, in the arc-spraying process, the coating achieves its density by deformation of the material droplets to the contour of the underlying surface upon impact. The density can then be increased further by the compressive force induced by the next impacting droplets, which assists in the splat compaction. The surface layer of the coating, however, was not further bombarded by the molten droplets, and therefore, tends to have larger intersplat pores. When the stainless steel 316 coating surface was ground down to achieve the surface roughness of approximately 0.2 μm Ra, the surface layer was removed. At the same time, the depth of the pit was also reduced with the new surface being denser with pores smaller in size. The shallower surface pit allows better circulation of the solution, which promotes the formation of the protective scale. The scale formation and breakdown cycle are not clearly visible in Figure 5, but a decrease in the corrosion rate as the test progressed suggests the presence of the protective film.

3. Effect of Ni electroplating on the corrosion behavior

Corrosion and corrosive wear protection process of a Ni plated coating is shown in Figure 6. Commonly the applications of the EAS coating were not permitted in immersion and high humidity condition, with an exception of a sacrificial anode, because the corrosive solution can penetrate through the intersplat pores in the coating to the substrate. After using the electroplating of Ni to seal the coating porosity, the corrosive solution can be retarded from penetrating through the pores. In corrosive wear condition, after the Ni plating is removed through wear process, some Ni plating remained in the pore, preventing the solution from penetrating into the coating and the substrate, which helps to improve the corrosion resistance of the thermal sprayed coating.

Figure 7 shows the test results on the sample group 2 (as-sprayed stainless steel 316 coating) and group 4 (Ni plated on as sprayed stainless steel 316 coating) tested in 2M NaOH to have similar potentials. For sample group 4, corrosion is now

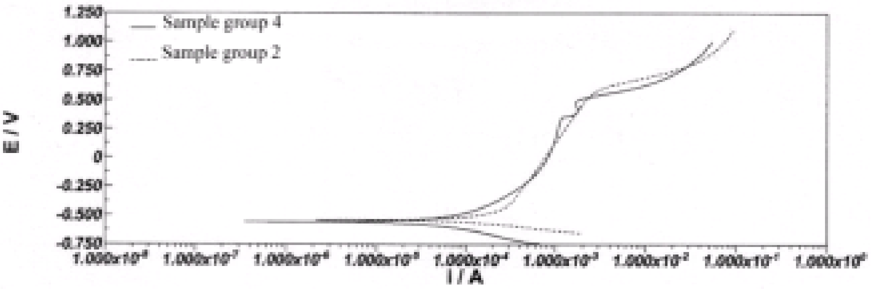

Figure 7. Polarization curves of sample group 2 (as sprayed stainless steel 316 coating) and group 4 (Ni plated on as sprayed stainless steel 316 coating) tested in 2M NaOH.

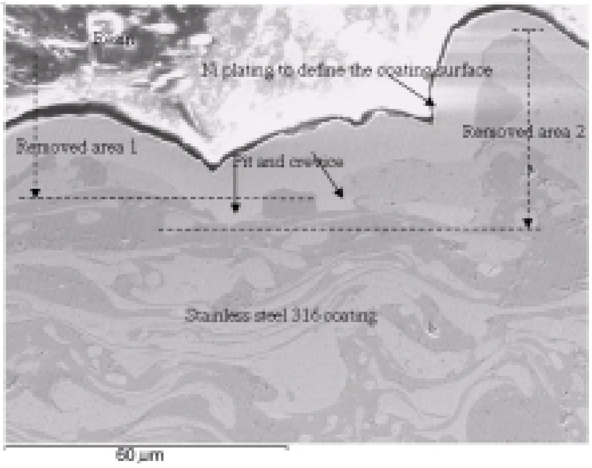

Figure 8. **Cross-section of the sample group 2 (as sprayed stainless steel 316 coating) after tested in 2M NaOH.**

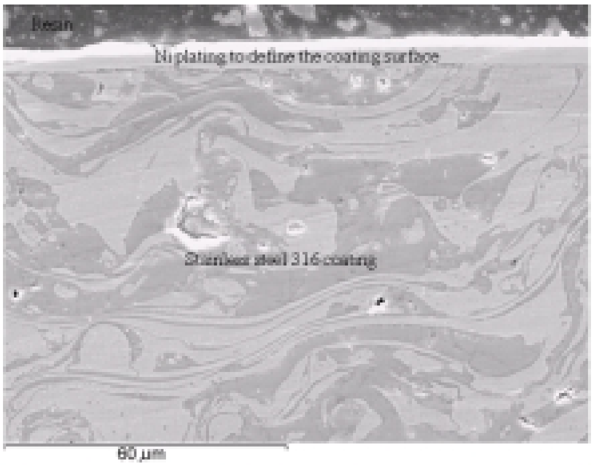

Figure 9. **Cross-section of the sample group 3 (ground stainless steel 316 coating) after tested in 2M NaOH.**

taking place on the Ni layer instead of the stainless steel 316 coating. The Ni plating exhibits a formation of the secondary passive film, with the possible passive layer of $Ni(OH)_2$ (Marijan, 1999) (Shreir, 1994).

4. Effect of coating surface roughness on the corrosion behavior

Previously in 2, it was found that the sample group 3 (ground stainless steel 316 coating) has better corrosion resistant property than the sample group 2 (as-sprayed stainless steel 316 coating) because the depth of the pit was reduced due to the new surface being denser with pores smaller in size, which can reduce pit and crevice effects. Figure 8 shows the cross-section of the sample group 2. The Ni-plating was done after the electrochemical test to benefit the microscopy where a sharper coating surface can be observed. If the surface was ground down to removed area 1, the coating will contain a higher pit depth than if area 2 was removed. Hence, grinding down pass the coating surface roughness is necessary to reduce the crevice effect. Figure 9 shows the cross-section of the sample group 3 after grinding to achieve a smooth surface. The new surface is denser because the loose outer layer splats and its intersplat pores were removed.

When the stainless steel 316 coating surface was ground down to achieve a smoother surface, followed by an electroplating of Ni, the potentiostat result shows an improvement in the corrosion behavior of the sample as evidence in Figure 10. The E_{corr} of sample group 5 (Ni plated on ground stainless steel 316 coating) is relatively high, reflecting a good resistance to corrosion in NaOH solution of the coating system. The corrosion rate was also improved as indicated by the shifting of the curve to a lower current density than the sample group 4 (Ni plated on as sprayed stainless steel 316 coating). The smoothened surface has a better corrosion resistant property than the rough as sprayed surface because of the smooth and near-defect-free surface of the Ni-plating layer, allowing less localized attack. As the corrosion becomes more uniform, the protective scale can also grow more uniformly and continuously. Also, with less localized attack occurring, the oxide scale can endure for longer and, therefore, provide an effective barrier against corrosion.

Figure 11 and 12 present the average E_{corr} values and the corrosion rates of the bulk stainless steel 304 substrate, the stainless steel 316 wire, the as-sprayed and ground stainless steel 316 coating, and the Ni plated on as-sprayed and ground stain-

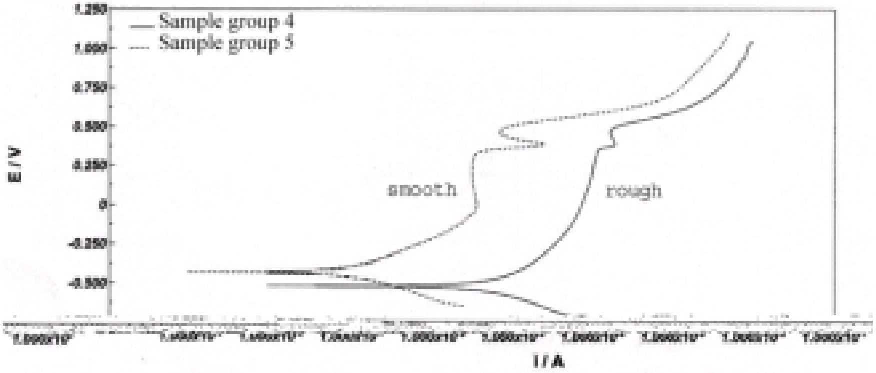

Figure 10. Polarization curves of sample group 4 (Ni plated on as sprayed stainless steel 316 coating) and 5 (Ni plated on ground stainless steel 316 coating) tested in 2M NaOH.

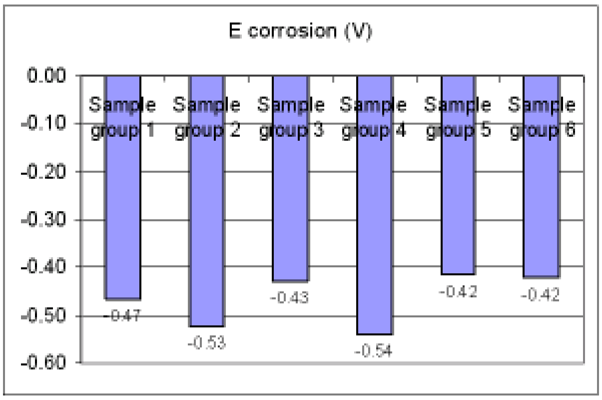

Figure 11. Corrosion potential (V) of the sample. The numbers designate the sample group where 1 is the bulk stainless steel 304 substrate, 2 is the as- sprayed stainless steel 316 coating, 3 is the ground stainless steel 316 coating, 4 is the Ni plated on as- sprayed stainless steel 316 coating, 5 is the Ni plated on ground stainless steel 316 coating and 6 is the stainless steel 316 wire.

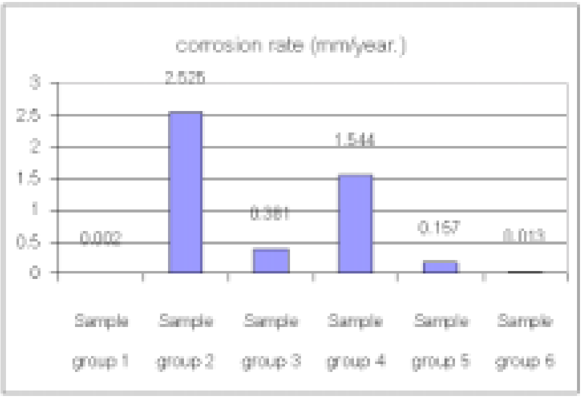

Figure 12. Corrosion rate (mm. per year) of the sample. The numbers designates the sample group according to Figure 11.

less steel 316 coating. The E_{corr} is the electrode potential when corrosion begins, which shows the susceptibility to corrosion of the sample, while the corrosion rates were calculated using Tafel extrapolation method and Equation 1. The E_{corr} of the sample group 1 (the bulk stainless steel 304 substrate) is lower than that of the sample group 6 (the stainless steel 316 wire). It indicates that the stainless steel 304 substrate corrodes easier than the stainless steel 316 wire. Nevertheless, the bulk stainless steel 304 substrate exhibits a lower corrosion rate than the stainless steel 316 wire.

The E_{corr} of the sample group 2 (the as-sprayed stainless steel 316 coating) is lower than the sample group 3 (the ground stainless steel 316 coating). It indicates that the rough EAS coating surface can corrode more easily than the smoothened EAS coating surface. Moreover, the corrosion rate of the as-sprayed stainless steel 316 coating is higher than the ground stainless steel 316 coating.

Sample group 4 (the Ni plated on as-sprayed stainless steel 316 coating) and sample group 5 (the Ni plated on ground stainless steel 316 coating) present the effect of coating surface roughness. The E_{corr} of the Ni plating on the as-sprayed stainless steel 316 coating is lower than the Ni plating on the ground stainless steel 316 coating. It means the rough EAS coating surface can corrode more easily than the smoothened EAS coating surface. The corrosion rate of the Ni plating on the as-sprayed stainless steel 316 coating is higher than the Ni plating on the ground stainless steel 316 coating. It shows that the smoothened EAS coating surface possesses higher durability than the rough EAS coating surface.

Comparison between sample group 2 (the as-sprayed stainless steel 316 coating) with sample group 4 (the Ni plated on as-sprayed stainless steel 316 coating) shows that the E_{corr} and the corrosion rate of the Ni plated sample are slightly lower than those of the un-plated sample, which shows that the Ni plated sample can start corroding more easily than the un-plated sample but its corrosion rate is slightly lower than that of the un-plated counterpart.

Conclusions

It was found that the corrosion resistance of stainless steel EAS coating can be improved using the electroplating of Ni with thickness of greater than 10 µm. The calculated result shows Ni plating on the EAS stainless steel 316 coating will start corroding more easily than the un-plated coating but the Ni plated sample processes higher durability than the un-plated coating, as can be observed in the lower corrosion rate. Moreover, grinding of the EAS coating followed by Ni plating can provide a better corrosion resistance because grinding of the coating surface can remove the large surface pores to an extent, but some small pores are still present. The electroplating of Ni on the ground coating can seal off the pores and provide a smooth finish to the sample, which improves the ability to form a protective scale and, in turn, enhances the corrosion resistance of the stainless steel 316 coating. Sealing of the stainless steel EAS coating using electroplating of Ni should extend the limit of EAS coating to use in immersion condition.

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