

The Oxidation Behaviour of Stainless Steel AISI 409 Coated By Decorative Nickel-Chromium Plating

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Abstract

The continuous and cyclic oxidation behaviour of ferritic stainless steel AISI 409 surface-coated by decorative nickel-chromium plating was studied. Firstly, the plated AISI 409 steel samples were cut into rectangular pieces of 20x10x3 mm. Nickel plating was electroplated with various times, i.e., 0, 5, 10 and 15 minutes; subsequently the decorative chromium plating was performed for 5 minutes. Then, the samples were exposed to 200°C and 300°C. The degradation of samples was evaluated by considering weight alteration after oxidation test. The oxidation product and surface of samples were characterized by optical microscope and scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX). From the results, it is obvious that the samples with the nickel pre-plating before chromium plating show higher oxidation resistance than the samples with only the chromium plating. Moreover, the oxidation resistance of the samples gradually increases with the thickness of nickel pre-plating. In addition, surface roughness of the samples prior to nickel and/or chromium plating and temperature of testing drastically affect oxidation rate. The best condition to approaching the high oxidation resistance and the beautiful appearance is that the samples have to be nickel pre-plated for 15 minutes subsequently they are immersed in the chromium plating bath for 5 minutes.

Keywords: Oxidation behaviour, Ferritic stainless steel AISI 409, Decorative nickel-chromium plating.

Introduction

Ferritic stainless steel is generally used in many industrial applications such as sink, washing-machine part, furniture and exhaust systems of motor vehicles because its price, mechanical property and corrosion resistance are reasonable.⁽¹⁾ In general, the ferritic stainless steel can be used to resist atmosphere and exhaust gas corrosion as well but the corrosion product, which is rust, on the surface is not desirable for decorative application.⁽²⁾ Therefore, surface modification has been extensively used for improvement of surface of engineering parts.

The most important technique using for surface improvement is chromium plating. The chromium plating is versatile and can be applied to a variety of substrates, including steel and stainless steel.⁽³⁾ However, it is easy to obtain flaws or cracks in the chromium surface plating. In order to improve chromium plating process and reduce defects, nickel is necessarily pre-plated prior to chromium plating.⁽⁴⁾ Moreover, it is well known that nickel not only protects the substrate from corrosion, but it also supports chromium plating to have a white color

that is desirable for decorative applications. Therefore, nickel - chromium plating is frequently made on the surfaces of automobile cars, electrical products and engineering parts for the purpose of improving the corrosion resistance of the basic materials and improving the decorative effect by combination with decorating.⁽⁵⁾ However, it still remains in question about the effective thickness of nickel pre-plating on the decorative chromium plating in particular for the exhaust tube system of motorcycle. In order to understand effect of Ni pre-plating on the oxidation behaviour of decorative chromium-nickel plating on AISI 409 stainless steel, firstly the samples were Ni pre-plated with various times, i.e., 0, 5, 10 and 15 minutes before they were Cr plated at a constant time of 5 minutes. Then, they were exposed to the temperatures of 200°C and 300°C, which are typical temperature ranges of the exhaust system of motorcycle, in the normal atmosphere of the tube furnace. After the oxidation test, degradation of the samples was evaluated by weight alteration of each sample. For oxidation products, they were characterized by optical microscope and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX).

Materials and Experimental Procedures

Sample Preparation

The AISI 409 ferritic stainless steel was selected to be a substrate in this study. The chemical composition of the AISI 409 steel was measured at the Center for Scientific and Technological Equipment, Suranaree University of Technology. The result is presented in Table 1.

Table 1. Chemical composition of the studied stainless steel AISI 409 (in wt. %)

Grade	Cr	Si	C	Mn	P	S	Fe
409	11.00	1.00	0.08	1.00	0.04	0.04	Bal.

Figure 1 shows the preparation of samples. Firstly, the samples were cut into rectangular pieces of 20x10x3 mm. Then, the samples were surface-prepared with alteration of surface roughness prior to the decorative nickel-chromium plating in order to monitor effect of surface roughness of substrate on degradation at temperature above room temperature of the decorative nickel-chromium plating. The samples were polished by a silicon carbide paper with various grit numbers such as 180, 600 and 1200 for preparing surface roughness of the substrate. In addition, a profile-meter (Veeco) model was used to measure surface roughness in terms of Ra (nm) of samples before and after plating.

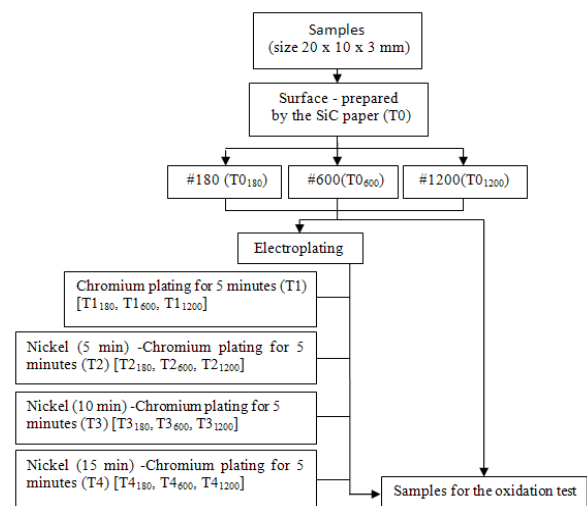


Figure 1. Flow chart of sample preparation.

For electroplating process, the samples were immersed in a nickel plating bath (pH 3.5) containing 250 g/l of nickel sulfate, 40 g/l of nickel chloride, 40 g/l of boric acid at 40°C and 3 A/dm² at various times, i.e., 0, 5, 10 and 15 minutes. After being nickel plating, the samples were then immersed in a chromium plating bath (pH 3.5) containing 250 g/l of Chromic acid, 2.5 g/l of sulfuric acid, at 46°C and 35 A/dm² at a constant time of 5 minutes. The thickness of nickel and/or chromium plating was measured by SEM and the results were presented in Table 2.

Table 2. Thickness of decorative Ni - Cr plating and surface roughness of samples before and after electroplating.

Samples	Thickness of decorative Ni-Cr plating (in μm)		Surface roughness (in Ra)	
	Ni	Cr	Before plating	After plating
T0 ₁₈₀	none	none	279.40	none
T0 ₆₀₀	none	none	207.58	none
T0 ₁₂₀₀	none	none	168.53	none
T1 ₁₈₀	none	0.10	294.32	157.91
T1 ₆₀₀	none	0.20	215.42	148.31
T1 ₁₂₀₀	none	0.20	167.53	90.21
T2 ₁₈₀	2.00	0.20	267.53	152.35
T2 ₆₀₀	2.00	0.20	198.60	138.86
T2 ₁₂₀₀	2.50	0.20	165.56	86.04
T3 ₁₈₀	3.00	0.30	225.30	148.88
T3 ₆₀₀	3.40	0.20	185.35	118.80
T3 ₁₂₀₀	3.60	0.20	156.74	70.65
T4 ₁₈₀	4.00	0.20	284.56	148.63
T4 ₆₀₀	5.00	0.20	195.45	114.47
T4 ₁₂₀₀	5.00	0.20	177.35	66.96

As shown in Table 2, it is clearly demonstrated that the surface roughness of the samples significantly changed with the SiC paper. For example, the samples polished with the SiC paper of up to number 180 have rougher surface than the samples that are polished with the SiC paper of up to number 600 and 1200, respectively. In addition, it is found that surface roughness of substrate prior to electroplating significantly affects roughness of the electroplating.

Experimental Procedure

The degradation of bare and coated AISI 409 stainless steel was studied by heating at the temperature of 200°C and 300°C in the normal atmosphere of the tube furnace (Carbolite, Scientific promotion co., Ltd.). The degradation of the samples was evaluated by measuring the weight alteration

per the exposure area ($\Delta W/S$) versus the oxidation time. Firstly, the weight and the exposure area of the samples were measured before oxidation test. Then, the samples were exposed to a given temperature with various exposure procedures, i.e., continuous and cyclic oxidation tests. Effect of exposure time on the degradation of the samples also has been evaluated. For example, the oxidation times were 45, 90, 135 and 180 hours for the continuous oxidation test. For the thermal-cycle test, the oxidation time were 90 cycles and each cycle is performed by heating for 2 hours at the given temperature; subsequently cooling in the tube furnace for 30 minutes and finally cooling in the air for 30 minutes. The deterioration of each sample was measured after high temperature exposure by weight measurement in each condition, i.e., every 45, 90, 135 and 180 hours for the continuous oxidation test and every cycle for thermal-cycle test.

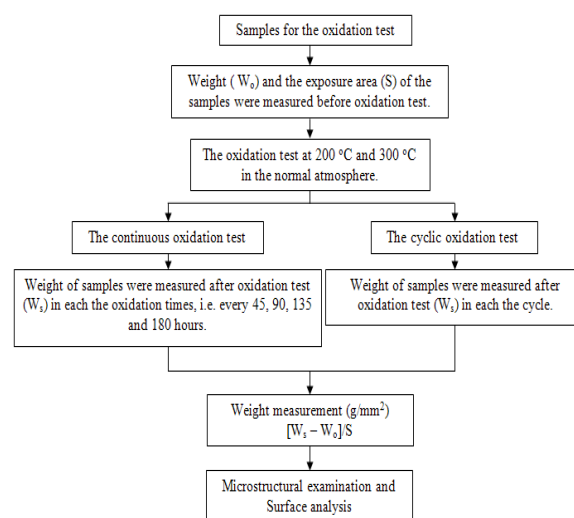


Figure 2. Experimental procedure.

Figure 2 shows the procedure of weight measurement and oxidation test. After exposure, the oxidation products were characterized by optical microscope, scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). Before mounting the samples for metallographic cross-section analyses, the samples were electroplated by copper in order to avoid evolution of oxide layer during grinding and

polishing. In addition, the copper electroplating is useful for a better optical contrast between oxide and mounting material.⁽⁶⁾

Results and Discussions

As described previously in the introduction and the experiment procedure, the degradation of bare and decorative plating samples in terms of weight change per exposure area have been studied with various parameters such as surface roughness, exposure temperature, thickness of nickel pre-plating and condition of oxidation test. The important results are shown as followings.

Oxidation Behaviour

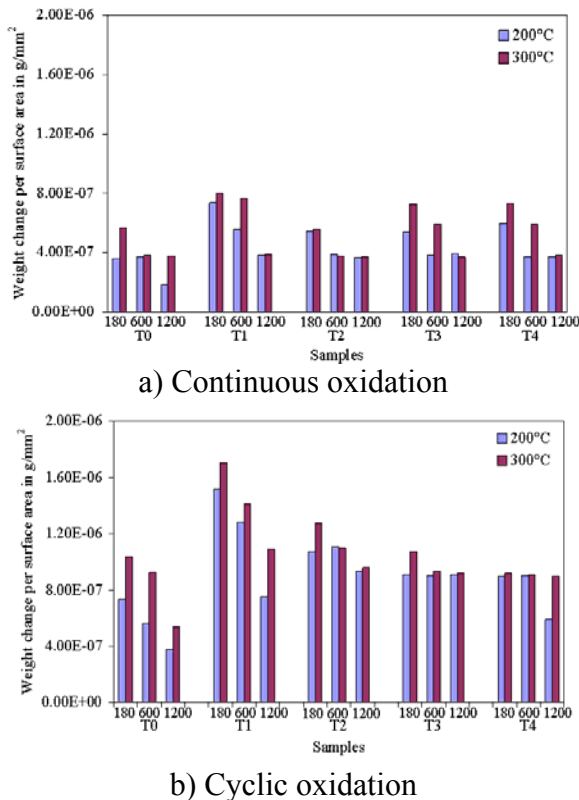


Figure 3. Weight change of bare, Cr plating and Ni - Cr plating samples at 200°C and 300°C for 180 hours with different exposure techniques: a) Continuous oxidation and b) Cyclic oxidation.

Figure 3 shows weight change of bare, Cr plating and Ni-Cr plating samples at 200°C and 300°C for 180 hours with different exposure techniques, i.e., continuous (180 hours) and cyclic oxidation (90 cycles). It is obvious that exposure techniques significantly affect oxidation rate, representing in terms of weight change per surface area (g/mm^2), of all samples. The oxidation rate of all samples tested under the cyclic oxidation test is higher than that of all samples tested under the continuous oxidation test. This might be explained that metal firstly reacts with oxygen in air at temperature above room temperature; subsequently metal oxide produces on such surface. At high temperature, the metal oxide is still ductile and it adheres on the surface. However, the metal oxide losses adhesion force between its self and metal substrate during cooling process due to the difference of thermal expansion coefficient between the metal substrate and metal oxide. As a result, the metal oxide is removed easily during the cyclic oxidation test.⁽⁷⁾ By considering surface roughness, it is obvious that surface roughness prior to electroplating significantly affects the oxidation rate. The samples prepared under the finer surface roughness, i.e., 600 and 1200, have lower oxidation rate than the samples prepared under the rough surface (180) for all exposure techniques (Figure 3a and Figure 3b). In addition, it is found that the surface roughness of all samples is changed to be finer, after the Cr and/or Cr-Ni plating have been applied to such surface of samples, as shown in Table 2. This implies that the oxidation resistance is better since the Cr and/or Ni-Cr plating have been coated on the surface of AISI 409 stainless steel. Those are certainly observed by monitoring weight change per surface area of T1, T2, T3 and T4 samples, respectively. It is found that the weight change per surface area is gradually decreased since the Cr and/or Ni-Cr plating have been applied on the surface. And, the best oxidation resistance can be found in T4 sample that is prepared by the nickel pre-plating for 15 minutes and chromium plating for 5 minutes. However, it

is remarkable that the bare sample shows higher oxidation resistance than the Cr and/or Ni-Cr plating samples for all conditions, i.e., at 200°C and 300°C and for continuous and cyclic exposures. This can be explained by considering EDX analysis of elements on surface of each sample as demonstrated in Table 3. It is clearly demonstrated that the bare sample (T0) and the Cr plating sample (T1) have the same elements on the surface in particular for silicon, while the Ni - Cr plating samples, i.e., T2, T3 and T4, do not have silicon on the surface after oxidation test. This implies that the silicon is a helpful element to reduce oxidation of AISI 409 stainless steel. This might be the fact that a silicon-rich layer was developed at the surface of bare sample (T0) during oxidation process. The reason why the silicon - rich layer occurred easily is that the silicon dioxide (SiO_2) has the largest negative value of ΔG^0 for the bare sample (T0). In addition, the SiO_2 produced on the surface of the bare sample (T0) is helpful to delay oxide fracture and to prevent the chromium diffusion away from the substrate.^(8,9) As a result, the bare sample (T0) has better oxidation resistance than the other samples. However, the Ni-Cr plating is still important for the decorative application because its appearance after high temperature exposure is more beautiful than the appearance of the bare sample as shown in Figure 4. From Figure 4, it can be seen that the color of the T0 and T1 samples changed from silver – white to dark - brown, while the T2 sample changed from silver - white to yellow. And, the color of Ni - Cr plating with the thickest of Ni is brighter than the other samples as can be seen in the T4 sample.

Table 3. EDX analysis of elements on surface of the samples (in %)

Element		T0	T1	T2	T3	T4
O	B-0	2.90	2.77	1.45	1.86	1.40
	C-2	3.10	3.08	1.76	2.24	1.48
	C-3	4.23	3.46	2.24	2.31	1.75
	D-3	3.39	3.29	1.48	1.94	2.10
Si	B-0	0.96	0.70	-	-	-
	C-2	1.01	0.71	-	-	-
	C-3	0.63	0.96	-	-	-
	D-3	0.87	0.72	-	-	-
Cr	B-0	10.66	11.10	1.89	1.44	1.01
	C-2	11.16	11.25	2.12	3.10	0.73
	C-3	10.89	10.77	1.00	2.12	0.69
	D-3	10.78	12.82	1.15	2.65	2.55
Fe	B-0	85.53	85.43	6.14	1.07	3.79
	C-2	84.73	84.96	6.25	1.14	1.98
	C-3	84.26	84.81	5.07	1.25	3.58
	D-3	84.96	83.16	5.35	1.22	1.03
Ni	B-0	-	-	90.52	95.63	93.81
	C-2	-	-	89.86	93.52	95.81
	C-3	-	-	91.47	94.32	93.98
	D-3	-	-	91.95	94.19	94.32

*Remarks: B-0 – Before oxidation, C-2 – Cyclic oxidation at 200°C, C-3 – Cyclic oxidation at 300°C and D-3 – Continuous oxidation at 300°C

From Figure 3, the Cr plating sample (T1) shows the highest weight change. This is due to the fact that such sample was only Cr plated. And, after the T1 sample was subjected to the given temperatures, the chromium layer was oxidized to chromium oxide easily.⁽¹⁰⁾ And, it is well known that the Cr layer, performed by electroplating method, normally has flaws or cracks in its layer.⁽⁵⁾ As a result, oxygen atoms diffuse through the flaws or cracks and chromium oxide to oxidize the substrate easily. In contrast to the chromium oxide, it is not easy for the oxygen atoms to diffuse through the SiO_2 and to react with the substrate.⁽⁹⁾ Therefore, the Cr plating sample (T1) shows higher weight change than the bare sample (T0).

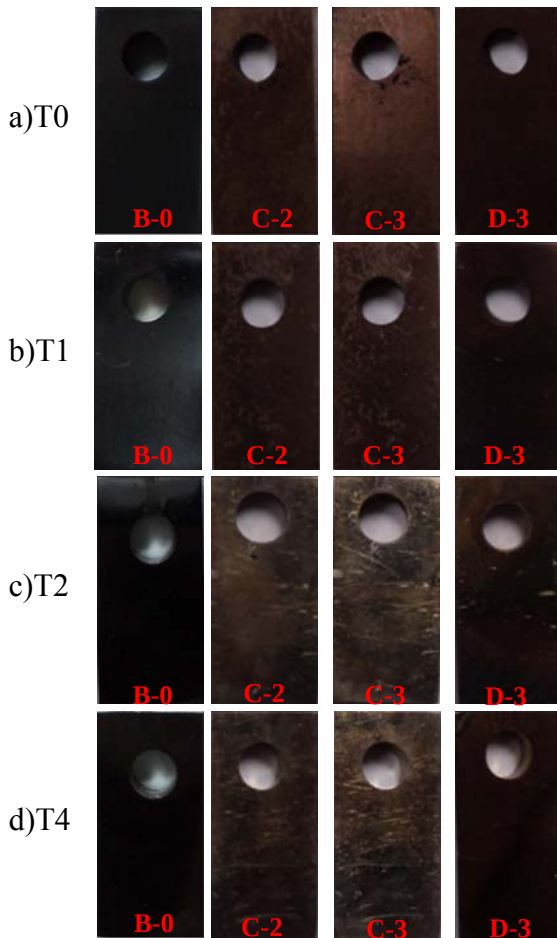
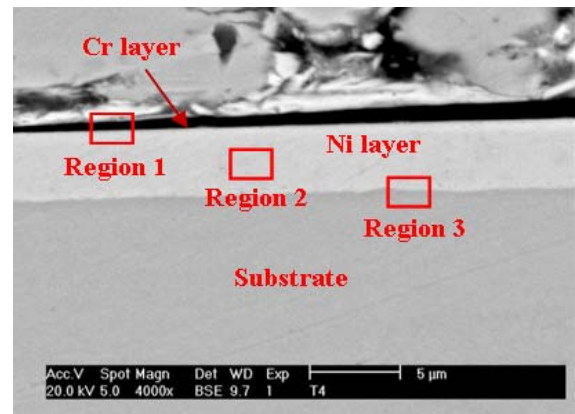


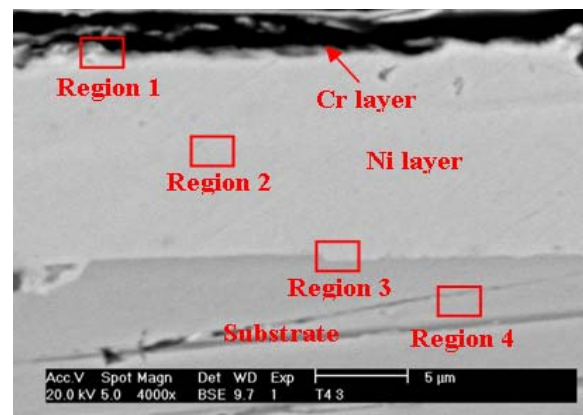
Figure 4. The surface color of samples after oxidation test at 300°C for 180 hours.

- a) Bare samples b) Cr plating samples
c) Ni-Cr plating samples (thinnest Ni layer)
d) Ni-Cr plating samples (thickest Ni layer)

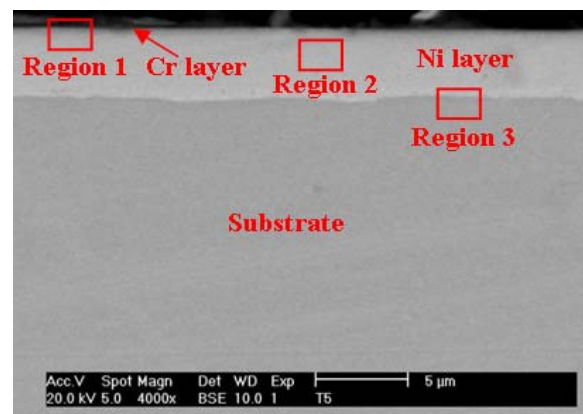
As to be expected, the weight change of all samples significantly increased with the test temperature. As shown in Figures 3a and Figure 3b, it is obvious that the oxidation rate of all samples at the temperature of 300°C is higher than that of all samples at the temperature of 200°C. This is due to the fact that the higher temperature atmosphere in general accelerates the diffusion of metal or oxygen atoms through the oxide layer than the lower temperature atmosphere.⁽¹¹⁾ This means that the metal reacted with the oxygen easily at the high temperature.



a) before the oxidation test



b) after the cyclic oxidation test



c) after the continuous oxidation test

Figure 5. The SEM images on cross-section of Ni-Cr plating samples with the thickest Ni layer (T4) tested at 300°C for 180 hours.

Table 4. EDX analysis of elements on cross section of each sample

Sample	Element	Region (in %)			
		1	2	3	4
T0 B-0	O	2.24	-	-	-
	Si	0.70	0.78	-	-
	Cr	10.04	11.08	-	-
	Fe	87.02	88.14	-	-
	Ni	-	-	-	-
T1 B-0	O	5.90	2.40	-	-
	Si	0.98	0.93	-	-
	Cr	14.72	11.09	-	-
	Fe	78.40	85.52	-	-
	Ni	-	-	-	-
T2 B-0	O	7.56	-	-	-
	Si	2.77	-	-	-
	Cr	2.15	1.98	9.42	-
	Fe	5.06	14.30	73.37	-
	Ni	71.04	83.72	17.21	-
T4 B-0	O	-	-	-	-
	Si	-	-	-	-
	Cr	2.81	0.80	9.57	-
	Fe	13.32	4.74	79.85	-
	Ni	70.89	94.46	10.58	-
T0 C-3	O	1.50	-	-	-
	Si	-	0.57	-	-
	Cr	10.68	10.85	-	-
	Fe	87.97	88.58	-	-
	Ni	-	-	-	-
T1 C-3	O	1.91	1.70	-	-
	Si	-	-	-	-
	Cr	10.57	10.55	-	-
	Fe	87.52	87.65	-	-
	Ni	-	-	-	-
T2 C-3	O	6.29	-	-	-
	Si	2.70	-	1.39	-
	Cr	2.60	2.45	8.91	-
	Fe	15.85	15.05	69.70	-
	Ni	72.56	82.50	20.00	-
T4 C-3	O	2.24	1.05	-	-
	Si	-	-	-	0.93
	Cr	2.76	-	8.86	10.61
	Fe	1.34	1.79	76.74	87.84
	Ni	93.65	97.16	14.41	1.08
T4 D-3	O	5.69	1.37	-	-
	Si	0.98	-	0.98	-
	Cr	1.44	0.49	8.48	-
	Fe	4.09	4.49	64.72	-
	Ni	87.80	93.65	25.81	-

*Remarks: B-0 – Before oxidation, C-2 – Cyclic oxidation at 200°C, C-3 – Cyclic oxidation at 300°C and D-3 – Continuous oxidation at 300°C

From Figure 3 and Figure 4, the Ni-Cr plating sample with the thickest Ni layer (T4) shows better oxidation resistance and better appearance than the other plating samples, i.e., T1, T2 and T3. In order to understand such behaviour, the T4 sample was cut and was chemical analyzed as shown in Figure 5. For a comparison, the other interesting samples such as T0, T1 and T2 also were cut and were chemical analyzed as shown in Table 4. As shown in Table 4 in particular for region 2 that is the Ni layer, it is obvious that the T4 has iron and chromium lower than T0, T1 and T2 after exposure to 300°C. This means that the ability to inhibit oxidation of iron and chromium depends on the thickness of the Ni layer. The thicker the Ni layer, the greater the oxidation resistance. Figure 5b and Figure 5c show that the sample tested under cyclic oxidation test exhibits much thicker oxide layer than the sample tested under continuous oxidation test. This can be used to confirm that the cyclic oxidation test is more aggressive than the continuous oxidation test.

Microstructure Evaluation

Figure 6 shows SEM images of surface of the bare (T0), the Cr plating only (T1) and the Ni-Cr plating samples (T2 and T4) before oxidation test. It is seen that at the same surface-prepared by polishing with SiC No. 180, i.e., T0-180, T1-180, T2-180 and T4-180, the plated samples have smoother surface than the bare sample. Moreover, it is found that the smoother surface of the plated samples can be approached by polishing the substrate with SiC No. 600 and 1200. Figure 7 shows the surface of the bare (T0), the Cr plating only (T1) and the Ni-Cr plating samples (T4) after oxidation test at 300°C for 180 hours (the worst case). It is obvious that the exposure procedures, i.e., continuous and cyclic oxidation tests, significantly affect the degradation of samples. The cyclic oxidation test is more severe than the continuous oxidation test. Those can be observed by considering the corrosion products and cracks produced on the sample surface. The corrosion products formed on

surface of the bare (T0) and Cr plating (T1) samples. Figure 8 shows the crack area of the bare sample after the cyclic oxidation test at 300°C for 180 hours. The EDX analysis confirms the content of Fe and O within corrosion products as shown in Figure 9.

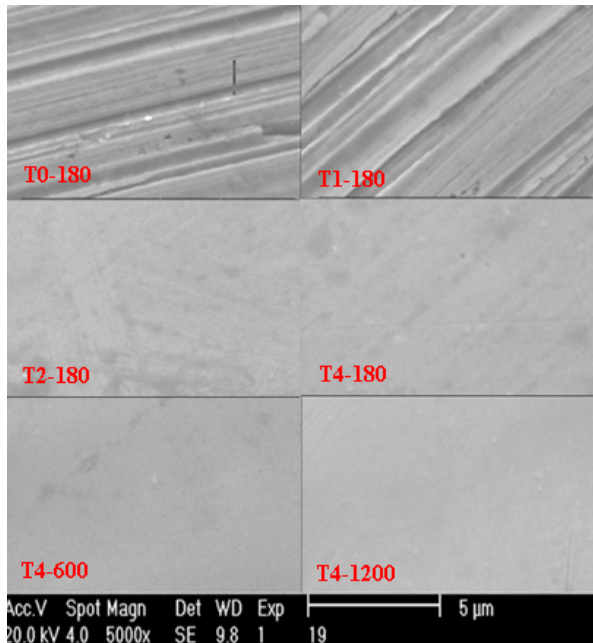
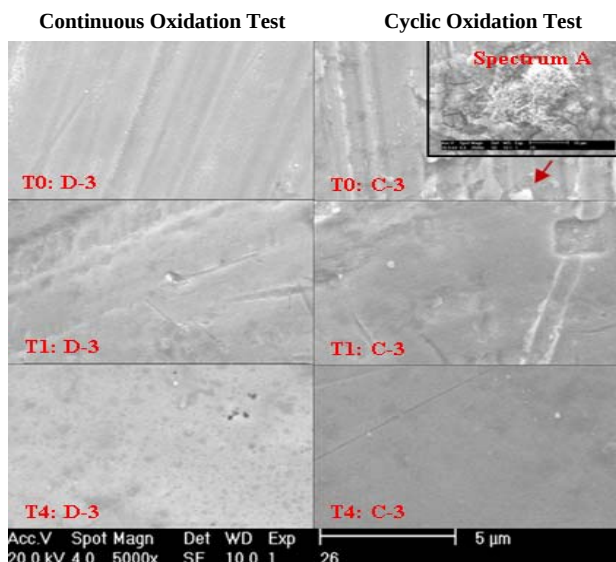


Figure 6. The SEM images of the samples before oxidation test.



*Remarks: C-3 – Cyclic oxidation at 300°C and D-3 – Continuous oxidation at 300°C

Figure 7. The SEM images of the samples after the oxidation test at 300°C for 180 hours.

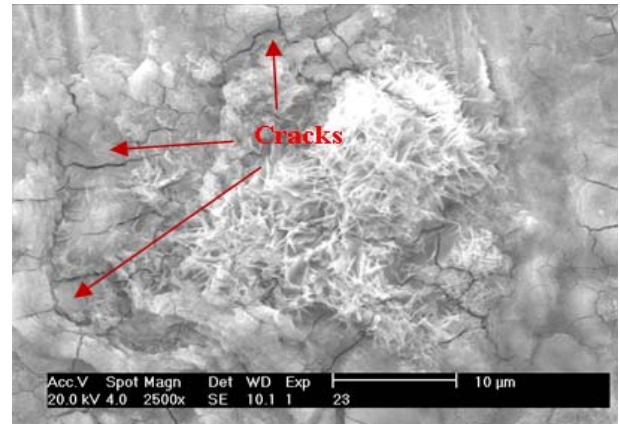


Figure 8. The SEM images of surfaces of the bare sample after the cyclic oxidation test at 300 °C for 180 hours.

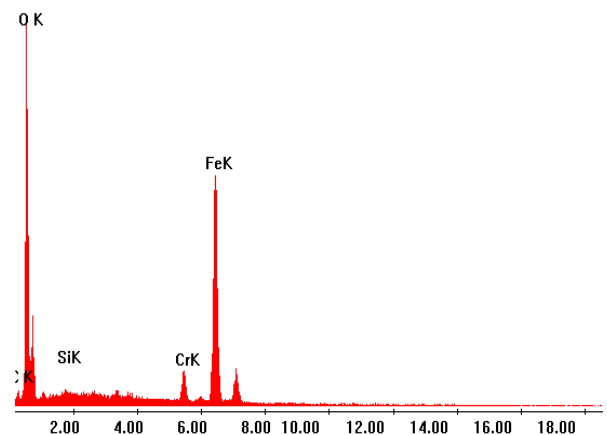


Figure 9. The EDX analysis of spectrum A.

Conclusions

From the first investigation of oxidation resistance of nickel-chromium decorative plating on AISI 409 stainless steel at the temperature of 200°C and 300°C in the normal atmosphere, the following conclusion can be drawn:

1. The surface roughness of substrate prior to decorative Ni-Cr plating significantly affected the oxidation resistance. The smoother substrate yielded better oxidation resistance.

2. The bare samples represented lower weight change than the Ni-Cr plating samples. However, the appearance of the Ni-Cr plating samples after oxidation test was more beautiful than that of the bare samples. As a result, the Ni-Cr plating is necessary for the exhaust tube system of motorcycle.

3. The surface roughness of the decorative Ni-Cr plating decreased with immersion time of nickel pre-plating prior to chromium plating. And, the Ni-Cr plating samples showed lower weight change than that of the Cr plating samples.

4. It was observed that the beautiful appearance and good oxidation resistance strongly depended on the thickness of nickel layer. And, the best condition for decorative Ni-Cr plating in this study was 15 minutes for Ni pre-plating and subsequently 5 minutes for Cr plating.

5. The oxidation of samples were strongly affected by exposure procedures, i. e. continuous and cyclic oxidation tests. The degradation of samples were increased significantly by the cyclic oxidation test.

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